

A

Ph.D. Thesis

entitled

**SYNTHESIS AND CHARACTERIZATION OF PVDF-
CaCu₃Ti₄O₁₂ NANOCOMPOSITE FOR HIGH ENERGY
DENSITY CAPACITORS**

THESIS SUBMITTED TO THAPAR INSTITUTE OF ENGINEERING &
TECHNOLOGY

DOCTOR OF PHILOSOPHY (Ph.D.)

IN

PHYSICS

by

SHOBHNEEK KAUR



THAPAR INSTITUTE
OF ENGINEERING & TECHNOLOGY
(Deemed to be University)

Under the Supervision of

Dr. DWIJENDRA PRATAP SINGH

(Associate Professor)

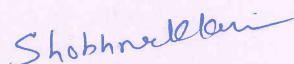
**School of Physics and Materials Science
Thapar Institute of Engineering & Technology
Patiala (Punjab)-147004**

OCTOBER, 2020

*DEDICATED TO MY
PARENTS*

DECLARATION

Certified that the thesis entitled " **SYNTHESIS AND CHARACTERIZATION OF PVDF-
CaCu₃Ti₄O₁₂ NANOCOMPOSITE FOR HIGH ENERGY DENSITY CAPACITORS**" submitted by Miss. Shobhneek Kaur is in the fulfillment for the degree of Doctor of Philosophy of this Institute. This work has been done under the supervision of Dr. Dwijendra Pratap Singh, Associate Professor, School of Physics and Materials Science, Thapar Institute of Engineering & Technology. The work presented in this thesis is original to the best of our knowledge and has not been submitted for any other degree of this or any other University.


(Shobhneek Kaur)

Candidate


(Dr. Dwijendra Pratap Singh)

Supervisor

ACKNOWLEDGEMENT

Firstly, I am thankful to the lord for providing me a strength in my whole life. It is an immense pleasure to express my deep sense of gratitude to my supervisor Dr. Dwijendra P. Singh, (Associate professor), School of Physics and Materials Science, Thapar Institute of Engineering and Technology, Patiala, for giving me such an invaluable guidance at every stage of the thesis. My cordial thanks to Dr. O. P. Pandey (Head of SPMS) who always encouraged and supported me throughout my complete course of Ph.D. thesis. I am grateful to Dr. Ashok Kumar, Sr. Scientist, Physico-Mechanical Metrology (NPL, Delhi) for providing the facilities of Impedance analyzer and P-E loop measurements. I appreciate the support that he allowed me work in his lab. I am also thankful to his students Ravikant, Vikas N Thakur and Charanjeet Singh for their cooperative behavior. I am also grateful to Dr. Amit Lochan. Sharma, Sr. Scientist, Optical Thin Film Group (CSIR, Chandigarh) for providing the facilities of XRD & FTIR and also for the continuous encouragement during my research work. I would like to thank Dr. S.D. Tiwari, Dr. Poonam Uniyal and Dr. Rajeev Mehta for being part of my thesis committee, as well as for all the fruitful discussions. I am thankful to Dr. Kulvir Singh, Dr. Puneet Sharma and, Dr. B.N. Chudasama for their support.

I would like to thank my closest and lovable friends Ms. Nisha, Ms. Navneet Kaur (aliens of my life) who always support and stand by me in every situation during the course of my thesis. I am especially grateful to my laboratory colleagues Sachin Jaidka and Lovepreet Kaur Dhugga for the assistance to my work. I am also grateful to Ms. Indu Gupta, Kushlendra Pandey, Santosh Kumar for their support and including all those people who have helped me directly or indirectly to complete my project work. I am grateful to my overseas close friend Mr. Bharat Manchanda to support me in resolving technical glitches & Ms. Avneet Kaur, Ms. Tamanna, Ms. Alankkrita Kumari, Mr. Rahul Vilecha, Mr. Deepak for their moral support.

I would like to put my heartiest gratitude to my parents (Mr. Amarjeet Singh & Mrs. Parmjeet Kaur). I am also thankful to my brother and sister-in-law (Mr. Kamaljeet Singh & Mrs. Kiranveer Kaur). My heartiest thanks to another brother and sis-in-law from Gurugram (Mr. Manmohandeep Singh & Mrs Pushpa Singh) for their lovable support and care for me whenever my presence was required in NPL, Delhi for some measurements. I especially thankful to my lovable aunt Prof. Manjeet Kaur who support me in my every up and down. Finally, the whole family for their constant support enthusiasm and encouragement.



Shobhneek Kaur

List of Publications

1. Effect of annealing temperature on dielectric behavior of PVDF thick films.

Shobhneek Kaur and Dwijendra Pratap Singh.

AIP Conference Proceedings, 1832, 120003 (2017).

doi.org/10.1063/1.4980688

2. Influence of annealing on dielectric and polarization behavior of PVDF thick films

Shobhneek Kaur, Ashok Kumar, Amit Lochan Sharma and Dwijendra Pratap Singh.

J. Mater. Sci: Mater Electron, 28, 8391-8396 (2017).

DOI 10.1007/s10854-017-6556-8

3. Dielectric and energy storage behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles for capacitor application.

Shobhneek Kaur, Ashok Kumar, Amit Lochan Sharma and Dwijendra Pratap Singh.

Ceramics International, 45, 7743-7747 (2019).

doi.org/10.1016/j.ceramint.2019.01.077

4. On structural, dielectric and energy storage behavior of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films.

Shobhneek Kaur and Dwijendra Pratap Singh.

Materials Chemistry and Physics, 239, 122301 (2020).

doi.org/10.1016/j.matchemphys.2019.122301

Other Publications

1. Enhanced dielectric properties of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films by quenching in ice water.

Shobhneek Kaur, Amit Lochan Sharma, Ashok Kumar and Dwijendra Pratap Singh.

Materials Chemistry and Physics, 254, 123530 (2020).

doi.org/10.1016/j.matchemphys.2020.123530

List of Conferences

Oral presentation in International Conferences

- Shobhneek Kaur and Dwijendra P. Singh, “Study the variation in dielectric behavior of PVDF-CCTO nanocomposite films by quenching ”, 6th Global Nanotechnology Congress and Expo held in Dubai, 2019.

Poster presentation in National and International Conferences

- Shobhneek Kaur and Dwijendra P. Singh, “Effect of annealing temperature on dielectric behavior of PVDF thick film”, 61st DAE Solid State Physics *Symposium*, KIIT University, Bhubaneswar, Odisha, 2016.
- Shobhneek Kaur and Dwijendra P. Singh, “Effect of annealing on structural and microscopic of PVDF thick film”, AMST held at Thapar University, 2016.
- Shobhneek Kaur and Dwijendra P. Singh, “To study the improvement in dielectric properties and energy density of PVDF-CCTO nanocomposite films by quenching, Singapore, 2019.
- Shobhneek Kaur, Gursimarn, and Dwijendra P. Singh, “Synthesis of monolayer graphene by low cost solution processing technique for electronic applications”, ICC held at Govt. Engineering College, Bikaner, 2017.
- Shobhneek Kaur and Dwijendra P. Singh, “Enhanced dielectric constant and energy density of quenched PVDF-CaCu₃Ti₄O₁₂ nanocomposite films”, ICONN held at SRM University, Chennai, 2017.
- Shobhneek Kaur and Dwijendra P. Singh, “To study the electrical properties of CaCu₃Ti₄O₁₂ (CCTO) at different calcining temperature”, ICN held at IIT Roorkee, 2017.

Schools and Workshops attended

- NWATSC held at Thapar University, Patiala, 2015.
- Summer School on Magnetism held in Nanyang Technical University Singapore, 2019.

PREFACE

Polymer ceramic nanocomposites are highly in demand due to its prospective applications in electrical and electronics engineering e.g. embedded electronics, varistors, sensors, and high energy density capacitors. Ceramic materials which are usually used as a filler in the polymer matrix such as lead zirconate titanate (PbZrTiO_3), lead titanate (PbTiO_3), barium titanate (BaTiO_3), barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$), etc. possesses a high dielectric constant. But, the dielectric strength of these ceramics is low due to their brittle nature. On the other side, polymers such as polyvinylidene fluoride (PVDF), polyvinylidenedifluoride-trifluoroethylene (PVDF-TrFE), biaxially oriented polypropylene (BOPP) etc shows high dielectric strength and low dielectric constants (i.e. < 10). So, incorporation of the ceramic materials in the polymer matrix could become a promising material for high energy density capacitor and other applications.

Among all the polymers, polyvinylidene fluoride (PVDF) is flexible in nature and, has high dielectric breakdown strength but low intrinsic permittivity. Besides this, it is very versatile in nature as it exist in different crystalline phase viz. α , β and γ -phases having different dielectric and polarization behavior. The evolution of these phases are controlled by different ways of processing e.g. quenching, annealing, stretching etc. The β and γ -phases are polar in nature, but the tangent loss of γ -phase is found to be less as compared to β -phase. The γ -phase of PVDF is found to be most suitable for energy storage applications. The dielectric and energy storage behavior of polymer ceramic nanocomposite based on PVDF have been widely investigated.

Among all dielectric ceramics, calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) ceramic shows colossal dielectric constant ($\epsilon \sim 10^4 - 10^5$) which is constant over a broad frequency ($10^2 \text{ Hz} - 10^6 \text{ Hz}$) and temperature range (100 K - 600 K). The incorporation of the CCTO nanoparticles in the PVDF matrix will be cause less area hysteresis loop by virtue of its non-ferroelectric nature and the composites with less area hysteresis loop have good energy storage properties. Therefore, the composite of calcium copper titanate with PVDF could be an alternative choice of a material for energy storage applications.

Earlier studies have confirmed that PVDF-CCTO nanocomposite have moderate dielectric constant, low tangent loss and high mechanical strength. But, the polarization and energy storage behavior of the PVDF-CCTO nanocomposites has not been investigated so far. Therefore, the synthesis and characterization of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite for high energy density capacitors has been studied in the present work.

The thesis consisting of all these studies has been composed in six chapters.

The first chapter gives the brief review of polymers, ceramics and polymer ceramic nanocomposite, which is related with their structural properties, dielectric and energy storage behavior. The aim of thesis is presented in the last section of this chapter.

The second chapter describes the details of synthesis and the characterization techniques employed for investigation of materials of interest viz. PVDF thick films, CCTO nanoparticles and PVDF-CCTO nanocomposite thick films.

The third chapter describes the comprehensive study of PVDF polymer thick films and CCTO nanoparticles. The effect of annealing temperature on structural, dielectric and polarization behavior of PVDF thick films has been studied. The annealing temperature in order to have very good dielectric and polarization behavior of PVDF thick film has been optimized. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits high dielectric constant, high breakdown electric field, along with very good capacitive behavior. Hence the particle size and phase purity of CCTO nanoparticles has also been optimized. The important outcomes of experimental investigation are concluded in the last section of this chapter.

The fourth chapter deals with the structural, dielectric and energy storage behavior of polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films. PVDF-CCTO nanocomposite films have been fabricated by solution casting method, where $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles are incorporated in the PVDF polymer matrix. Synthesized films have been structurally, morphologically, and electrically characterized. Dielectric constant of PVDF-CCTO nanocomposite films are found to increase with increase in loading of CCTO nanoparticles in the frequency range 100 Hz - 1 MHz. Obtained dielectric constant of composites has also been fitted in various theoretical models. Unlike dielectric behaviour, polarization does not show the ordered variation with the loading of CCTO nanoparticles. Enhanced energy density and polarization are attributed to increase dipole moment due to ordering of α , β , γ -phases of PVDF in PVDF-CCTO nanocomposite films. The final conclusion of the experimental studies and, its analysis is given in the last section.

The fifth chapter describes the effect of functionalization on dielectric and energy storage behavior of PVDF-CCTO nanocomposite thick films. CCTO nanoparticles are functionalized by $-\text{NH}_2$ functional group by using ethylenediamine. These nanoparticles are incorporated in the PVDF matrix for synthesizing functionalized PVDF-CCTO nanocomposite thick films. The comparative study of functionalized PVDF-CCTO nanocomposite films and normal PVDF - CCTO nanocomposite thick films have been carried out on different parameters viz. structural, dielectric and energy storage behavior. The dielectric constant, electrical displacement, energy density, and efficiency has been found to be increased appreciably in functionalized PVDF-CCTO nanocomposite films as compared to normal PVDF-CCTO nanocomposite films. Improved dielectric and energy storage behavior of functionalized PVDF-CCTO nanocomposite thick films is assigned to modification among the interfaces between PVDF and CCTO

nanoparticles. The chapter ends with important conclusions obtained from the analysis of experimental data.

The sixth chapter describes, the summary of all experimental investigation, methodology and, their outcomes of the studies on "Synthesis and characterization of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite for high energy density capacitors". Still, there is scope of further investigation on PVDF-CCTO nanocomposites, which would be very important from academic, scientific and technological point of view. The scope of these future investigations have also been suggested.

CONTENTS

CHAPTER 1 : INTRODUCTION

1.1	INTRODUCTION	1
1.2	DIELECTRIC POLYMERS	2
1.3	POLYVINYLIDENE FLUORIDE PROPERTIES AND APPLICATIONS	2
1.3.1	Crystalline phases of polyvinylidene fluoride	3
1.3.2	Dielectric and polarization behavior of polyvinylidene fluoride	4
1.3.3	Polyvinylidene fluoride ceramic nanocomposite	6
1.4	STUDIES ON CALCIUM COPPER TITANATE CRYSTAL	9
1.4.1	Calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) crystal structure	9
1.4.2	Dielectric behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$	10
1.5	AIM OF THESIS	11
	References	13-18

CHAPTER 2 : EXPERIMENTAL DETAILS

2.1	INTRODUCTION	19
2.2	SYNTHESIS OF MATERIAL	19
2.2.1	Synthesis of polyvinylidene fluoride thick films	19
2.2.2	Synthesis of calcium copper titanate nanoparticles	20
2.2.3	Synthesis of polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films by solution casting	21
2.2.4	Functionalization of calcium copper titanate nanoparticles	21
2.3	CHARACTERIZATION TECHNIQUES	22
2.3.1	Structural characterization	22
2.3.1.1	X-ray diffraction	22
2.3.1.2	Scanning electron microscopy	23
2.3.1.3	Electron dispersive X-ray spectroscopy analysis	23
2.3.1.4	Transmission electron microscope	24

2.3.1.5 Fourier transform infrared spectroscopy	24
2.3.2 Electrical properties	25
2.3.2.1 Low field measurements	25
2.3.2.1.1 Dielectric measurements	25
2.3.2.1.2 Current -voltage characteristics	26
2.3.2.2 High field measurements	26
2.3.2.2.1 Displacement vs Electric field	26
References	27
 CHAPTER 3 : STUDIES ON SYNTHESIS AND CHARACTERIZATION OF POLYVINYLIDENE FLUORIDE THICK FILMS AND $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANOPARTICLES	
3.1 INTRODUCTION	29
3.2 STUDIES ON POLYVINYLIDENE FLUORIDE THICK FILMS	31
3.2.1 EXPERIMENTAL	31
3.2.1.1 Synthesis of polyvinylidene fluoride thick films	31
3.2.1.2 Structural studies	31
3.2.1.3 Dielectric measurements	31
3.2.1.4 Polarization vs Electric field measurements	32
3.2.2 RESULT AND DISCUSSION	32
3.2.2.1 Structural studies	32
3.2.2.1.1 X-ray diffraction	32
3.2.2.1.2 Scanning electron microscope	33
3.2.2.1.3 Fourier transform infrared spectroscopy	34
3.2.2.2 Electrical properties	35
3.2.2.2.1 Dielectric behavior of polyvinylidene fluoride thick films	35
3.2.2.2.2 Polarization behavior of polyvinylidene fluoride thick film	36
3.3 CALCIUM COPPER TITANATE NANOPARTICLES	37
3.3.1 EXPERIMENTAL	38
3.3.1.1 Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	38

3.3.1.2 Structural studies	38
3.3.1.3 Dielectric measurements	38
3.3.1.4 Current voltage and charging- discharging measurements	38
3.3.2 RESULTS AND DISCUSSION	39
3.3.2.1 Structural studies	39
3.3.2.1.1 X-ray diffraction	39
3.3.2.1.2 High resolution transmission electron microscopy	40
3.3.2.1.3 Energy dispersive spectroscopy	41
3.3.2.1.4 Raman spectroscopy	41
3.3.2.2 Electrical properties	42
3.3.2.2.1 Dielectric behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	42
3.3.2.2.2 Studies on electrical transport	43
3.3.2.2.3 Studies on charging - discharging behavior	44
3.4 CONCLUSION	45
References	47-50

CHAPTER 4 : STUDIES ON DILECTRIC AND ENERGY STORAGE BEHAVIOR OF PVDF - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANOCOMPOSITE

4.1 INTRODUCTION	51
4.2 EXPERIMENTAL	52
4.2.1 Synthesis of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	52
4.2.2 Structural studies of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	52
4.2.3 Electrical studies	52
4.3 RESULT AND DISCUSSION	53
4.3.1 Structural studies	53
4.3.1.1 X-ray diffraction	53
4.3.1.2 Scanning electron microscope	54
4.3.1.3 Fourier transform infrared spectroscopy	54
4.3.2 Electrical properties	55
4.3.2.1 Studies on dielectric behavior	55
4.3.2.2 Studies on electrical displacement and energy storage behavior	58

4.4	CONCLUSION	61
	References	62-63
CHAPTER 5 : STUDIES THE EFFECT OF FUNCTIONALIZATION OF $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANOPARTICLES IN PVDF - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANOCOMPOSITE ON DILECTRIC AND ENERGY STORAGE BEHAVIOR		
5.1	INTRODUCTION	64
5.2	EXPERIMENTAL	66
5.2.1	Synthesis of functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	66
5.2.2	Synthesis of functionalised $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles in polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	66
5.2.3	Structural studies	66
5.2.4	Electrical studies	66
5.3	RESULT AND DISCUSSION	67
5.3.1	Structural studies	67
5.3.1.1	X-ray diffraction	67
5.3.1.2	Scanning electron microscope	67
5.3.1.3	Fourier transform infrared spectroscopy	68
5.3.2	Electrical studies	69
5.3.2.1	Studies on dielectric behavior	69
5.3.2.2	Studies on electrical displacement and energy storage behavior	71
5.4	CONCLUSION	73
	References	75-76
CHAPTER 6 : SUMMARY AND FUTURE SCOPE		
6.1	INTRODUCTION	77
6.2	COMPONENT OF STUDY	77
6.2.1	Synthesis of materials	77
6.2.1.1	Synthesis of polyvinylidene fluoride thick films and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	77
6.2.1.2	Synthesis of polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	78

6.2.1.3 Synthesis of functionalised $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles in polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	78
6.2.2 Structural and morphological studies	78
6.2.3 Electrical Studies	78
6.3 RESULTS	78
6.3.1 Polyvinylidene fluoride thick films and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	78
6.3.1.1 Structural studies	78
6.3.1.2 Dielectric studies	79
6.3.1.3 Displacement vs Electric field studies	79
6.3.1.4 Current-voltage studies	79
6.3.2 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films	79
6.3.2.1 Structural studies	79
6.3.2.2 Dielectric studies	79
6.3.2.3 Displacement vs Electric field loop	80
6.3.3 Functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles incorporated with polyvinylidene fluoroide - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	80
6.3.3.1 Structural and morphological studies	80
6.3.3.2 Dielectric studies	80
6.3.3.3 Displacement vs Electric field loop	80
6.4 CONCLUSION	80
6.4.1 Polyvinylidene fluoride thick films	80
6.4.2 Calcium copper titanate nanoparticles	81
6.4.3 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films	81
6.4.4 Functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles incorporated with polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films	82
6.5 FUTURE SCOPE OF THESIS	83

List of Figures

Fig 1.1	Schematic representation of the α , β , and γ -phases of PVDF.	3
Fig1.2	X-ray diffraction and Fourier transform infrared spectroscopy of different crystalline phase of PVDF (α , β , and γ).	3
Fig 1.3	Schematic diagram of polarizability and its dominance in various frequency range.	4
Fig 1.4	Dielectric constant and tangent loss of different crystalline phases of PVDF (α , β and γ).	5
Fig 1.5	Hysteresis loop of different crystalline phases of PVDF (α , β and γ).	6
Fig 1.6	Dielectric permittivity, dielectric loss of the PVDF, D-BT/PVDF, and D-h-BT.	8
Fig 1.7	(a) Unipolar polarization loop (b) energy density and incorporated energy efficiency of PVDF film, D-BT/PVDF, and D-h-BT/PVDF nanocomposite film.	8
Fig 1.8	Crystal cubic structure of Calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$).	9
Fig 2.1	Schematic diagram of polyvinylidene fluoride thick films prepared by solution casting method.	20
Fig 2.2	Schematic representation of solution-casting process for making polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick film.	21
Fig 2.3	Schematic representation of functionalization of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles by ethylenediamine.	22
Fig 2.4	Schematic diagram to calculate the discharged energy density.	27
Fig 3.1	X-ray diffractrogram of PVDF thick film annealed at different temperatures.	32
Fig 3.2	Scanning electron microscope micrographs of PVDF annealed films at different temperatures.	33

Fig 3.3	Fourier transform infrared spectra of PVDF annealed films at different temperatures.	34
Fig 3.4	Frequency dependent dielectric constant of PVDF thick films annealed at different temperatures	35
Fig 3.5	Tangent losses of PVDF thick films annealed at different temperatures	35
Fig 3.6	Unipolar polarization vs electric field loops of PVDF thick films annealed at different temperatures	36
Fig 3.7	Schematic diagram of the charging–discharging experiment	38
Fig 3.8	X-ray diffraction of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder calcined at 800°C and 1000°C	39
Fig 3.9	X-ray diffraction of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanopowder calcined at 900°C (Inset is showing Williamson & Hall plot)	40
Fig 3.10	(a) High resolution transmission electron microscopic image, (b) Particle size distribution, (c) high resolution fringes and selected area electron diffraction pattern of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles (d) Scanning micrographs of sintered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellet at 900°C.	40
Fig 3.11	Energy dispersive spectroscopy spectrum of synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles	41
Fig 3.12	Raman spectra of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles at room temperature	41
Fig 3.13	Variation in dielectric constant and tangent loss with frequency of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellet at room temperature	42
Fig 3.14	Current density vs electric field curve of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellet at room temperature	43
Fig 3.15	Discharging current response with time, (b) discharged energy density with time of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ capacitor with inset of charged energy density with time at an applied electric field 3000 (V/cm)	45
Fig 4.1	X-ray diffraction patterns of CCTO, (a) PVDF- 4CCTO, (b) PVDF- 8CCTO, (c) PVDF- 12CCTO and, (d) PVDF- 15CCTO nanocomposite films	53
Fig 4.2	SEM micrographs of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO, and PVDF-15CCTO nanocomposite films	54

Fig 4.3	Fourier transform infrared spectra of CCTO, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12 CCTO and, (d) PVDF-15 CCTO nanocomposite films	55
Fig 4.4	Frequency dependent dielectric constant of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF- 12CCTO and, (d) PVDF-15 CCTO nanocomposite films	55
Fig 4.5	Frequency dependent tangent loss of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films	56
Fig 4.6	Frequency dependent ac conductivity of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films	57
Fig 4.7	Variation of effective dielectric constant at 1 kHz of PVDF-CCTO nanocomposite films with different vol% of CCTO ceramic in PVDF-CCTO nanocomposite	57
Fig 4.8	Displacement loops of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films	59
Fig 4.9	Energy density of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films	59
Fig 4.10	Efficiency of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films	60
Fig 5.1	X-ray diffraction of the (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, (b) pure PVDF, (c) PVDF-8CCTO, and (d) PVDF-8FCCTO nanocomposite films	67
Fig 5.2	Scanning electron microscope micrographs (a) PVDF-8CCTO, and (b) PVDF-8FCCTO nanocomposite film	67
Fig 5.3	Fourier transform infrared spectra of (a) non-functionalized, and (b) functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder	68
Fig 5.4	Fourier transform infrared spectra of (a) PVDF, (b) PVDF-8CCTO, and PVDF-8FCCTO nanocomposite films	69
Fig 5.5	Frequency dependent dielectric constant of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films	69
Fig 5.6	Frequency dependent tangent loss of PVDF-8CCTO and PVDF-8FCCTO nanocomposite film	70

Fig 5.7	Ac conductivity of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films	71
Fig 5.8	Unipolar D-E loop of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films	71
Fig 5.9	Energy density of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films	72
Fig 5.10	Energy efficiency under applied electric field of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films	72

List of Tables

Table 1.1	Comparison of polymers dielectric constant and losses, at 1 kHz	2
Table 1.2	X-ray diffraction and Fourier transform infrared spectroscopy data of different crystalline phases of polyvinylidene fluoride	4
Table 1.3	Represents the comparative results of polyvinylidene fluoride based composite at 20 vol%	7
Table 1.4	Represent the comparative study of different methods to prepare $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder and sintering temperature effects on its electrical studies	10
Table 3.1	Remnant and maximum polarization of PVDF thick films annealed at different temperatures	36

CHAPTER 1

INTRODUCTION

1.1 INTRODUCTION

The regular development and demand for the smaller size of electronic devices based on dielectric materials have gained attention towards the materials which have high dielectric constant, low tangent losses, high mechanical strength and, are easy to process. The importance of these materials emerged due to prospect of their immense applications in electrical engineering, microelectronics, high energy density capacitors, varistors, charge storage etc.¹⁻⁶. The polymer-ceramic composites have been widely investigated due to their moderate dielectric constant, low losses, high dielectric strength and high energy density^{3,5,7-11}. The static energy density of a dielectric materials is given by;

$$U_D = \frac{1}{2} \epsilon_0 \epsilon_r E_b^2 \dots\dots\dots (1.1)$$

where ϵ_0, ϵ_r are known for the vacuum permittivity ($8.854 \times 10^{-12} \text{ F.m}^{-1}$), the dielectric permittivity whereas E_b is known for dielectric strength. It shows that the energy density is found to vary directly with dielectric constant and square of breakdown field/dielectric strength. Breakdown field is also related with mechanical strength. Usually, the ceramics used in polymer matrix are such as PbZrTiO_3 , PbTiO_3 , BaTiO_3 , $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3$ - PbTiO_3 , etc. possesses a high dielectric constant¹²⁻¹⁴. However, the dielectric strength of these ceramics is low due to their brittle nature. On the other hand, there are certain polymers (such as polyvinylidene fluoride (PVDF), polyvinylidenedifluoride-trifluoroethylene (PVDF-TrFE), biaxially oriented polypropylene (BOPP), polyvinyl alcohol (PVA), polyvinyl chloride (PVC), etc) shows dielectric behavior and, they are flexible in nature, easy to process and have high dielectric strength and low dielectric constants (i.e. < 10)¹⁵⁻¹⁸. So the combination of the high dielectric ceramic with these polymers could be a promising material for high energy density capacitors and other electrical and electronic applications. The composite of high dielectric ceramic and low dielectric polymer could provide a material which shows reasonable dielectric constant and good mechanical strength. Among all ceramic fillers, calcium copper titanate (CCTO) shows colossal dielectric constant ($\epsilon \sim 10^4$ - 10^5) which is constant in a broad frequency (10^2 - 10^6 Hz) and temperature range (100 K-600 K)^{19,20}. But its application in various electronic devices is hindered due to its high tangent loss. The present chapter discusses briefly about the properties of dielectric polymers with

special emphasis on the PVDF, dielectric ceramic materials, PVDF ceramic composite. The aim of the thesis is given in the last section.

1.2 DIELECTRIC POLYMERS

There are large number of polymers showing dielectric behavior such as polyvinylidene fluoride (PVDF), polyvinylidene difluoride–trifluoroethylene (PVDF-TrFE), biaxially oriented polypropylene (BOPP), polyvinyl alcohol (PVA), polystyrene (PS), polyvinyl chloride (PVC), etc are the polymers used for thin-film capacitor applications^{15,22,28}. Table 1.1 shows the dielectric constant and dielectric loss of various polymers. Polymers are lightweight, low cost, and easy to process. Among these polymers PVDF is very

Table: 1.1 Comparison of polymers dielectric constant and losses, at 1 kHz.

Polymers	Dielectric constant at 1 kHz (~)	Dielectric loss at 1 kHz (~)	References
BOPP	2.2	0.0002	²¹
PVDF	11	0.02-0.2	^{22,23}
P(VDF/TrFE)	13.2	0.023	²⁴
PS	2.6	0.02	²⁵
PVC	5	0.02	²⁶
PVA	5	0.01	²⁷

versatile as it possesses different crystalline phase with varying dielectric and polarization behavior^{18,22,29–32}. Therefore, its properties are tunable. The subsequent section will discuss about PVDF and its physical, structural, dielectric and polarization properties.

1.3 POLYVINYLIDENE FLUORIDE PROPERTIES AND APPLICATIONS

Polyvinylidene fluoride (PVDF) is a polymer with a long carbon chain having fluorine and hydrogen atom attached to it. Its chemical formula $-(C_2H_2F_2)_n-$. Its properties are as follows:

- PVDF is stable at room temperature and its melting temperature is 180°C.

- It exhibits in five crystalline forms denoted as α , β , γ , δ and ϵ depending on the process ³³. Among which α -phase is non-polar in nature whereas β and γ -phases are polar. A schematic diagram of α , β , and γ -

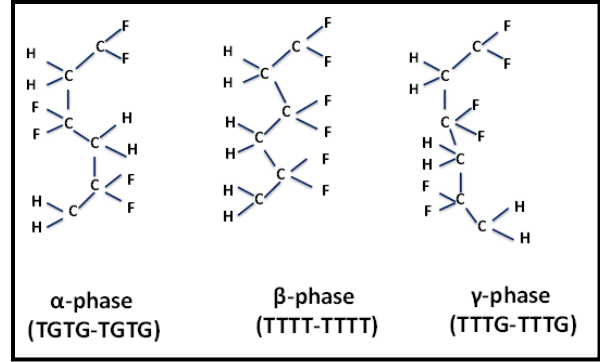


Fig. 1.1 Schematic representation of the α , β , and γ -phases of PVDF.

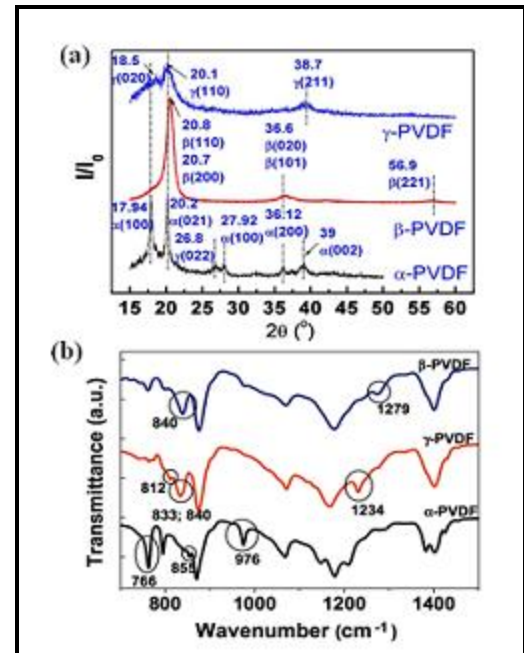
phases of PVDF has been given in fig. 1.1.

- It is very easy to process, and the processing conditions decides the formation of various crystalline phases of PVDF.

PVDF is semi-crystalline in nature and it demonstrate piezoelectric, pyroelectric and ferroelectric ^{22,34} properties which are used in the fabrication of multifunctional sensors for practical applications such as PVDF capacitive pressure sensors, structural health monitoring of civil, aerospace structures biomedical sciences (as an artificial membrane), PVDF membrane also used as sensors ^{35–37}. The various crystalline phases of PVDF and its dielectric or polarization behavior have been discussed in the subsequent sub sections.

1.3.1 Crystalline phases of polyvinylidene fluoride

PVDF exhibits in five crystalline forms denoted as α , β , γ , δ and ϵ depending on the process ³³. Among all five phases, β -phase exhibits excellent piezoelectric and has all *trans-trans* (TTTT) configuration and polar whereas α -phase has *trans-gauche* (TGTG) configuration and nonpolar in nature. The γ -phase is also polar due to (TTTG) configuration. The δ phase also exhibits TGTG' configuration and the arrangement of all dipoles parallel to each other ³⁸. The evolution of these



phases in PVDF depends on various processing condition such as temperature, poling and quenching etc^{30,38–40}. The crystalline phases of PVDF are determined by using X-ray diffraction. (XRD) and fourier transform

Table 1.2 X-ray diffraction and Fourier Infrared spectroscopy data of different crystalline phases of PVDF.

PVDF	2 θ (°)	Wavenumber (cm ⁻¹)
α -phase	17.9 (110), 18.4 (020), 20.2 (021), 27.9 (111), 36.1 (200), 39.0 (002)	408, 532, 614, 764, 796, 855, 976
β -phase	20.7 (110, 200), 36.6 (020,101), 56.9 (221)	444, 512, 776, 812, 833, 840
γ -phase	18.5 (020), 20.1 (110), 38.7 (211)	431, 484, 512, 776, 812, 840, 880, 1234, 1401

infrared spectroscopy (FTIR). Figure 1.2 represents the XRD and FTIR data showing the crystalline phases of PVDF^{41,42}. The table 1.2 shows the different lattice planes corresponding different crystalline phases of PVDF along with their angular position in XRD^{41,42}. and absorption bands corresponding to these phases in FTIR.

1.3.2 Dielectric and polarization behavior of polyvinylidene fluoride

The dielectric constant in a material occurs by virtue of polarizability. The total polarizability defined into three parts: electronic, ionic, and dipolar polarization as shown fig 1.3⁴³. When the displacement of the electron shell relative to the nucleus is known as electronic polarization whereas displacement of a charged ion with respect to other ions known as ionic polarization. Dipolar polarization occurs due to molecules with a permanent electric dipole moment that can change orientation of the dipoles with respect to applied electric field. In heterogeneous materials due to the

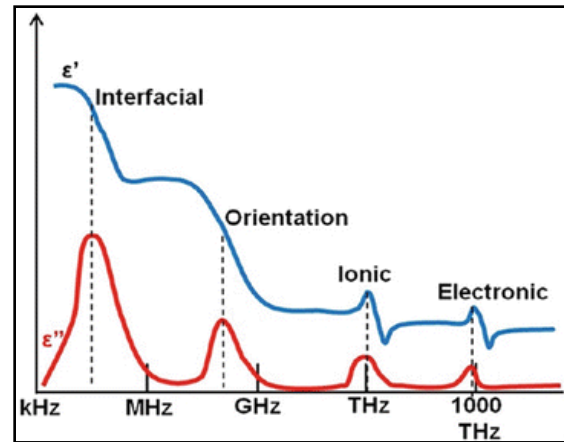


Fig. 1.3 Schematic diagram of polarizability and its dominance in various frequency range. [43]

accumulation of charge at structural interfaces creates the interfacial polarization⁴⁰ and mostly heterogeneous materials are insulating in nature. Interface or space polarization usually happens at the grain boundaries or any other interface such as electrode-material interface.

A schematic representation of polarizability and its dominance in various frequency range is shown in fig. 1.3. The dielectric behavior of PVDF is

mainly dominated by interfacial and orientational polarizability. The lower frequency dielectric behavior is governed by interfacial polarization, whereas its behavior in high frequency (< 10 MHz) is mainly dominated by orientation polarizability. Usually the dielectric constant is found to be higher in lower frequency (< 1 kHz) range and it decreases in high frequency region ($> 10^5$ Hz)⁷. High dielectric constant in the low frequency range is due to the Maxwell-Wagner-Sillars (MWS), interfacial polarization, and space polarization^{44–46}. Fig 1.4 shows the variation of the dielectric constant and tangent loss of the various phases of PVDF at room temperature with respect to frequency³⁴. The dielectric constant of α and β phase of PVDF is found to be significantly higher as compared to the γ -phase of PVDF. At lower frequency, the dielectric constant is higher due to the interfaces among PVDF. Decrease of dielectric constant in high frequency region is attributed to the lack of response of dipoles of nanocomposite film with respect to frequency of applied electric (ac.) field. The losses are lower at low frequency and then increases at high frequency ($> 10^5$ Hz). The tangent loss of γ -phase of PVDF is found to be less as compared to α and β phase. The tangent loss is basically arising due to combined effect of conduction of electron, interfacial polarization and dipolar relaxation, whereas conduction electron and interfacial polarization are dominant in the frequency range ($< 10^5$ Hz).

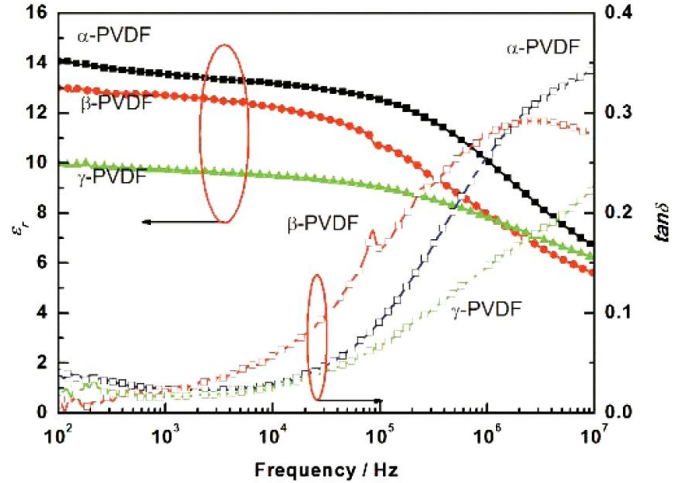


Fig. 1.4 Dielectric constant and tangent loss of different crystalline phases of polyvinylidene fluoride (α , β and γ). [34]

Figure 1.5 represents the polarization vs electric field hysteresis loop of α , β and γ -phases of PVDF⁴⁷. The β -phase shows the highest saturation polarization which is found to be $\sim$

8 $\mu\text{C}/\text{cm}^2$ at 150 MV/m then the α and γ -phases. This loop is also confirming the ferroelectric nature β -phase of PVDF. Though β -phase of PVDF possesses very good ferroelectric and piezoelectric behavior³⁰, but it not very good for energy storage in form of capacitor. The formation of large area ferroelectric loop leads to more energy loss and compromises with energy efficiency¹⁰. On the other hand it is observed

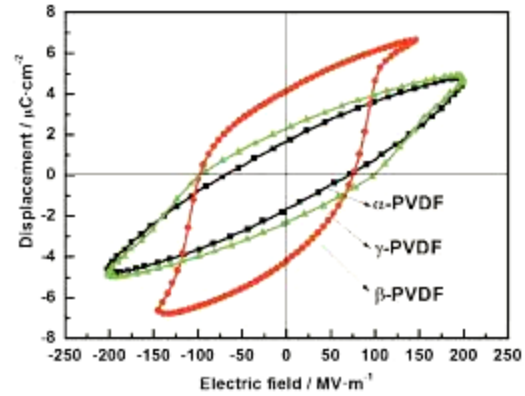


Fig. 1.5 Hysteresis loop of different crystalline phases of PVDF (α , β and γ). [47]

that γ - phase of PVDF exhibits better energy storage properties such as discharge energy density and energy efficiency⁴⁸. The stability, versatility and ease of processability make PVDF polymer as most suitable matrix for making polymer ceramic nanocomposite. The subsequent section discusses briefly about PVDF ceramic nanocomposites.

1.3.3 Polyvinylidene fluoride ceramic nanocomposite

Polymer ceramic nanocomposite is formed by using different polymers such as PVDF, P(VDF-TrFE), (BOPP), PVA, PS, PVC, etc.^{15,16,18,26,49}. But the polymer ceramic composite consisting of PVDF as polymeric matrix provides better tenability of structural, dielectric, and energy storage properties^{48,50–54}. It is already mentioned that PVDF polymer has low tangent loss (~ 0.01) and low dielectric constant (~ 11). Only the lower dielectric constant prevents it to be used for high energy density capacitor applications. Moreover, the ceramic material such as lead zirconate titanate (PbZrTiO_3), lead titanate (PbTiO_3), barium titanate (BaTiO_3), lead magnesium niobate-lead titanate $\text{Pb}(\text{Mg}_{0.33}\text{Nb}_{0.67})\text{O}_3\text{-PbTiO}_3$, barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$), and calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) etc. possesses high dielectric constant^{9,55–57}. But they are having low dielectric strength due to their brittle nature. The composite of PVDF with ceramic materials may exhibit moderate dielectric constant and high dielectric strength. Moreover, the polarization can sustain at high fields. Therefore, PVDF ceramic composites are very good choice for developing high energy density capacitor materials.

In the introduction of this chapter the formula for static energy density is given. But when the polarization/electric displacement changes with electric field, then to calculate the energy

storage density by using this formula will not give the accurate result. The charging and discharging energy density is calculated from area under charging and discharging curve in unipolar displacement vs electric field data ^{10,47,58}.

The energy density of the dielectric materials calculated as:

$$U = \int E dD \dots\dots\dots (1.2)$$

The energy efficiency is given by formula;

$$\eta(\%) = \frac{\text{Discharging energy density}}{\text{Charging energy density}} * 100 \dots\dots\dots (1.3)$$

The micro size ceramic filler in polymer ceramic composite possesses high dielectric constant, but dielectric strength is compromised ⁶². Therefore, the size of ceramic filler in the nanocomposite plays an important role to utilize it for high energy density capacitor applications. Polymer ceramic nanocomposite based on PVDF has been widely investigated and found to exhibit excellent dielectric energy storage behavior ^{10,63,64}. The

Table 1.3 Represents the comparative results of polyvinylidene-fluoride based composite at 20 vol%

Composites	Dielectric constant at 1 kHz (~)	Tangent loss at 1kHz (~)	Energy density (J/cm ³) (~)	References
PVDF-BaTiO ₃ (20 vol%)	20	0.003	3.5	59,60
PVDF-Ba _{0.6} Sr _{0.4} TiO ₃ (20 vol%)	19	0.2	0.28	55
PVDF-CCTO (20 vol %)	31	0.08	Not investigated	61

ceramic fillers such as PbZrTiO₃, PbTiO₃, BaTiO₃, Pb (Mg_{0.33}Nb_{0.67})O₃-PbTiO₃, (Ba_xSr_{1-x}TiO₃), and (CaCu₃Ti₄O₁₂) are used in the PVDF polymer matrix to study the electrical properties ^{9,55–57,65}. Mostly, PVDF- Ba_xSr_{1-x}TiO₃ nanocomposite with PVDF have been studied for high energy density capacitor applications ^{5,55,66}. The results of PVDF polymer based nanocomposite dielectric constant (ϵ_r), tangent loss (δ), and discharging energy density (U_D) are given in table 1.3.

Figure 1.6 represents the data of room temperature dielectric constant and dielectric loss of polyvinylidene fluoride (PVDF) and its nanocomposite with D-BT(BaTiO₃ nanoparticles modified with a titanate coupling agent DN-101) and D-h-BT (BaTiO₃ functionalized by H₂O₂ group and then modified with a titanate coupling agent DN-101), which are denoted by D-BT/PVDF and D-h-BT/PVDF respectively⁵⁸.

All these sample are taken in the form of free-standing films. At 1 kHz the dielectric constant is found to be ~ 22 for functionalized BaTiO₃ nanocomposite whereas losses are found to be almost same for the frequency range 1-10⁷ Hz for all the three samples.

Figure 1.7 (a) represents the data of the polarization vs electric field unipolar loop of PVDF film, D-BT/PVDF, and D-h-BT/PVDF nanocomposite film. The highest saturation polarization is ~6.41 $\mu\text{C}/\text{cm}^2$ at 240 MV/m found in the D-h-BT/PVDF which 127% higher than pure PVDF. Figure 1.7 (b) also represents that highest energy density is 7.65 Jcm^{-3} at 240 MV/m found in the D-h-BT/PVDF nanocomposite which is 138% larger than pure PVDF. The D-h-BT/PVDF nanocomposite also show stable efficiency when the electric field is above 200 MVm^{-1} ⁵⁸. The interfacial modification by the coupling agent and surface functionalization of ceramic particles are ascribed to improved dielectric and energy storage behavior. The interfacial modification among the interfaces of polymer ceramic nanocomposite has been achieved by adopting

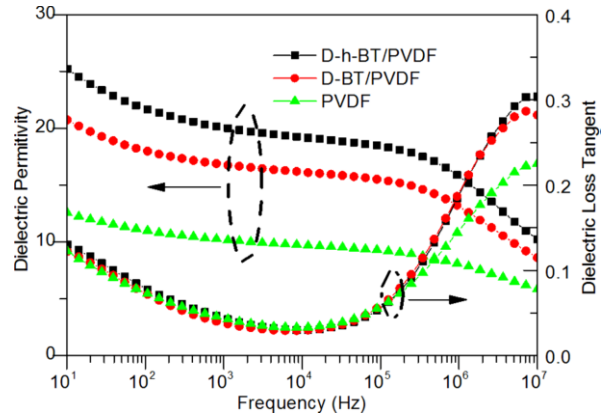


Fig. 1.6 Dielectric permittivity, dielectric loss of the PVDF, D-BT/PVDF, and D-h-BT. [58]

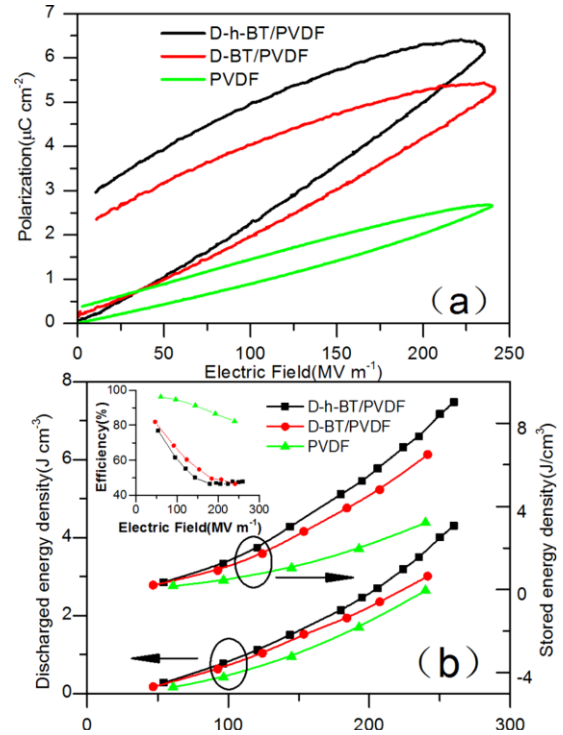


Fig. 1.7 (a) Unipolar polarization loop (b) energy density and incorporated energy efficiency of PVDF film, D-BT/PVDF, and D-h-BT/PVDF nanocomposite film. [58]

different processing ways such as sonification, quenching, and functionalization etc.^{40,67,68}. Among them, surface functionalization of ceramic nanoparticles with different functional groups (such as $-\text{OH}$, $-\text{NH}_2$, $-\text{SO}_3\text{H}$ etc.) before incorporating it into the polymer matrix affects the dielectric and energy storage properties significantly^{11,69,70}. As above discussion the functionalized BST nanofiber shows high dielectric constant, energy density and efficiency.

Among all ceramic materials $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ has very high dielectric constant ($\sim 10^5$) over a wide frequency and temperature range. Obviously, its loss is very high. But the interfacial modification in its composite with PVDF could minimize the dielectric loss. This material could also be a better choice as ceramic filler in the PVDF based composite to develop the material for high energy density capacitor applications. The subsequent section will briefly describe crystal structure, method of processing and its effect on dielectric behavior and origin of very high dielectric constant.

1.4 STUDIES ON CALCIUM COPPER TITANATE

The crystal structure and the dielectric behavior of calcium copper titanate (synthesized by various methods) are discussed in the subsections.

1.4.1 Calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) crystal structure

Subramanian *et al.*, discovered a calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) from the same family of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ family^{19,20}. Deschanvers *et al.*, were discovered $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) when it replace A with Ca of $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ family⁷¹. Admas *et al.*, study the symmetry of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ compound⁷². An ideal cubic perovskite structure ($\text{A}'\text{A}''\text{BO}_3$) represents the crystal structure of CCTO with Ca^{2+} ions Cu^{2+} ions sharing the A-site cations which lead to a 4-coordinate square-planar and Ti^{4+} sits at the B site. The difference in the size of the Ca^{2+} and Cu^{2+} ion leads to the tilting of TiO_6 octahedra which leads to a body centered cubic cell with space group $\text{Im}\bar{3}$. This tilting, (at an angle of 141°) leads to a 4-coordinate square planar environment for Cu and a 12-coordinate

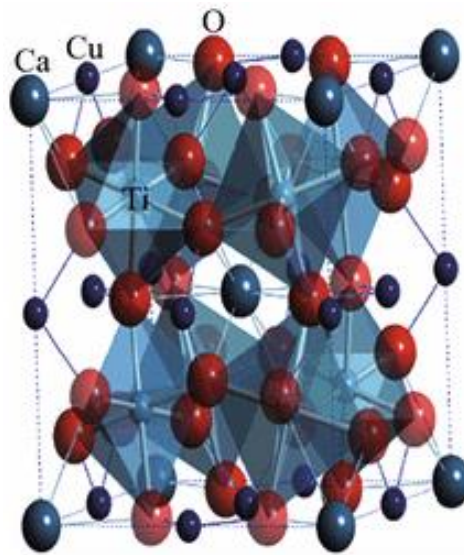


Fig. 1.8 Crystal cubic structure of calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$). [56]

icosahedral environment for Ca. Also, due to this tilting the Ti^{4+} ions occupy a centrosymmetric position in the octahedra sites. The Ti^{4+} ions can be easily displaced off the center along their one-threefold axis and hence this transition is not purely ferroelectric as the displacements occur along with four different directions. So, CCTO has a perovskite structure, and its dielectric constant increases due to the tension of Ti-O bonds. The crystal structure of CCTO is shown in fig 1.8 ⁵⁶.

1.4.2 Dielectric behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

Subramanian *et al.* discovered the single -crystal $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) with high dielectric constant ($\sim 10^5$) and its stable with a temperature range of 100~600 K ^{19,73}. Some important facts of the CCTO material are as follows;

- CCTO with a giant dielectric constant in the range of $\sim 10^5$ for polycrystalline and single crystal material. Dielectric constant remains stable at higher temperature range 100 K and 600 K and stable in low frequency region 10^2 - 10^5 Hz.
- CCTO is non-ferroelectric nature so it is stable at higher temperatures ⁷⁴. There is no phase transition upto $\sim 800^\circ\text{C}$ whereas in ferroelectric material there is a phase change at curie temperature.
- High tangent loss found to be ~ 0.1 of CCTO material but it can be overcome by adapting suitable synthesis, calcinations, and sintering temperature.

There are various methods have been adopted to synthesize the micro and nanosize CCTO powders.

Table 1.4 Represent the comparative study of different methods to prepare $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder and sintering temperature effects on its electrical studies.

Methods	Particle size	Dielectric constant at 1 kHz (~)	Tangent loss at 1kHz (~)	Sintering Temperature ($^\circ\text{C}$)	References
Solid-state	3 μm	12400	0.6	1120	^{75,76}
Wet chemistry	4-15 μm	39008	0.05	1030	⁷⁴
Sol-gel	50 nm	30000	0.091	1050	^{76,77}
Sol-gel combustion	189-300 nm	6800	0.21	1000	⁷⁷
Co-precipitation	2-5 μm	12300	0.2	1100	⁷⁸

The method of synthesis and sintering temperature is found to affect dielectric properties. Table 1.4 shows different methods of synthesis, particle size and corresponding dielectric behavior of CCTO ceramic materials.

Vangchgyia *et al.*,⁷⁹ have found that nonlinear coefficient and dielectric behavior is influenced by sintering time, where microstructure shows the micron size of particle. Nanoparticle of giant dielectric material CCTO has also been synthesized by sol gel technique. Where the size of nanoparticles is found to be in the range of 80 - 120 nm. Sun *et al.*,⁸⁰ has prepared the CCTO powder by sol-gel method. He has also found that the sintering time has an influence on the dielectric constant, breakdown field and non-linear coefficient. Grain boundary barrier layer (GBBL) capacitor model supporting current-voltage (I-V) and cole-cole plots results are also discussed. The physical phenomena that is responsible for very high dielectric constant is extrinsic or intrinsic in nature, is not very clear till date. It is still a matter of investigation. Sinclair *et al.*,⁸¹ have envisaged that the high dielectric constant of CCTO due to internal barrier layer capacitance (IBLC). Several research groups have interpreted the observed value of very high dielectric constant in various ways. They are as follows:

- Synthesis and sintering temperature^{19,82} difference between grain interiors and grain boundaries⁸¹.
- The space charge lie between the surface of sample and the electrodes contacts^{83,84}.
- Due to lattice distortions⁸⁵ and, oxygen vacancies contribution in the dipolar polarization^{86,87}.
- Due to incomparable ionic radius of Ca/Cu sometimes Cu occupying the Ca site contributing to the high dielectric constant.

1.5 AIM OF THESIS

As discussed above the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles could be a prospective ceramic filler in PVDF matrix to make PVDF-CCTO nanocomposite. Thorough and detailed investigation of dielectric and energy storage behavior of this nanocomposite could be of very much importance for academic scientific and technological community. CCTO materials exhibit very high dielectric constant and non-ferroelectric in nature. Non ferroelectric behavior of CCTO in the nanocomposite leads to low energy loss in PVDF-CCTO nanocomposite, which

could improve the energy efficiency. One underlying problem of CCTO is pertinent to mention here i.e. its high dielectric loss. This problem of CCTO could be minimized with its nanocomposite with CCTO and interfacial modification. The PVDF-CCTO nanocomposite could be promising material for high energy density capacitors. The interfacial modification of ceramic filler in the polymer matrix is found to affect the dielectric and energy storage behavior. The size of ceramic filler should also be as small as possible in order to withstand the dielectric and mechanical strength of the nanocomposites. The detailed investigation of energy storage behavior is yet to be carried out.

Considering these perspectives, the aim of the thesis is as follows;

- a) To synthesize and characterize the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles.
- b) To investigate the effect of surface functionalization of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ on dielectric behavior of PVDF based nanocomposite.
- c) To investigate the energy storage behavior of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite for high energy density capacitors.

References

- 1 M. Arbatti, X. Shan and Z. Cheng, *Adv. Mater.*, 2007, **19**, 1369–1372.
- 2 A. Srivastava, K. K. Jana, P. Maiti, D. Kumar and O. Parkash, *J. Eng.*, 2015, **2015**, 9.
- 3 W. Xia and Z. Zhang, *IET Nanodielectr*, 2018, **1**, 17–31.
- 4 N. Ortega, A. Kumar, J. F. Scott, D. B. Chrisey and M. Tomazawa, , DOI:10.1088/0953-8984/24/44/445901.
- 5 L. Wang, F. Gao, J. Xu, K. Zhang, J. Kong, M. Reece and H. Yan, *Compos. Sci. Technol.*, 2018, **158**, 112–120.
- 6 N. Yadav, K. Mishra and S. Hashmi, *High Perform. Polym.*, 2018, **30**, 957–970.
- 7 Z. H. Dai, T. Li, Y. Gao, J. Xu, J. He, Y. Weng and B. H. Guo, *Compos. Sci. Technol.*, 2019, **169**, 142–150.
- 8 H. Luo, X. Zhou, C. Ellingford, Y. Zhang, S. Chen, K. Zhou, D. Zhang, C. R. Bowen and C. Wan, *Chem. Soc. Rev.*, 2019, **48**, 4424–4465.
- 9 P. Gupta, A. Kumar, M. Tomar, V. Gupta and D. P. Singh, *J. Mater. Sci. Mater. Electron.*, 2017, **28**, 11806–11812.
- 10 H. Tang and H. A. Sodano, *Nano Lett.*, 2013, **13**, 1373–1379.
- 11 and Z. W. Liu Shaohui, Zhai Jiwei, Wang Jinwen, Xue Shuangxi, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1533–1540.
- 12 R. Ranjan, S. K. Mishra and D. Pandey, *J. Appl. Phys.*, 2002, **92**, 3266.
- 13 H. Tang, Z. Zhou and H. A. Sodano, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5450–5455.
- 14 A. Wu, P. M. Vilarinho, I. M. M. Salvado and J. L. Baptista, *J. Am. Ceram. Soc.*, 2000, **83**, 1379–1385.
- 15 P. Dias, A. Hiltner, E. Baer, J. Van Dun, H. Chen and S. P. Chum, *Annu. Tech. Conf. -*

ANTEC, Conf. Proc., 2006, **5**, 2660–2664.

- 16 S. Gahlot, V. Kulshrestha, G. Agarwal and P. K. Jha, *Macromol. Symp.*, 2015, **357**, 173–177.
- 17 N. M. K. Abdel-Gawad, A. Z. E. Dein, D. E. A. Mansour, H. M. Ahmed, M. M. F. Darwish and M. Lehtonen, *IEEE Trans. Dielectr. Electr. Insul.*, 2017, **24**, 3490–3499.
- 18 W. Li, Q. Meng, Y. Zheng, Z. Zhang, W. Xia and Z. Xu, *Appl. Phys. Lett.*, 2010, **96**, 94–97.
- 19 M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, *J. Solid State Chem.*, 2000, **151**, 323–325.
- 20 A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt and S. M. Shapiro, *Solid State Commun.*, 2000, **115**, 217–220.
- 21 X. Zhang, Y. Zhao, Y. Wu and Z. Zhang, *Polymer (Guildf)*, 2017, **114**, 311–318.
- 22 P. Martins, A. C. Lopes and S. Lanceros-Mendez, *Prog. Polym. Sci.*, 2014, **39**, 683–706.
- 23 S. Lanceros-Méndez, J. F. Mano, A. M. Costa and V. H. Schmidt, *J. Macromol. Sci. Part B*, 2001, **40**, 517–527.
- 24 Z. Zhang, H. Yang, H. Wang, X. Ding, Q. Zhang and Z. Zhu, *J. Mater. Sci. Mater. Electron.*, 2019, **30**, 2501–2511.
- 25 G. Subodh, V. Deepu, P. Mohanan and M. T. Sebastian, *Polym. Eng. Sci.*, 2009, **49**, 1218–1224.
- 26 A. M. El Sayed and W. M. Morsi, *Polym. Compos.*, 2013, **34**, 2031–2039.
- 27 R. Nangia, N. K. Shukla and A. Sharma, *IOP Conf. Ser. Mater. Sci. Eng.*, 2017, **225**, 012044.
- 28 M. K. Mohanapriya, K. Deshmukh, K. Chidambaram, M. B. Ahamed, K. K. Sadasivuni, D. Ponnammam, M. A. A. AlMaadeed, R. R. Deshmukh and S. K. K. Pasha,

- J. Mater. Sci. Mater. Electron.*, 2017, **28**, 6099–6111.
- 29 X. Cai, T. Lei, D. Sun and L. Lin, *RSC Adv.*, 2017, **7**, 15382–15389.
 - 30 S. Satapathy, S. Pawar, P. K. Gupta and K. B. R. Varma, *Bull. Mater. Sci.*, 2011, **34**, 727–733.
 - 31 H. Parangusan, D. Ponnammam and M. Al Ali Almaadeed, *RSC Adv.*, 2017, **7**, 50156–50165.
 - 32 S. L.-M. V. Sencadas, R. Gregorio Jr, *J. Macromol. Sci. Part B Phys.*, 2015, **2348**, 514–525.
 - 33 P. Singh, H. Borkar, B. P. Singh, V. N. Singh and A. Kumar, *AIP Adv.*, 2014, **4**, 087117.
 - 34 J. Li, Q. Meng, W. Li and Z. Zhang, *J. Appl. Polym. Sci.*, 2011, **122**, 1659–1668.
 - 35 C. Dung and E. Sasaki, *Sensors*, 2016, **16**, 601.
 - 36 G. dong Kang and Y. ming Cao, *J. Memb. Sci.*, 2014, 463, 145–165.
 - 37 D. Hernández-Rivera, G. Rodríguez-Roldán, R. Mora-Martínez and E. Suaste-Gómez, *Sensors (Switzerland)*, , DOI:10.3390/s17051009.
 - 38 Y. Li, C. Liao and S. C. Tjong, *Nanomaterials*, 2019, **9**, 952.
 - 39 P. Y. Raval, A. R. Makadiya, P. R. Pansara, P. U. Sharma, N. H. Vasoya, J. A. Bhalodia, S. Kumar, S. N. Dolia and K. B. Modi, *Mater. Chem. Phys.*, 2018, **212**, 343–350.
 - 40 F. Shi, J. Ma, P. Wang and Y. Ma, *J. Taiwan Inst. Chem. Eng.*, 2012, **43**, 980–988.
 - 41 S. Lotfian, C. Giraudmaillet, A. Yoosefinejad, V. K. Thakur, H. Y. Nezhad and U. K. Bedford, *ACS Omega*, 2018, **3**, 8891–8902.
 - 42 W. X. and Z. X. Wenjing Li, Qingjie Meng, Yuansuo Zheng, Zhicheng Zhang, *Appl. Phys. Lett.*, 2010, **96**, 192905.

- 43 J. Yuan, S. Yao and P. Poulin, in *Polymer Nanocomposites: Electrical and Thermal Properties*, Springer International Publishing, 2016, pp. 3–28.
- 44 K. W. Wagner, *Arch. für Elektrotechnik*, 1914, **2**, 371–387.
- 45 T. Mizutani, T. Nagata and M. Ieda, *J. Phys. D. Appl. Phys.*, 1984, **17**, 1883–1887.
- 46 J. J. T. J.C. Maxwell, 1892, **1**, 1–500.
- 47 W. X. and Z. X. Wenjing Li, Qingjie Meng, Yuansuo Zheng, Zhicheng Zhang Zhang, *Appl. Phys. Lett.*, 2010, **96**, 192905.
- 48 S. L. Zhong, Z. M. Dang, W. Y. Zhou and H. W. Cai, *IET Nanodielectrics*, 2018, **1**, 41–47.
- 49 M. Xiao, L. Sun, J. Liu, Y. Li and K. Gong, *Polymer (Guildf)*, 2002, **43**, 2245–2248.
- 50 H. Tang and H. A. Sodano, *Nano Lett.*, 2013, **13**, 1373–1379.
- 51 J. Fu, Y. Hou, M. Zheng, Q. Wei, M. Zhu and H. Yan, *ACS Appl. Mater. Interfaces*, 2015, **44**, 24480–24491.
- 52 J. Zhang, J. Ma, L. Zhang, C. Zong, A. Xu, Y. Zhang, B. Geng and S. Zhang, *RSC Adv.*, 2020, **10**, 7065–7072.
- 53 S. Chen, J. Hu, L. Gao, Y. Zhou, S. Peng, J. He and Z. Dang, *RSC Adv.*, 2016, **6**, 33599–33605.
- 54 W. B. Li, D. Zhou, L. X. Pang, R. Xu and H. H. Guo, *J. Mater. Chem. A*, 2017, **5**, 19607–19612.
- 55 G. Hu, F. Gao, J. Kong, S. Yang, Q. Zhang, Z. Liu, Y. Zhang and H. Sun, *J. Alloys Compd.*, 2015, **619**, 686–692.
- 56 M. Ahmadipour, M. F. Ain and Z. A. Ahmad, *Nano-Micro Lett.*, 2016, **8**, 291–311.
- 57 P. S. Dobal and R. S. Katiyar, *J. Raman Spectrosc.*, 2002, **33**, 405–423.
- 58 L. Gao, J. He, J. Hu and Y. Li, *J. Phys. Chem. C*, 2014, **118**, 831–838.

- 59 K. Yu, H. Wang, Y. Zhou, Y. Bai and Y. Niu, *J. Appl. Phys.*, 2013, **113**, 034105.
- 60 C. V. Chanmal and J. P. Jog, *Express Polym. Lett.*, 2008, **2**, 294–301.
- 61 C. Yang, H. S. Song and D. B. Liu, *Compos. Part B Eng.*, 2013, **50**, 180–186.
- 62 W. Yang, S. Yu, R. Sun and R. Du, *Acta Mater.*, 2011, **59**, 5593–5602.
- 63 P. Thomas, S. Satapathy, K. Dwarakanath and K. B. R. Varma, *Express Polym. Lett.*, 2010, **4**, 632–643.
- 64 S. S. Chen, J. Hu, L. Gao, Y. Zhou, S. M. Peng, J. L. He and Z. M. Dang, *RSC Adv.*, 2016, **6**, 33599–33605.
- 65 H. L. W. Chan, M. C. Cheung and C. L. Choy, *Ferroelectrics*, 1999, **224**, 113–120.
- 66 S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai and Z. An, *RSC Adv.*, 2015, **5**, 40692–40699.
- 67 L. Tshwenya and O. A. Arotiba, *RSC Adv.*, 2017, **7**, 34226–34235.
- 68 L. Xie, X. Huang, C. Wu and P. Jiang, *J. Mater. Chem.*, 2011, **21**, 5897–5906.
- 69 S. Liu, S. Xue, S. Xiu, B. Shen and J. Zhai, *Nat. Publ. Gr.*, 2016, 1–11.
- 70 J. Li, J. Claude, L. E. Norena-Franco, S. Il Seok and Q. Wang, *Chem. Mater.*, 2008, **20**, 6304–6306.
- 71 P. Thongbai, J. Jumpatam, B. Putasaeng, T. Yamwong, V. Amornkitbamrung and S. Maensiri, *J. Mater. Sci. Mater. Electron.*, 2014, **25**, 4657–4663.
- 72 T. B. Adams, D. C. Sinclair and A. R. West, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2006, **73**, 094124.
- 73 C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto, S. Wakimoto, M. A. Subramanian and A. P. Ramirez, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2003, **67**, 092106.
- 74 J. Liu, R. W. Smith and W. N. Mei, *Chem. Mater.*, 2007, **19**, 6020–6024.
- 75 S. Kawrani, M. Boulos, D. Cornu and M. Bechelany, *ChemistryOpen*, 2019, **8**, 922–

950.

- 76 W. Q. Ni, X. H. Zheng and J. C. Yu, *J. Mater. Sci.*, 2007, **42**, 1037–1041.
- 77 M. Ahmadipour, M. Hatami and K. V. Rao, *Adv. Nanoparticles*, 2012, **01**, 37–43.
- 78 B. Barbier, C. Combettes, S. Guillemet-Fritsch, T. Chartier, F. Rossignol, A. Rumeau, T. Lebey and E. Dutarde, *J. Eur. Ceram. Soc.*, 2009, **29**, 731–735.
- 79 S. Vangchangyia, E. Swatsitang, P. Thongbai, S. Pinitsoontorn, T. Yamwong, S. Maensiri, V. Amornkitbamrung and P. Chindaprasirt, *J. Am. Ceram. Soc.*, 2012, **95**, 1497–1500.
- 80 D. L. Sun, A. Y. Wu and S. T. Yin, *J. Am. Ceram. Soc.*, 2008, **91**, 169–173.
- 81 D. C. Sinclair, T. B. Adams, F. D. Morrison and A. R. West, *Appl. Phys. Lett.*, 2002, **80**, 2153–2155.
- 82 T. B. Adams, D. C. Sinclair and A. R. West, *J. Am. Ceram. Soc.*, 2006, **89**, 2833–2838.
- 83 P. Lunkenheimer, R. Fichtl, S. G. Ebbinghaus and A. Loidl, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2004, **70**, 1–4.
- 84 P. Lunkenheimer, V. Bobnar, V. Bobnar, A. V. Pronin, A. V. Pronin, A. I. Ritus, A. A. Volkov and A. Loidl, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2002, **66**, 521051–521054.
- 85 S. Y. Chung, *Appl. Phys. Lett.*, 2005, **87**, 2003–2006.
- 86 L. Fang, M. Shen and W. Cao, *J. Appl. Phys.*, 2004, **95**, 6483–6485.
- 87 R. Schmidt, M. C. Stennett, N. C. Hyatt, J. Pokorny, J. Prado-Gonjal, M. Li and D. C. Sinclair, *J. Eur. Ceram. Soc.*, 2012, **32**, 3313–3323.

CHAPTER 2
EXPERIMENTAL
TECHNIQUES

2. 1 INTRODUCTION

This chapter presents details of the various techniques used for the preparation and characterization of ceramics and polymer nanocomposites. Polyvinylidene fluoride (PVDF) polymer films are prepared by the solution casting method. Ceramic calcium copper titanate (CCTO) nanoparticles are prepared by the sol-gel method. The CCTO nanoparticles further incorporated in the PVDF matrix to make polymer - ceramic nanocomposite. PVDF-CCTO nanocomposite films are prepared by solution casting process. X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscope (TEM) measurements are used to investigate the crystallographic structure, surface morphology, and particle size of CCTO nanoparticles and PVDF-CCTO nanocomposite films. Fourier transform infrared spectroscopy (FTIR) measurement is employed to investigate the bonding and different polymorph present in the PVDF-CCTO nanocomposite films. The dielectric measurement is used to understand the capacitive and dielectric behavior of CCTO pellets and PVDF-CCTO nanocomposite films. Displacement vs electric field measurement is carried out to find the discharging and charging, energy density, energy efficiency of the capacitor based on PVDF-CCTO nanocomposite films. Current-voltage (I-V) measurement is used to investigate the transport behavior of CCTO pellets. In this chapter, a brief description of all experimental techniques which have been done to understand the behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles and PVDF-CCTO nanocomposite films in order to make a reliable material for high energy density capacitor.

2. 2 SYNTHESIS OF MATERIAL

Polyvinylidene fluoride (PVDF), calcium copper titanate (CCTO) nanoparticles, and PVDF-CCTO nanocomposite films are synthesized for studying the dielectric and energy storage behavior of these materials. The following methods have been used in the synthesis of PVDF, CCTO nanoparticles, and PVDF-CCTO nanocomposite films. Functionalization of CCTO nanoparticles has also been carried out to investigate their effect on dielectric and energy storage behavior.

2.2.1 Synthesis of polyvinylidene fluoride thick films

PVDF thick films are prepared by solution casting method. 2 grams of PVDF powder is dissolved in 100 ml of N-N Dimethylformamide (DMF), (Sigma Aldrich). This solution is magnetically stirred at 50°C. When the solution becomes thick, it is poured into the petridish.

This solution is dried at 160°C in a vacuum oven to evaporate the DMF. PVDF thick film of thickness of 20-30 µm is separated out from petridish. These films have been annealed at 50°C, 90°C, 100°C, 110°C and 130°C respectively for 5 hours in air. A schematic diagram for the synthesis of thick film prepared by solution casting is shown in fig. 2.1.

2.2.2 Synthesis of calcium copper titanate nanoparticles

CaCu₃Ti₄O₁₂ (CCTO) nanoparticles are prepared by using sol-gel technique. Calcium nitrate tetrahydrate (Ca(NO₃)₂·4H₂O), copper nitrate trihydrate (Cu(NO₃)₂·3H₂O) and titanium (IV) isopropoxide (C₁₂H₂₈O₄Ti) (all from Sigma Aldrich) are used as a raw materials. A stoichiometry ratio of calcium nitrate tetrahydrate and copper nitrate trihydrate is dissolved in ethanol separately.

When both the solutions became homogenous, they are mixed and labeled as solution I. A second solution of titanium isopropoxide in acetylacetone is prepared and labeled as solution II. Solutions I and II are mixed at a room temperature and a sol is formed by heating the mixture at 90°C. Then, diluted ethanol is added dropwise in the above solution to obtain a gel. The formed gel is dried at 140°C for 5 hours to get the precursor of CaCu₃Ti₄O₁₂, which is grinded in an agate mortar to get a fine powder. The obtained precursor powder is then calcined at 900°C for 3 hours to get brown colored CaCu₃Ti₄O₁₂ powder. CCTO powder is calcined at three different temperatures 800°C, 900°C and 1000°C for 3 hours to attain a pure phase of CCTO. The pure phase of CCTO is attained by calcining the CCTO powder at 900°C for 3 hours. Calcination is a process of heating a substance to a high temperature but below the melting or fusing point, causing loss of moisture, reduction or oxidation, and dissociation into simpler substances. The calcined CCTO powder is pelletized, compressed, and sintered for same temperature which is used for calcination. Time and temperature for calcination and sintering are same to avoid the crystalline growth of CCTO.

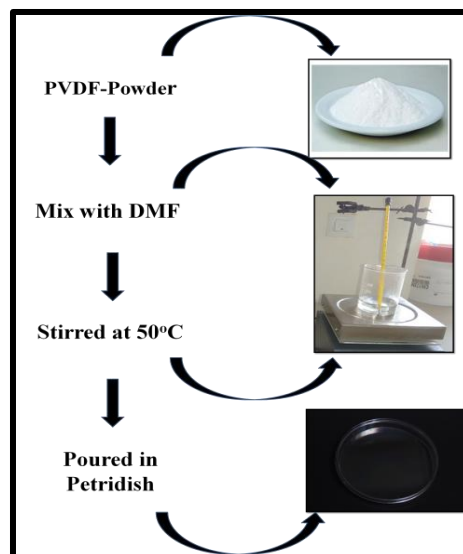


Fig. 2.1 Schematic diagram of polyvinylidene fluoride thick films prepared by solution casting method

2.2.3 Synthesis of polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films by solution casting

PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films with different vol% loading of CCTO nanoparticles are prepared by solution casting technique. Initially, the poly(vinylidene fluoride) (PVDF) powder is dissolved in N, N-Dimethylformamide (DMF) and stirred for 2 hours at a room temperature by using a magnetic stirrer. The different volume fraction of CCTO nanoparticles (4, 8, 12, and 15 vol %) are added in PVDF solvent. After the addition of CCTO nanoparticles, the solutions are sonicated for 1 hour for ensuring the proper dispersion of CCTO

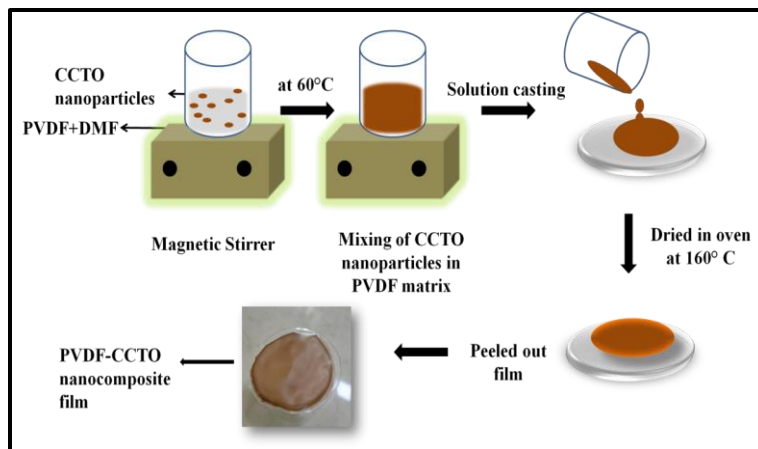


Fig. 2.2 Schematic representation of solution-casting process for making polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick film

nanoparticles in PVDF solvent to form the matrix. The sonicated solution is stirred for 3-4 hours at 60°C for the homogenous mixing of CCTO nanoparticles in PVDF matrix. This process makes the solution viscous, which is poured into petridish. It is dried at 160°C in a vacuum oven to evaporate rest of the DMF. The dried nanocomposite thick films are easily peeled off from the petridish at room temperature. The thickness of the dried nanocomposite films is ~ 80 µm. A schematic diagram for the synthesis of PVDF-CCTO nanocomposite thick films is shown in fig. 2.2

2.2.4 Functionalization of calcium copper titanate nanoparticles

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles are prepared by sol-gel method. The 5 grams of CCTO powder is dispersed in 500 ml N, N-Dimethylformamide (DMF) through sonication for 15 minutes. This solution is stirred with magnetic stirrer at room temperature for 1 hour and 500 ml ethylenediamine (EDA) is added in stirred solution. This solution is subjected to continuous stirring further for 1 hour. This solution is heated to 60°C along with continuous stirring for 6 hours. The stirred and heated solution is allowed to cool down to room temperature. Cooled solution is subjected to centrifugation at 9000 rpm for 10 min. The centrifuged product is

dried at 60°C for 12 hrs, which result in functionalized CCTO nanoparticles with amine (---NH₂) group. A schematic diagram for the synthesis of CCTO nanoparticles functionalized by amine (----NH₂) group is shown in fig. 2.3. Finally, the

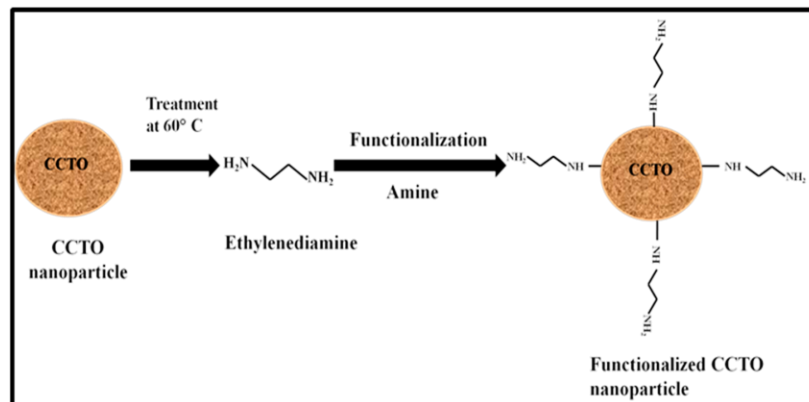


Fig: 2.3 Schematic representation of functionalization of CaCu₃Ti₄O₁₂ nanoparticles by ethylenediamine.

functionalized CCTO nanoparticles are loaded into the polymer matrix at the 8 vol% and casting process for making PVDF-CCTO nanocomposite film is done same as mentioned in above section 2.2.2.

2.3 CHARACTERIZATION TECHNIQUES

The characterization of synthesized samples is broadly divided into three categories viz. structural, thermal, and electrical characterization.

Structural characterization includes x-ray diffraction (XRD), scanning electron microscope (SEM), electron dispersive x-ray spectroscopy (EDXS), transmission electron microscopy (TEM), and fourier transform infrared spectroscopy (FTIR). Electrical characterization includes dielectric, displacement vs electric field, and I-V measurements.

2.3.1 Structural characterization

X-ray diffraction (XRD) has been used for crystallographic phase identification of any material. SEM is used to detect the surface morphology, whereas TEM is employed to investigate the particle size & morphology of the material.

2.3.1.1 X- ray diffraction

X-ray diffraction is basically used to find out the crystal structure of the material. These X-rays are generated by a cathode ray tube, which are filtered to produce monochromatic radiation. The monochromatic radiation is collimated and directed towards the samples¹. When the incident rays interact with the sample it produces constructive interference which is satisfied by Bragg's law

$$n\lambda = 2d \sin\theta \dots\dots\dots (2.1)$$

Here, d is the spacing between diffracting planes, θ is the incident angle, n is an integer, and λ is the wavelength of the beam. X-rays are used to produce the diffraction pattern because their wavelength λ is typically of the same order of magnitude (1-100 angstroms) with spacing (d) between planes in the crystal. Diffraction peak positions are accurately measured with XRD, which makes it best method for characterizing homogeneous and inhomogeneous strains.

In this work, X-ray diffraction pattern (PANalytical) has been used for identification of crystallographic phases of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles and PVDF-CCTO nanocomposite thick films.

2.3.1.2 Scanning electron microscope

A scanning electron microscope (SEM) is one of the resourceful instruments that is used to the analysis of the microstructure and surface morphology of the sample. SEM utilizes accelerated electrons at high voltage instead of light to form an image³. The focused electron beam hits the surface of the sample, the interaction between an electron beam and sample generates varied signals, and these signals are detected by the detectors to get the information about the sample composition, surface topography. Secondary electrons are emitted from the surface of the sample during interaction plays an important role to detecting the morphology and topography of the sample whereas backscattered electron shows contrast in the composition of the elements of the sample. Detectors collect these backscattered electrons, diffracted backscattered electrons, secondary electrons and convert them into a signal that is sent to a screen. Final image of the sample is achieved.

In this work, JEOL JSM-6610LV, SEM has been used to analyze the microstructure and surface morphology of CCTO nanoparticles and PVDF- CCTO nanocomposite thick films.

2.3.1.3 Electron dispersive X-ray spectroscopy analysis

Energy dispersive X-ray spectroscopy (EDXS) is an analytical technique to determine the elemental composition of the individual elements present in a sample⁴. When an electron beam interacts with the surface of the sample, it emits the X-rays of specific wavelength, which are the characteristics of the atomic structure which is most probably known as Moseley's law². Spectrum of X-ray energy versus counts is evaluated to determine the elemental composition of the sampled volume.

In this work, Agilent Resolution Pro Cary 660, EDX has been used to detect the chemical composition of calcium (Ca), Copper (Cu) and titanate (Ti) and oxygen (O) in $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles.

2.3.1.4 Transmission electron microscope

Transmission electron microscope (TEM) has a much higher spatial resolution than SEM and facilitates the study of the inner structure and analysis of the features on the atomic scale (in the range of few nanometers). TEM provides high resolution image of the specimen and is used to study the growth layers, their composition, and defects in semiconductors as well as in various other fields of materials science ⁵. In TEM a beam of electrons (60-350 keV) is transmitted through the specimen to form a monochromatic image, which provides details of morphological, compositional, and crystallography information of the sample. Sometimes TEM can reveal the finest details of internal structure (i.e. as small as individual atoms).

In this work Tecnai G2, F30 high resolution TEM is used for investigating the particle size and its distribution of CCTO nanoparticles. The sample for TEM has been prepared by adding small amount of ethanol in CCTO nanoparticles and dropping this solution onto carbon coated grids.

2.3.1.5 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) absorption or transmission spectra is used to characterize the chemical changes and to determine the functional group present in any compound/sample. The wavelength and wave number ranges of the IR are 2.5- 25 μm and 4000 cm^{-1} - 400 cm^{-1} respectively. When IR radiation is incident on the sample, it absorbs only particular wavelengths of IR radiation which is characteristic of the sample ⁶. The remaining radiations is either transmitted or reflected from the sample, which gives the information regarding the vibrations of atomic and molecular species such as change in bond length (stretching) and change in bond length (bending). Interferometer technique (Michelson interferometer) is used to record the transmission spectra of a sample.

In this work, fourier transform infrared spectroscopy (Agilent Resolution Pro Cary 660) has been employed to investigate the bonding and different polymorph present in the PVDF-CCTO nanocomposite thick films. Functionalized CCTO nanoparticles by the amine (--- NH_2) group has also been confirmed by using FTIR measurements.

2.3.2 Electrical properties

The electrical studies are carried out at low field and high field in order to understand transport, dielectric, and energy storage behavior of PVDF, CCTO and PVDF-CCTO nanocomposite thick films.

2.3.2.1 Low field measurements

The dielectric measurement i.e. dielectric constant (permittivity), dielectric loss (tangent loss) and I-V (current-voltage) is measured at low field.

2.3.2.1.1 Dielectric measurements

The dielectric constant is defined as the ratio of the permittivity of the substance to the permittivity of the free space. The capacitance of a parallel plate capacitor is measured as $C = \epsilon_r \epsilon_0 A/d$, where A is the area, ϵ_0 is the absolute permittivity of the free space equal to 8.854 pFm^{-1} and d is the separation between the plates. The dielectric constant is a complex quantity given by $\epsilon = \epsilon' - i\epsilon''$, where ϵ' is related to the amount of electric energy stored in the materials so it is known as storage component and ϵ'' is known as loss component. The dielectric constant measurement of the material involves different types of polarization (i.e. electronic, ionic, orientational/dipolar, and interfacial polarization). Dielectric properties of material are dependent on phases, shape, size, and interfaces among the sample. In low frequency range only electronic and ionic polarization, dipolar polarization occurs, but the microstructure of material also has a large influence on the dipolar, space charge, and ionic polarization. Usually the dielectric constant is measured by LCR meter or impedance analyzer, where the sample is placed in parallel plate configuration and excited by very small voltage i.e. 0.5 V- 5 V. Formation of interfaces in polymer-ceramic nanocomposite also affects the dielectric behavior significantly. Frequency dependent dielectric constant gives information about the relaxation phenomena in different kind of materials.

The dielectric loss or dissipation factor is expressed by tangent loss ($\tan \delta$) and it is defined as;

$$\tan \delta = \frac{\epsilon''}{\epsilon'} \dots\dots\dots(2.2)$$

The total tangent loss is given as;

$$\delta = \delta_{dc} + \delta_{MW} + \delta_{dip} \dots\dots\dots(2.3)$$

Where δ_{dc} and δ_{MW} are the losses interrelated to dc conductivity and interfacial polarization respectively, δ_{dip} represents the loss due to dipolar relaxation⁷. Dielectric properties of CCTO pellet and PVDF-CCTO nanocomposite thin films are measured with an applied voltage of 1.0 V in the frequency range of 10^2 – 10^6 Hz by using Hioki 353250, LCR meter. The silver electrodes are applied on both sides of the pellets and the nanocomposite films by using silver paint to investigate the dielectric properties. The thickness of CCTO pellets and PVDF-CCTO nanocomposite thick films subjected for measuring dielectric behavior are ~ 2 mm and ~ 70 -80 μm respectively.

2.3.2.1.2 Current -voltage characteristics

Current-voltage (I-V) characteristics measurement gives the information about the mechanism of electrical transport i.e. ohmic transport, space charge transport, trap charge transport, etc. Keithley's 2410 source measuring unit is used for the measurement of I-V characteristics of the CCTO pellets in the voltage range (0 V-1100 V). The current-voltage (I-V) characteristics can be converted into current density vs electric field (J-E) characteristics by taking dimension of sample in consideration.

In present work J-E characteristics are used to find out the breakdown voltage and non-linearity of pelletized CCTO samples. Both factors are very important to use a dielectric material for capacitor and other applications. The nonlinear current-voltage behavior indicates the non-Ohmic transport in CCTO as represented as ⁸;

$$I = KV^\alpha \dots\dots\dots (2.4)$$

Where "K" is proportionality constant, and " α " is nonlinear coefficient. The nonlinear coefficient is calculated by using formula ;

$$\alpha = \frac{\partial(\ln I)}{\partial(\ln V)} \dots\dots\dots (2.5)$$

2.3.2.2 High field measurements

The displacement vs electric field measurements have been carried out at high electric field (up to 600 kV/cm), which gives static and electric field dependent energy density, respectively.

2.3.2.2.1 Displacement vs Electric field

The electric displacement is given by $D = \epsilon_0 E + P$, if $\epsilon_0 E \gg P$; the $D \sim P$ [10]. When the dielectric material has high permittivity then D is approximate to P. The energy density is

calculated for nonlinear dielectrics such as ferroelectric and non-ferroelectric materials which exhibits some energy dissipation. In fig. 2.4 the area inside the loop represents the energy loss (U_{loss}) and area above the loops at a maximum value of electric field known as discharging energy density (U_D), and it can be calculated by integrating the effective area between the charging and discharging curves of the displacement loops¹⁰. The energy density of a capacitor is calculated by $U = \int E dD$, where U is the total stored energy density, E is the applied electric field and D is the electric displacement. The charging energy density, discharging energy density and energy loss are schematically represented in fig. 2.4.

The efficiency of the material is also calculated from the displacement loops as represented in equation 2.6. It is defined as the ratio of discharged energy to the total stored energy (i.e. discharged energy and charged energy density).

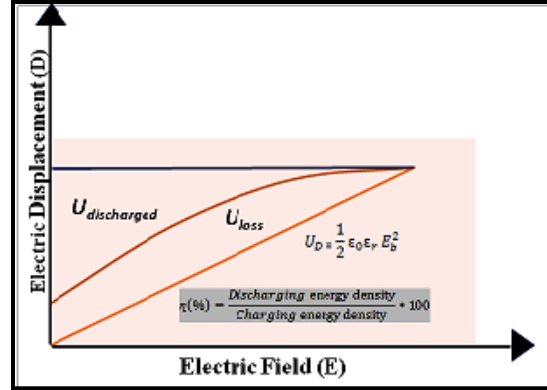


Fig. 2.4 Schematic diagram to calculate the discharged energy density.

$$\eta(\%) = \frac{\text{Discharging energy density}}{\text{Charging energy density}} * 100 \quad \dots\dots\dots (2.6)$$

In this work, displacement loops (D-E) are measured by using premier Radiant-II ferroelectric tester by applying a triangular wave of the frequency of 10 Hz to investigate the energy storage behavior.

References

1. B. D. Cullity, *Elements of X-Ray Diffraction*, Addison-wesley 1956.
2. D. Keith Bowen, Keith D. Bowen, And Brain K Tanner, *High Resolution X-Ray Diffraction and Topography*, Taylor & francis 1998.
3. C. W. Oatley, *The Scanning Electron Microscope, Part1, The instrument*, Cambridge University Press, Cambridge, U.K. 1972.
4. John C. Russ, *Fundamentals of Energy Dispersive X-ray Analysis*, Butterworth-Heinemann 1984.
5. Carter, Barry, Williams, David B, *Transmission Electron Microscopy: A Textbook for Materials Science*, Springer Science & Business Media 2009.
6. J. M. Chalmers, N. J. Everalla, K. Hewitson, M. A. Chestersb, M. Pearsonb, A. Grady, B. Ruzicka, Fourier transform infrared microscopy: some advances in techniques for characterization and structure–property elucidations of industrial material, 1998, **123**, 579–586
7. Y. Li, X. Huang, Z. Hu, P. Jiang, S. Li, T. Tanaka, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4396–4403.
8. Y.H. Lin, J. Cai, M. Li, C.W. Nan, *Appl. Phys. Lett.* 2006, **88**,172902.
9. H. Palneedi, M. Peddigari, G.T. Hwang, D. Y. Jeong, J. Ryu, *Adv. Funct. Mater.* ,2018, **28**, 1803665.
10. X. Zhang, B. W. Li, L. Dong, H. Liu, W. Chen, Y. Shen, and C. W. Nan, *Adv. Mater. Interfaces*, 2018, **5**, 1800096.

CHAPTER 3

***STUDIES ON SYNTHESIS
AND CHARACTERIZATION
OF
POLYVINYLIDENE
FLUORIDE THICK FILMS
AND
 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$
NANOPARTICLES***

3.1 INTRODUCTION

Polymer ceramic nanocomposite has drawn a lot of attention of the scientific community due to its prospect of application in high energy density capacitor, and embedded electronics^{1,2}. Therefore, in order to have a material for the high energy density capacitor, it must have a moderate dielectric constant and high breakdown strength. The ceramic materials have high dielectric constant but low breakdown strength such as materials like BaTiO₃, Ba_xSr_{1-x}TiO₃, PbTiO₃, and CaCu₃Ti₄O₁₂³⁻⁶. Ceramic materials are also used as ceramic filler in polymer ceramic composites to enhance the dielectric constant. On the other hand, polymers such as polyvinylidene fluoride (PVDF), polyvinylidene fluoride-trifluoroethylene (PVDF- TrFE), polyvinyl alcohol (PVA) etc.,⁷⁻⁹ have a low dielectric constant and high breakdown strength. Among these polymers, PVDF is flexible and, has high dielectric breakdown strength but low intrinsic permittivity. PVDF is typically crystallizes with five distinct crystalline structure named as α , β , γ , δ , and ϵ phases⁸. Among them, ϵ and δ phases are rarely studied due to their poor stability¹⁰. The β crystalline form possesses strong polarization, which has a zigzag (all-trans-TTTT) confirmation of the polymer chain and having a net non-zero dipole moment. The development of β -phase content has always attracted great interest; because electro active properties depend on β -phase content. The β -phase form in PVDF could be obtained by stretching, quenching, and polling under a high electric field^{11,12}. For synthesizing polymer ceramic nanocomposite, CaCu₃Ti₄O₁₂ (CCTO) could be promising ceramic filler by virtue of its very high dielectric constant ($\sim 10^4$) over wide temperature range (100 K - 600 K) and frequency range (10^2 Hz - 10^6 Hz)^{13,14}. The PVDF-CCTO nanocomposite is of high interest as novel material for high energy density capacitors. Several studies have been carried out on phase formation in PVDF and synthesis of CCTO particles in nanometer range. The solvent used for processing of PVDF film and the temperature has found to affect PVDF film formed from dimethylformamide (DMF) by solution casting which has been reported to have a stable β -phase at low temperature ($\sim 50^\circ\text{C}$), where the porosity of film is very high, preventing it from electrical applications¹⁵. Effect of annealing temperature on phase transition in poly(vinylidene fluoride) film has been widely studied by different research groups^{8,16,17}. Satapathy *et al.*,⁸ have observed the changes in phase content in the PVDF film formed by using dimethyl sulfoxide (DMSO) at

different annealing temperature that affects the polarization behavior. The crystalline phase transformation and dielectric properties of α and β -phase have also been investigated^{18,19}. Guan *et al.*,¹⁸ have studied the effect of crystalline phase orientation on dielectric and energy storage behavior in PVDF based copolymer. Apart from PVDF, the investigation on synthesis, dielectric and breakdown behavior of calcium copper titanate (CCTO) is also reported in literature^{20–26}. The giant dielectric constant material calcium copper titanate (CCTO) has been synthesized by various methods i.e. like solid state method, sol-gel method, combustion method and co-precipitation method etc.^{21,26–28}. Dielectric behavior of CCTO ceramic prepared by different technique has been widely studied^{23,29,30}. Vangchgyia *et al.*, have found that nonlinear coefficient and dielectric behavior is influenced by sintering time, where microstructure shows the micron size of particle. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramic with high breakdown field of 4032 V/cm and nonlinear coefficient of 7.05 along with high dielectric constant and low loss has also been reported¹⁵. Nanoparticles of giant dielectric material CCTO has also been synthesized by sol gel technique. Where the size of nanoparticles are found to be in the range of 80 - 120 nm^{15,16}.

The dielectric constant of polymer ceramic nanocomposite is increased by adding higher vol % of ceramic fillers but the higher loading of ceramic mostly decreases the breakdown and mechanical strength of the nanocomposite¹⁴, which might prevent its application for high energy density capacitors. The PVDF-CCTO nanocomposite is of high interest as novel material for high energy density capacitors, but before investigating the dielectric and energy storage behavior of PVDF-CCTO nanocomposite following investigations are essential:

1. The effect of annealing temperature on crystalline phase, dielectric and polarization behavior of PVDF thick film which could ultimately affect the energy storage behavior.
2. Size of ceramic filler should be as small as possible as well as its dielectric behavior should be very good. Therefore, optimization of synthesis of CCTO nanoparticles is also essential.

This chapter presents the effect of annealing on structural, dielectric, and polarization behavior of PVDF. It also presents the synthesis, dielectric and energy storage behavior of CCTO nanoparticles. Therefore, this chapter is broadly divided in to two section viz. Sec 3.2 and Sec 3.3, which are as follows:

3.2 STUDIES ON POLYVINYLIDENE FLUORIDE THICK FILMS

The effect of annealing on structural, crystalline, dielectric and polarization behavior of PVDF thick films has been investigated. The studies on PVDF thick films annealed at different temperature has been discussed in below section.

3.2.1 EXPERIMENTAL

The experimental studies include the synthesis of polymer, structural, dielectric and energy density of PVDF thick films, which are described in the following sections:

3.2.1.1 Synthesis of polyvinylidene fluoride thick films

PVDF thick films are prepared by solution casting method. 2 gm PVDF powder is dissolved in 100 ml of N-N Dimethylformamide (DMF), Sigma Aldrich. This solution is magnetically stirred at 50°C. When the solution becomes thick it is poured into the petridish. This solution is dried at 160°C in a vacuum oven in order to evaporate the DMF. PVDF thick films of thickness of 20 - 30 μm are separated out from petridish. These films have been annealed at 50°C, 90°C, 100°C, 110°C and, 130°C respectively for 5 hours in the air.

3.2.1.2 Structural studies

X-ray diffractions (XRD), scanning electron microscope (SEM) studies have been carried out to confirm the phases and surface morphology respectively. Fourier transform infrared spectroscopy (FTIR) has been done in order to find out the various functional groups and bonds present in the material.

3.2.1.3 Dielectric measurements

Dielectric constant is the measure of the amount of electric potential energy, in the form of induced polarization that stored in the material (Sec 2.3.2.1.1).⁵ The PVDF thick film is of rectangular shape. The gold electrodes of area (0.25 cm^2) are sputtered on both sides of films by using Auto fine coater-JEOL, JEC-3000FC.

3.2.1.4 Polarization vs Electric field measurements

The polarization vs electric field studies are carried out in order to understand the effect of annealing on polarization behavior. The details of the polarization vs electric field measurement are already discussed in the Sec.2.3.2.1.

3.2.2 RESULT AND DISCUSSION

PVDF thick films has been prepared by a solution casting method. The prepared films are subjected to be annealing at different temperatures such as 50°C, 90°C, 100°C, 110°C and 130°C for 5 hours. The effect of annealing on structural, dielectric and polarization behavior of the PVDF thick films are discussed in the following sections.

3.2.2.1 Structural studies

The results of X– ray diffraction (XRD), scanning electron microscope (SEM), and Fourier transform infrared spectroscopy (FTIR) are discussed in the subsequent sections.

3.2.2.1.1 X-ray diffraction

Figure 3.1 shows the X-ray diffractogram of PVDF thick films annealed at different temperatures.

Two peaks appearing at $2\theta = 18.4^\circ$ and 20° corresponds to α -phase of PVDF and are corresponding to (0 2 0) and (1 1 0) planes respectively³¹. The peaks of γ -crystalline phase appears at $2\theta = 18.5^\circ$ (0 2 0) and 20.1° (1 1 0); whereas the presence of β -phase is confirmed by peaks at 20.7° (2 0 0) and 20.8° (1 1 0)^{8,32,33}.

In our case, the PVDF film annealed at 90°C shows prominent peak corresponding to β -phase at $2\theta = 20.7^\circ$ (2

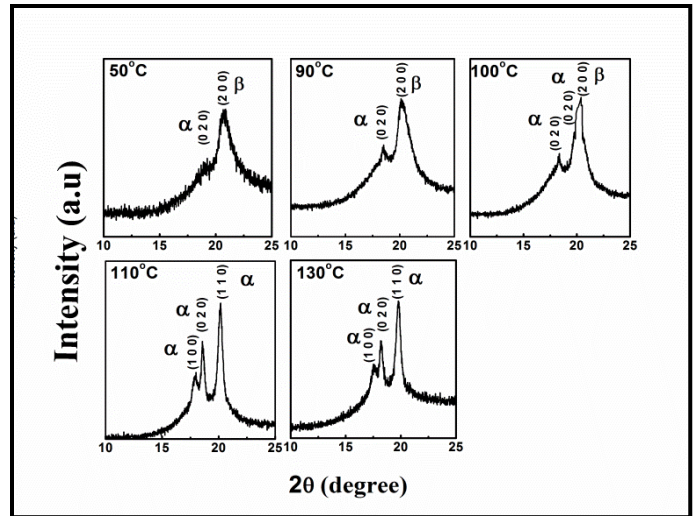


Fig. 3.1 X-ray diffractogram of PVDF thick film annealed at different temperatures.

0 0) and weak peak at $2\theta = 19.1^\circ$ (1 1 0) corresponds to α -phase. When the annealing temperature is increased, the peak of α -phase ($2\theta = 19.1^\circ$) is becoming prominent along with β -phase.

The increase in annealing temperature usually promotes the growth of crystallite size. The broadening in the peak of β -phase for the film annealed at 90°C is smaller than the film annealed at 50°C ; which confirms that crystalline size of β -phase for the film annealed at 90°C is larger than the film annealed at 50°C . But for the film annealed at 100°C , no intense peak of β -phase of PVDF has been observed. Two peaks of α -phase are occurring along with β -phase for the film annealed at 100°C ; which indicates that α -phase is growing at the cost of β -phase. The conversion of β -phase into α -phase may be arising due to thermally induced chain reorientation³¹. When the annealing temperature is increased upto 110°C , the peak of β -phase PVDF i.e. $2\theta = 20.7^\circ$ (2 0 0) completely disappeared. The XRD studies have made it clear that α and β -phase of PVDF are in coexistence for the film annealed upto 100°C ; but β -phase completely disappears for the film annealed at temperature greater or equal to 110°C .

3.2.2.1.2 Scanning electron microscope

Scanning electron microscope (SEM) micrographs of PVDF film annealed at different temperatures is shown in fig 3.2. Film annealed at 50°C exhibits randomly oriented grain of $\sim 6\ \mu\text{m}$. The sizes of grains decrease with increase in annealing temperature upto 100°C .

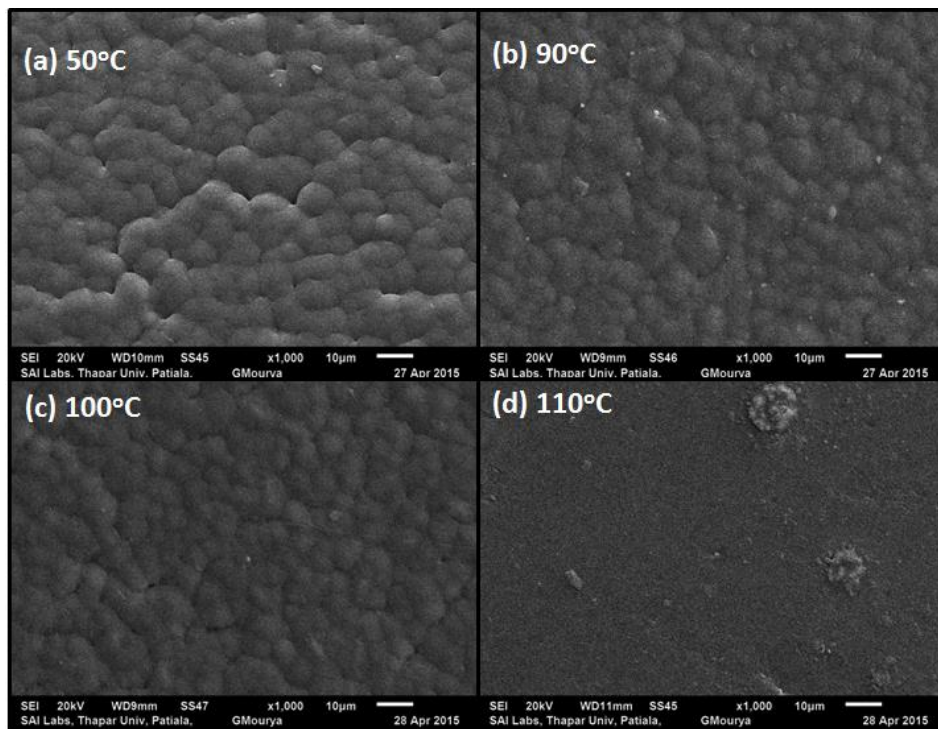


Fig. 3.2 Scanning electron microscope micrographs of PVDF annealed films at different temperatures.

When the annealing temperature is increased upto 100°C, the density of grain boundary increases whereas its thickness decreases. This effect of annealing temperature will also affect the polarizing behavior of PVDF thick film. For annealing temperature at 100°C; the grains either coalesces with each other or too small to be observed³⁴.

3.2.2.1.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is carried out for investigating the phase transformation and chain orientation in PVDF film annealed at different temperatures. The absorbance band at 490, 530, 615, 766, 795, 974, 1149, 1210, 1383, 1402, and 1455 cm^{-1} are related to α -phase³⁵. The bands at 613 and 765 cm^{-1} are the bending and wagging vibration of CF_2 and rocking vibration of PVDF chain respectively. The bands at 840, 878, 1171 and 1232 cm^{-1} corresponds to β -phase of PVDF. The absorption band at 872 cm^{-1} was assigned to CH_2 and CF_2 group generated

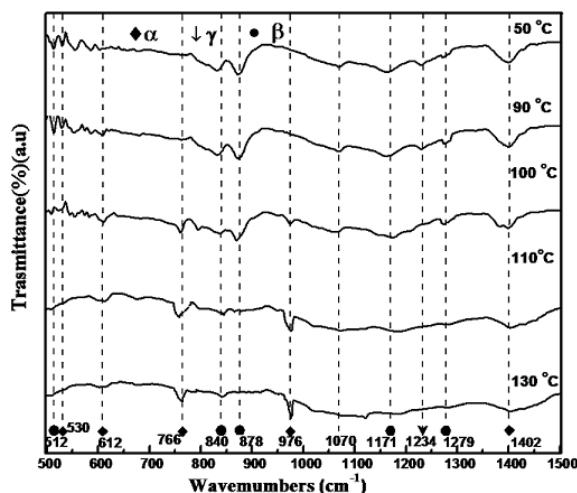


Fig. 3.3 Fourier transform infrared spectra of PVDF annealed films at different temperatures.

from the CH_2 rocking and CF_2 stretching; while the band at 1171 and 1234 cm^{-1} were related to CH_2 group ascribing its wagging and rocking³⁶. The band at 1402 cm^{-1} is related with in plane bending or scissoring of CH_2 group; whereas the band at 1070 cm^{-1} attributed to the bending of C-C-C²⁴. The absorption band in the range 1230-1240 cm^{-1} may either be related to β or γ - phase of PVDF, whereas absorption band in the range 1275-1280 cm^{-1} confirmly corresponds to β -phase of PVDF^{25,26}. Figure 3.3 shows the FTIR spectra of PVDF film annealed at different temperature. The absorption band corresponds to β -phase of PVDF (840, 878, 1171, 1234 and 1279 cm^{-1}) predominantly appears for the film annealed at 50°C, 90°C, 100°C respectively. For film annealed at 100°C the intensity of the peak corresponding β -phase at 840 and 878 cm^{-1} has been decreased; whereas two peaks of α - phase at 766 and 976 cm^{-1} of PVDF has appeared. The prominent occurrence of α -phase of PVDF has also been observed in X-ray diffraction at annealing temperature greater than 100°C. The FTIR results also shows the peak of β -phase has almost disappeared; whereas the prominent peaks of α -phase are still present for film annealed at 110°C. The results

observed by XRD and FTIR are supporting each other. All the absorption band of β -phase of PVDF except at 840 cm^{-1} , disappears for the film annealed at 110°C and 130°C .

3.2.2.2 Electrical properties

The electrical studies include dielectric behavior and polarization vs electric field (D-E) studies. These studies are essential for employing PVDF thick films for capacitor-based applications. The results are discussed in the following sections.

3.2.2.2.1 Dielectric behavior of polyvinylidene fluoride thick films

The dielectric constant and tangent loss with frequency of PVDF thick films annealed at different temperature has been studied for understanding their dielectric behavior. The dielectric constant in the lower frequency range is found to be large than the higher frequencies for all films. It is almost constant in frequency range 10^3 - 10^5 Hz as shown in fig 3.4. The value of dielectric constant for the film annealed at 100°C is found to be highest. Dielectric constant for all films is decreasing for the frequency $\geq 10^6$ Hz; which is assigned to α_c relaxation of PVDF thick film. Dielectric constant is mostly governed by two factors (a) interface between α and β crystalline phase, (b) interface between crystalline/ amorphous region. The dielectric constant for the film annealed at 100°C is ~ 11 in frequency range of 10^3 - 10^5 Hz. The interface between α -phase and β -phase increases the effective dipole moment; which in turn increases the local electric field.

Hence, large number of polar/nonpolar interface might be increasing the dielectric constant. The interface between polar β -phase and amorphous region

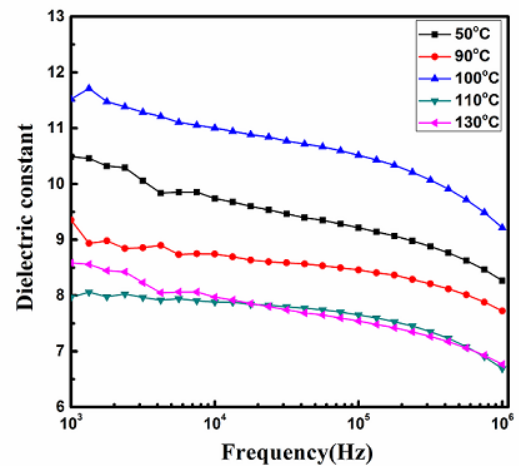


Fig. 3.4 Frequency dependent dielectric constant of PVDF thick films annealed at different temperatures.

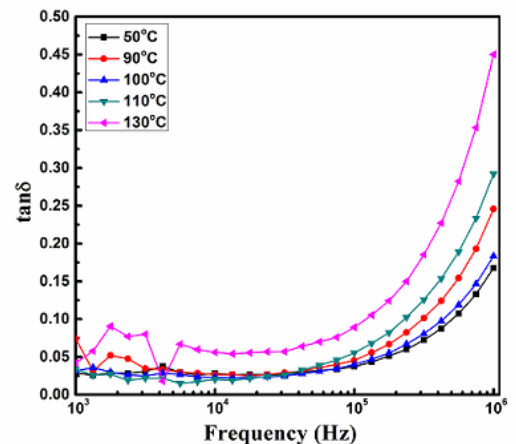


Fig. 3.5 Tangent losses of PVDF thick films annealed at different temperatures.

might also be contributing to the enhanced dielectric constant. Figure 3.5 shows the tangent loss of PVDF thick film annealed at different temperature. The tangent loss corresponding to PVDF film annealed at 90°C and 100°C is lowest in whole frequency range ($10^2 - 10^6$ Hz). The loss tangent for the film annealed at 100°C is ~ 0.025 in frequency range 10^3 to 10^5 Hz. The loss tangent is almost constant in frequency range 10^3 to 10^5 Hz and increases towards a peak value at frequency $\geq 10^6$ Hz; which is typical feature of α_c relaxation of PVDF^{37,38}. The total tangent loss is the result of conduction of electron, interfacial polarization and dipolar relaxation³³. The conduction electron and interfacial polarization are dominant only upto frequency $\sim 10^5$ Hz. The losses due to dipolar relaxation i.e. (CH_2 and CF_2 dipoles of PVDF) are dominant at higher frequency.

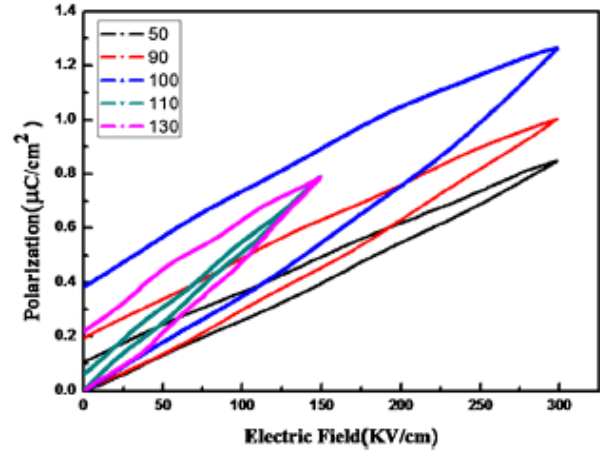


Fig. 3.6 Unipolar polarization vs electric field loops of PVDF thick films annealed at different temperatures.

3.2.2.2.2 Polarization behavior of polyvinylidene fluoride thick film

Polarization behavior of synthesized PVDF thick films, annealed at different temperature has been investigated by polarization vs electric field studies. Figure 3.6 shows the unipolar loop of PVDF thick films which makes it clear that annealing temperature affects the polarization behavior under the same electric field 250 kV/cm. The maximum polarization ($P_{\max}$) as well as remnant polarization (P_r) is found to be highest for the film annealed at 100°C. The values of maximum polarization ($P_{\max}$) and remnant polarization (P_r) for the

Table 3.1 Remnant and maximum polarization of PVDF thick films annealed at different temperatures.

PVDF thick film annealed at different temperature are given in table 3.1. The annealing temperature might be increasing the crystallite size as well as crystallinity. The β -phase crystallite of PVDF are increasing in size with increase

S. No.	Annealing Temp.(°C)	P_r	$P_{\max}$
1	50	0.10	0.85
2	90	0.19	1.00
3	100	0.38	1.27
4	110	0.06	0.79
5	130	0.21	0.79

of annealing temperature from 50°C to 90°C; thereby increasing the dipole moment. The increased dipole moment enhances the maximum polarization.

The α -phase starts growing at the cost of β -phase for the film annealed at 100°C, where the vector sum of dipole moments of CH₂ and CF₂ dipoles at α/β interface as well as crystalline amorphous interface is contributing for more increase in dipole moment as compared to film annealed at 90°C. The increase in dipole moment may be attributed to highest maximum polarization for this film. When annealing temperature becomes greater > 100°C, the β -phase PVDF film convert into α -phase thereby exhibiting smallest value of polarization. The remnant polarization for 100°C is also highest ($\sim 0.39 \mu\text{C}/\text{cm}^2$); which is approximately $\sim 30\%$ of maximum polarization ($\sim 1.27 \mu\text{C}/\text{cm}^2$). The small crystallite and amorphous dipoles are polarized by low electric field, whose contents are very low. Most of these dipoles are reversible due to their small size. The high electric field improves the polarization dramatically by orienting large polar crystallite. However, most of oriented crystals could not be disoriented due to lack of sufficient free space between crystallite grains. Hence, remnant polarization for the film annealed at $\sim 100^\circ\text{C}$ is quite high ⁵. The observed polarization behavior is found to be in agreement with dielectric and structural observation. The film annealed at temperature > 100°C, completely converts into α -phase thereby exhibiting low values of maximum and remnant polarization. The structural observations i.e. XRD and FTIR results are also supported by dielectric and P-E data for the PVDF film annealed at different temperatures. One important point that must be noted, film annealed at 100°C shows better interconnectivity and mechanical strength as compared to film annealed at lower temperature ⁵. The observation of improved dielectric and polarization behavior of the film annealed at 100°C may be useful for high power electronics application.

3.3 CALCIUM COPPER TITANATE NANOPARTICLES

The synthesis of calcium copper titanate (CCTO) nanoparticles is carried out in order to optimize its phase, size and dielectric behavior. Structural and dielectric properties of CCTO nanoparticles has been investigated. Apart from this, transport behavior and charging-discharging behavior of capacitor formed by CCTO pellet is also studied in order to have better understanding about nonlinearity and energy storage behavior of CCTO nanoparticles. The

energy storage behavior of CCTO nanoparticles cannot be studied by displacement vs electric field data (Sec. 2.3.2.1) since it is non-ferroelectric in nature. The experiments carried out and their results are discussed following sections.

3.3.1 EXPERIMENTAL

The experimental studies include the synthesis of calcium copper titanate CCTO nanoparticles, structural, dielectric measurements, and current-voltage measurements which are discussed in sections.

3.3.1.1 Synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

Calcium copper titanate ($\text{CaCu}_3\text{Ti}_4\text{O}_{12}$) nanoparticles are prepared by using sol-gel technique. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$) Copper nitrate trihydrate ($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and Titanium (IV) Isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) from sigma aldrich are used as raw materials. The synthesis process of CCTO nanoparticles was already discussed in experimental Sec. 2.2.1.

3.3.1.2 Structural studies

X-ray diffractions (XRD), scanning electron microscope (SEM), and high-resolution transmission electron microscopy (HRTEM) studies have been carried out to confirm the crystalline phase and surface morphology respectively.

3.3.1.3 Dielectric measurements

The calcined CCTO powder pressed into pellet at 7000 psi and sintered at 900°C for 3 hours. The gold electrodes are coated on both sides of pellet of 6 mm diameter. The thickness of the pellet was ~ 2 mm. The details of dielectric measurements are already discussed in the Sec. 2.3.2.1.1.

3.3.1.4 Current voltage and charging-discharging measurements

The current-voltage measurements are done to study breakdown, nonlinearity and transport

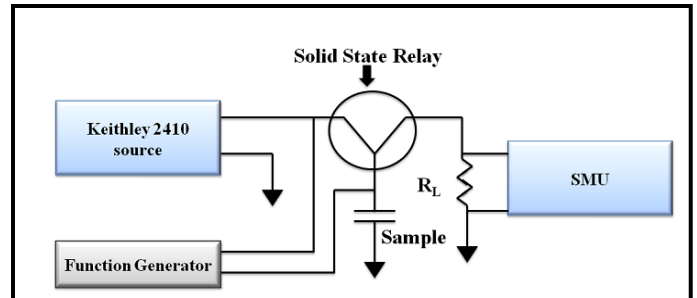


Fig. 3.7 Schematic diagram of the charging-discharging experiment.

behavior of CCTO pellet prepared from CCTO powder. The details of current-voltage measurements are already discussed in Sec. 2.3.2.1.2.

The charging and discharging behavior of capacitor formed by $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellets. The electrodes applied on the both sides of the pellet to form a capacitor structure. The high voltage trigger pulse of 500V is applied by Keithley 2410 high voltage source measuring unit. This has been done by applying a 10 Hz and 2 V p-p square wave pulse by function generator, which excites solid state relay to apply the voltage on sample (CCTO pellet capacitor). A load resistance of $R_L = 50 \text{ k}\Omega$ is applied in parallel to capacitor. The charging and discharging current vs time data is recorded by using another source measuring unit Keithley 2400. The schematic diagram off charging-discharging experiment is shown in figure 3.7. The same kind of experimental set-up will be used elsewhere ³⁹.

3.3.2 RESULTS AND DISCUSSION

The results of structural and electrical studies are discussed in the following sections.

3.3.2.1 Structural studies

X-ray diffractions (XRD), scanning electron microscope (SEM), fourier transform infrared spectroscopy (FTIR), high resolution transmission electron microscopy (HRTEM), and Raman spectroscopy studies have been carried out to confirm the phases and surface morphology respectively. Their results are discussed in the following subsequent sections.

3.3.2.1.1 X-ray diffraction

X-ray diffraction (XRD) pattern of CCTO nanoparticles is shown in fig 3.8. The CCTO nanoparticles has observed to exhibit cubic crystal structure with lattice parameter, $a = 7.38 \text{ \AA}$. Broadening in peak profile is used to determine the crystalline size. The crystalline size can be directly evaluated by using Scherrer formula ⁴⁰.

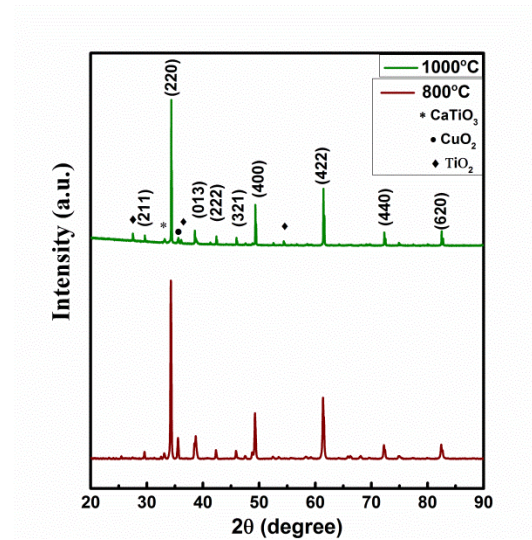


Fig. 3.8 X-ray diffraction of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder calcined at 800°C and 1000°C.

CCTO powder has been calcined at three different temperatures i.e. 800°C, 900°C and 1000°C. The calcined powder at 800°C and 1000°C show the presence of impurity phases of CaTiO_3 , CuO , TiO_2 (fig. 3.8) ⁴¹ whereas the powder synthesized at 900°C shows a pure phase of CCTO (fig. 3.9). Pure phase of CCTO has been used for further investigations. The plot of $W_{hkl} \cos \theta$ versus $4 \sin \theta$ is popularly called as W-H plot ⁴². The

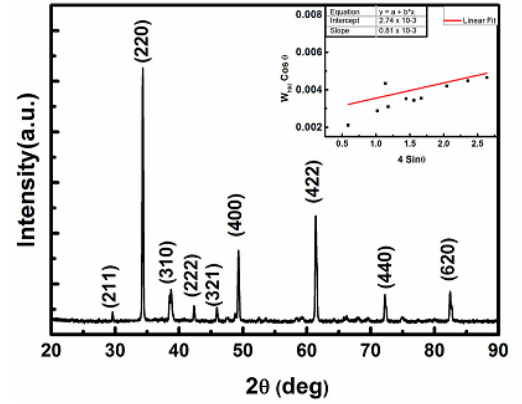


Fig. 3.9 X-ray diffraction of of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanopowder calcined at 900°C (Inset is showing Willamson & Hall plot).

inset of fig. 3.9 shows the W–H plot for CCTO nanoparticles calcined at 900°C. The slope and intercept along y-axis have been determined from the

linear fit of the scattered results. The crystalline size is estimated from the intercept along y-axis, and the strain is determined from the slope of the fit. The crystalline size of CCTO is found to be ~ 53 nm with corresponding strain value of 0.813×10^{-3} .

3.3.2.1.2 High resolution transmission electron microscopy

High resolution transmission electron microscopy (HRTEM) image of CCTO nanoparticles is shown in fig 3.10. The HRTEM image reveals the microstructure of CCTO nanoparticles; where the curved edges cylindrical particles are present. The particles are also showing very weak agglomeration. The size of particle has been measured by considering the distribution in HRTEM images: which has been shown in fig. 3.10 (b). The particle sizes are in the range of 20–120 nm, but majority of particles are lying in the range of 50–60 nm.

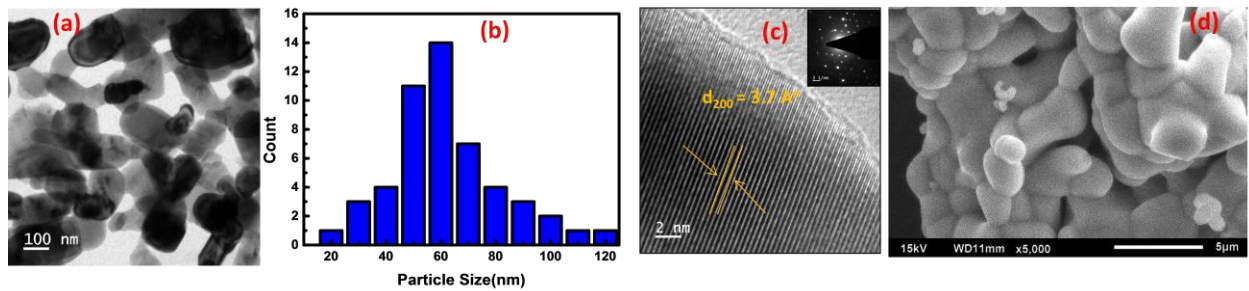


Fig: 3.10 (a) High resolution transmission electron microscopic image, (b) Particle size distribution, (c) high resolution fringes and selected area electron diffraction pattern of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles, (d) scanning micrograph of sintered CCTO pellet at 900°C for 3 hours.

The average particle size obtained from HRTEM, are in good agreement with the crystallite size determined from XRD. The SAED pattern in inset of fig. 3.10 c shows the crystalline feature of CCTO particles; HRTEM images exhibit very good (clear) lattice fringes (shown in fig. 3.10 c) with interplanar spacing $\sim 3.7 \text{ \AA}$ which corresponds to $[2\ 0\ 0]$ plane of CCTO. The fringes are not exhibiting any interconnecting zone as it has been observed in other research reports^{30,43}.

3.3.2.1.3 Energy dispersive spectroscopy

Fig 3.11 shows the energy dispersive spectroscopy (EDS) analysis of CCTO nanoparticles synthesized by modified sol-gel route. The atomic percentage of Ca, Cu, Ti are found to be 4.39, 17.66 and 17.57 with respective

percentage error of 1, 2.21 and 2.4. The ratio of Ca/Cu+Ti resembles with its ratio in standard $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Any impurity peak has not been observed in EDS spectra. EDS studies confirm the elemental stoichiometry in synthesized sample.

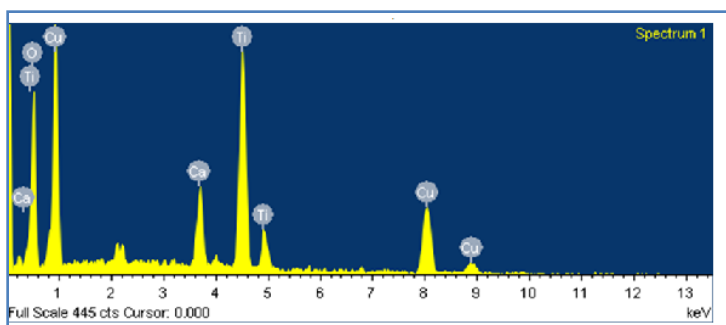


Fig. 3.11 Energy dispersive spectroscopy spectrum of synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles.

Sintering of CCTO pellet at 900°C for 3 hours (same as

that of calcinations) leads to a homogeneous morphological structure shown in fig 3.10 (d). The average grain size has been found to be $\sim 220 \text{ nm}$. The grains and grain boundaries are clearly visible in sintered CCTO ceramic pellet.

3.3.2.1.4 Raman spectroscopy

Raman spectra of synthesized CCTO nanoparticles is shown in fig. 3.12. The optical branches of CCTO split two A, two E and four F Raman active modes^{44,45}. The peak of Raman spectra at 451 cm^{-1} , 516 cm^{-1} are assigned to A_g symmetry; where atomic motion is related to rotation like TiO_6 octahedra. The peak at 579

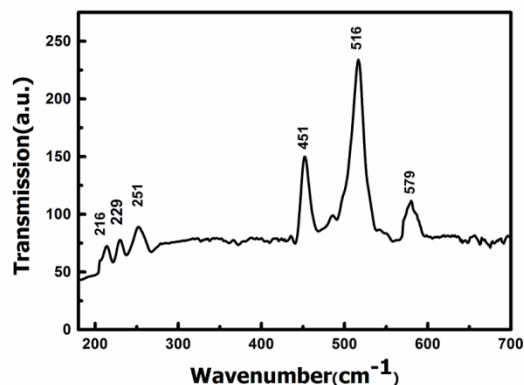


Fig. 3.12 Raman spectra of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles at room temperature.

cm^{-1} related to F_g symmetry where antistretching between O-Ti-O takes place. Strongly damped mode between wave number $200\text{--}300 \text{ cm}^{-1}$ (i.e. 216 , 229 and 251 cm^{-1}) are also observed⁴⁶.

These modes might be a result of interference between Raman scattering from two vibration modes. The interference arises from an anharmonic coupling between A and F - symmetries⁴⁷. Where the Raman mode appearing in wave number 186 - 270 cm^{-1} are assigned to interference between Raman scattering from A-type of symmetries via anharmonic interactions. Therefore, Raman spectra is also confirming the formation of CCTO nanoparticles.

3.3.2.2 Electrical properties

Dielectric studies and current- voltage characteristics have been studied in order to understand dielectric, nonlinearity, and breakdown behaviors of CCTO pellet formed by its powder. The charging & discharging behavior of capacitor formed by CCTO pellet is studied for understanding the energy storage properties. The results of these studies are discussed in the following subsections.

3.3.2.2.1 Dielectric behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

The dielectric constant and tangent loss with frequency of the pellet formed by CCTO nanoparticles have been studied for understanding their dielectric behavior. The frequency dependent dielectric behavior of CCTO pellets is shown in fig. 3.13. The CCTO nanopowder has pelletized and sintered at 900°C for 3 hrs. The temperature and time have been kept same as of calcination in order to prevent the increase in size of CCTO crystallites in pellet. The value of dielectric constant and tangent loss at 1 kHz, has been found to be ~ 7990 and ~ 0.096 respectively. The value of dielectric constant has been found to be in agreement with earlier reports in literature^{23,29,48}. The occurrence of high dielectric constant in polycrystalline CCTO is not associated with intrinsic property of crystal^{28,48}; but it is attributed to the creation grain boundary inter barrier layer capacitance (IBLC). According to this model the dielectric constant of a material can be expressed as⁴⁹:

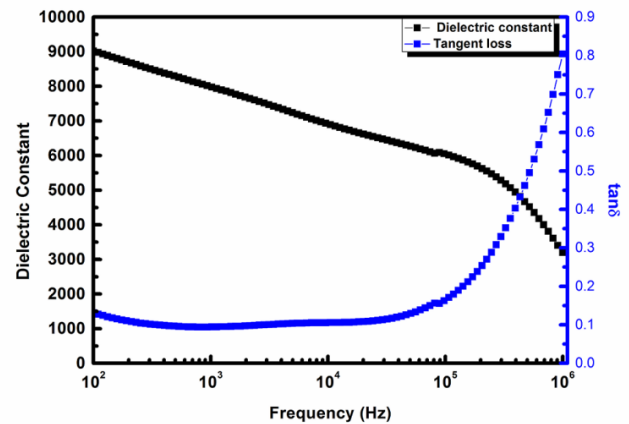


Fig. 3.13 Variation in dielectric constant and tangent loss with frequency of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellet at room temperature.

$$\varepsilon = \frac{d\varepsilon_g}{t} \dots\dots\dots (3.1)$$

Where "d" is the grain size and "t" is the thickness of grain boundary and ε_g is the dielectric constant of the grain boundary layer. The dielectric constant in our case is not a high as reported elsewhere^{28,48} but tangent loss of (~ 0.096) at 1 kHz is moderately small. In reports, where high dielectric constant has been found, CCTO is sintered at high temperature ($\sim 1100^\circ\text{C}$) for long duration ≥ 6 hours. But in our case sintering temperature and time is same as that of synthesis temperature of CCTO powder in order to avoid the crystalline growth. The smaller grain in ceramic lead to larger number of thin grain boundary. According to eqn.3.1, the combination of small grain size and thin grain boundary might be leading to moderate dielectric constant ~ 7990 and low tangent loss (~ 0.096) at 1 kHz.

3.3.2.2.2 Studies on electrical transport

Electrical transport studies have been carried out in order to understand the nature of transport behavior, nonlinearity and breakdown voltage. Current – voltage characteristics of CCTO pellet is measured, which is converted into current density vs electric field by using sample dimensions. Figure 3.14 shows the current density vs electric field curve at room temperature synthesized CCTO pellet. The nonlinear current - voltage behavior indicates the non-ohmic transport in CCTO; which is represented as⁴⁹;

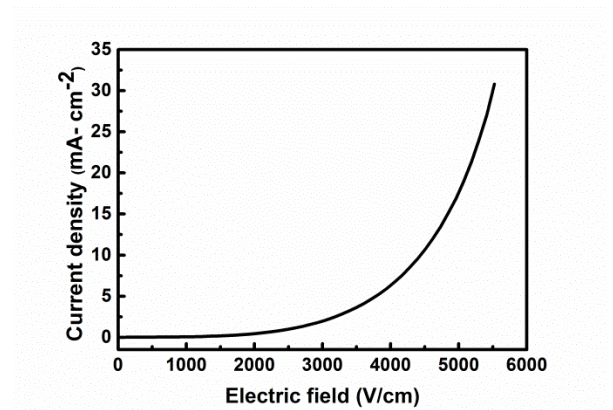


Fig. 3.14 Current density vs electric field curve of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ pellet at room temperature.

$$I = KV^\alpha \dots\dots\dots (3.2)$$

Where "K" is proportionality constant, and " α " is nonlinear coefficient. The nonlinear coefficient is calculated below;

$$\alpha = \frac{\partial(\ln I)}{\partial(\ln V)} \dots\dots\dots (3.3)$$

The value of the nonlinear coefficient calculated from current, voltage characteristics is found to be ~ 6.30 . The values of breakdown electric field (E_b) is recorded from current density vs electric field

curve at 10 mA/cm². The breakdown electric field has been found to be ~ 4400 V/cm. This value of breakdown field is highest to the best of our knowledge^{20,28,50–52}. Existence of electron energy band structure across an insulating grain boundary is reported in CCTO ceramic⁵¹, which is equivalent to n-i-n structure with acceptor like interface trapping of the electron in the grain boundary region. The high value of breakdown electric field and nonlinear coefficient might be arising due to formation of large number of energy bands in grain boundary that traps the electrons at grain/grain boundary interface.

3.3.2.2.3 Studies on charging –discharging behavior

The Metal-CCTO-Metal capacitor structure is fabricated. The capacitance and energy storage behavior of capacitor formed by CCTO has also been investigated. The discharge behavior of capacitor is one of the important parameters for its application. The discharge speed and discharge energy density is measured by using; capacitor discharge circuit reported in literature^{53,54}.

A pulse of 500 V is applied across the capacitor formed by CCTO, and decay of discharging current with time has been measured. The data of discharging current vs time is shown in fig.3.15 (a). The curve has been fitted in expression $I = I_0 \exp(-t/\tau)$. The value of time constant (τ) has been found to be ~ 0.339 ms. In this circuit current is discharged through a load resistance $R_L \sim 50 \text{ k}\Omega$ in series with CCTO sample.

The stored energy density in a capacitor is given by using formula:

$$U_D = \frac{1}{2} \epsilon_0 \epsilon_r E_b^2 \dots\dots\dots (3.4)$$

By taking $\epsilon_r = 9000$, value of dielectric constant at 100 Hz; and $E_b \sim 4400 \text{ V/cm}$ is value of breakdown strength recorded from current density vs electric field data. The stored static energy density has been found to be ~ 7.7 mJ/cc. Energy density can also be calculated from polarization vs electric field curve by using formula of energy density $E_d = \int E dP$, where "E" is electric field strength and "P" is polarization. But the polarization of pure CCTO does not depend on electric field⁵⁵. Alternate way of calculating the energy density can be performed from charging /discharging current vs time at fixed voltage (electric field) as follows. The power is calculated by using formula:

$$P = i^2 (R_L + R) \dots\dots\dots (3.5)$$

Where R_L is load resistance and R is resistance of CCTO pellet. The discharge energy density is calculated by equation:

$$E_d = \frac{1}{V} \int P dt \dots\dots\dots (3.6)$$

The value of E_d is calculated from discharging current vs time curve, where V is volume and P is power. Discharge energy density vs time curve has been shown in fig.3.15 (b). The experimental energy discharge time, i.e. $\tau_{0.9}$ is defined as time for discharge energy density in load to reach 90 % of its maximum value. The energy discharging time has been found to ~ 0.34 ms; which is smaller even as compared to PVDF- SrTiO_3 composites³⁹. The discharging time is dependent on capacitance by $\tau = R_L C$ (where $R_L = 50 \text{ k}\Omega$, $C = 8 \text{ nF}$); which gives $\tau \sim 0.40$ ms, this value is approximately similar to that obtained from the discharging curve (fig. 3.15 (a)).

The maximum value of energy density measured from the discharge curve (Fig. 3.15 b) is 6.8 J/cc. The energy density of CCTO based capacitor is found to be much higher as compared to energy density of BaTiO_3 based capacitor⁵⁶. The inset of fig. 3.15 (b) shows the charging

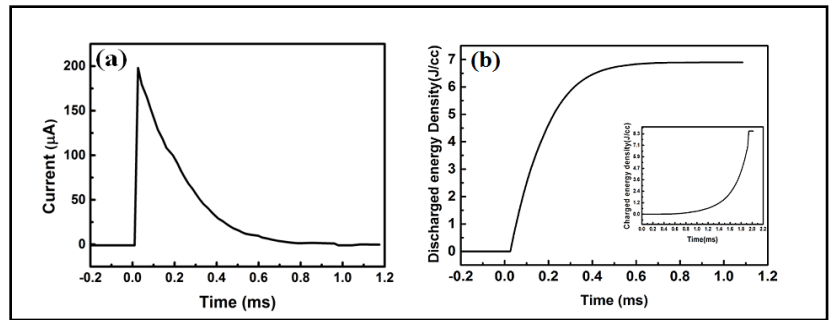


Fig. 3.15 Discharging current response with time, (b) discharged energy density with time of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ capacitor with inset of charged energy density with time at an applied electric field 3000 (V/cm).

density vs time curve. The maximum value of charging energy density has been found to be ~ 8.3 J/cc. Therefore, the efficiency can be calculated by using formula;

$$\eta = \frac{\text{Discharging energy density}}{\text{Charging energy density}} \dots\dots\dots (3.7)$$

Which comes $\sim 82 \%$ at an electric field of 3000 V/cm.

3.4 CONCLUSION

The effect of annealing temperature on structural, dielectric and polarization behavior of PVDF thick films have been investigated. Coexistence of polar β -phase along with α -phase is observed upto an annealing temperature of 100°C . Films annealed at temperature $> 100^\circ\text{C}$ completely

converts into α -phase. The dielectric constant (~ 11 at 1 kHz) and polarization ($\sim 1.27 \mu\text{C}/\text{cm}^2$) is found to be highest for the film annealed at 100°C , which might be attributed to increased dipolar contribution at α/β interfaces as well as amorphous crystalline interface. Therefore, annealing temperature of 100°C has been optimized in order to have very good dielectric and polarization behavior. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles has been synthesized by sol- gel method. The particle size varies in the range of 50-60 nm of synthesized powder annealed at 900°C . Moreover, it also exhibits pure CCTO crystalline phase. The dielectric constant and tangent loss of CCTO at 1 kHz are found to be ~ 7790 and ~ 0.096 respectively. The breakdown electric field and non-linear coefficient are found to be $\sim 4400 \text{ V}/\text{cm}$ and ~ 6.3 , respectively. Discharging time and discharged energy density are found to be $\sim 0.34 \text{ ms}$ and $\sim 6.8 \text{ J}/\text{cc}$ respectively. Therefore, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits high dielectric constant, high breakdown electric field, along with very good capacitive behavior. Hence the particle size, phase purity and dielectric behavior of CCTO has also been optimized. These CCTO nanoparticles will be used as ceramic filler for making PVDF-CCTO nanocomposite thick films, the film will be annealed at 100°C in order to have very good dielectric and polarization behavior.

References

- 1 S. Kumar, S. Supriya and M. Kar, *Compos. Sci. Technol.*, 2018, **157**, 48–56.
- 2 T. B. Adams, D. C. Sinclair and A. R. West, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2006, **73**, 094124.
- 3 L. Wang, F. Gao, J. Xu, K. Zhang, J. Kong, M. Reece and H. Yan, *Compos. Sci. Technol.*, 2018, **158**, 112–120.
- 4 W. Yang, S. Yu, R. Sun and R. Du, *Acta Mater.*, 2011, **59**, 5593–5602.
- 5 C. V. Chanmal and J. P. Jog, *Express Polym. Lett.*, 2008, **2**, 294–301.
- 6 Y. Bai, Z. Y. Cheng, V. Bharti, H. S. Xu and Q. M. Zhang, *Appl. Phys. Lett.*, 2000, **76**, 3804–3806.
- 7 J. Seo, J. Y. Son and W. H. Kim, *Mater. Lett.*, 2019, **238**, 294–297.
- 8 S. Satapathy, S. Pawar, P. K. Gupta and K. B. R. Varma, *Bull. Mater. Sci.*, 2011, **34**, 727–733.
- 9 S. Gahlot, V. Kulshrestha, G. Agarwal and P. K. Jha, *Macromol. Symp.*, 2015, **357**, 173–177.
- 10 A. J. Lovinger, *Macromolecules*, 1982, **44**, 40–44.
- 11 M. Mahmoud, H. Saidi, K. Zaman and M. Dahlan, 2002, **75**, 85–92.
- 12 Y. Li, C. Liao and S. C. Tjong, *Nanomaterials*, 2019, **9**, 952.
- 13 M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, *J. Solid State Chem.*, 2000, **151**, 323–325.
- 14 P. Gupta, A. Kumar, M. Tomar, V. Gupta and D. P. Singh, *J. Mater. Sci. Mater. Electron.*, 2017, **28**, 11806–11812.
- 15 S. Chen, K. Yao, F. E. H. Tay and C. L. Liow, *J. Appl. Phys.*, 2007, **102**, 104108.
- 16 W. M. Prest and D. J. Luca, *J. Appl. Phys.*, 1975, **46**, 4136–4143.
- 17 V. Tiwari and G. Srivastava, *J. Polym. Res.*, 2014, **21**, 587.
- 18 F. Guan, J. Pan, J. Wang, Q. Wang and L. Zhu, *Macromolecules*, 2010, **43**, 384–392.

- 19 W. M. Prest and D. J. Luca, *J. Appl. Phys.*, 1978, **49**, 5042–5047.
- 20 Z. Tang, Y. Huang, K. Wu and J. Li, *J. Eur. Ceram. Soc.*, 2018, **38**, 1569–1575.
- 21 C. Kumar, *J. Mater. Sci. Mater. Electron.*, 2011, **22**, 579–582.
- 22 C. Yang, H. S. Song and D. B. Liu, *Compos. Part B Eng.*, 2013, **50**, 180–186.
- 23 S. Jesurani, S. Kanagesan, R. Velmurugan and T. Kalaivani, *J. Mater. Sci. Mater. Electron.*, 2012, **23**, 668–674.
- 24 J. Zhang, J. Zheng, Y. Liu, C. Zhang, W. Hao, Z. Lei and M. Tian, *Mater. Res. Bull.*, 2019, **115**, 49–54.
- 25 M. Ahmadipour, M. F. Ain and Z. A. Ahmad, *Nano-Micro Lett.*, 2016, **8**, 291–311.
- 26 R. Jia, X. Zhao, J. Li and X. Tang, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, 2014, **185**, 79–85.
- 27 C. C. Homes, T. Vogt, S. M. Shapiro, S. Wakimoto and A. P. Ramirez, *Science (80-.)*, 2001, **293**, 673–676.
- 28 D. L. Sun, A. Y. Wu and S. T. Yin, *J. Am. Ceram. Soc.*, 2008, **91**, 169–173.
- 29 X. Ouyang, P. Cao, S. Huang, W. Zhang, Z. Huang and W. Gao, *J. Electron. Mater.*, 2015, **44**, 2243–2249.
- 30 E. Swatsitang, A. Niyompan and T. Putjuso, *J. Mater. Sci. Mater. Electron.*, 2013, **24**, 3514–3520.
- 31 R. Gregorio, *J. Appl. Polym. Sci.*, 2006, **100**, 3272–3279.
- 32 R. Gregorio, *J. Mater. Chem. A*, 1999, **100**, 4489–4500.
- 33 J. Li, Q. Meng, W. Li and Z. Zhang, *J. Appl. Polym. Sci.*, 2011, **116**, 2674–2684.
- 34 S. L.-M. V. Sencadas, R. Gregorio Jr, *J. Macromol. Sci. Part B Phys.*, 2015, **2348**, 514–525.
- 35 P. Martins, A. C. Lopes and S. Lanceros-Mendez, *Prog. Polym. Sci.*, 2014, **39**, 683–706.
- 36 B. Luo, X. Wang, Y. Wang and L. Li, *J. Mater. Chem. A*, 2014, **2**, 510–519.
- 37 Z. Zhang and T. C. M. Chung, *Macromolecules*, 2007, **40**, 783–785.

- 38 Z. Zhang and T. C. Mike Chung, *Macromolecules*, 2007, **40**, 9391–9397.
- 39 S. Liu and J. Zhai, *J. Mater. Chem. A*, 2015, **3**, 1511–1517.
- 40 B.D. Cullity, *Elements of X-ray Diffraction*, Addison-Wesley, Boston, 1956.
- 41 W. Q. Ni, X. H. Zheng and J. C. Yu, *J. Mater. Sci.*, 2007, **42**, 1037–1041.
- 42 G.K. Williamson, W.H. Hall, X-Ray Line broadening from filled aluminium and wolfram, *Acta Metall.* 1 (1953) 22–31.
- 43 Y. Tian, X. Zhang, Y. Yang, Z. Liu and X. Huang, in *Integrated Ferroelectrics*, 2011, **129**, 188–195.
- 44 A. F. L. Almeida, P. B. A. Fechine, M. P. F. Graça, M. A. Valente and A. S. B. Sombra, *J. Mater. Sci. Mater. Electron.*, 2009, **20**, 163–170.
- 45 N. Kolev, R. P. Bontchev, A. J. Jacobson, V. N. Popov, V. G. Hadjiev, A. P. Litvinchuk and M. N. Iliev, *Phys. Rev. B - Condens. Matter Mater. Phys.*, 2002, **66**, 1–4.
- 46 B. Hilczer, J. Kulek, M. Polomska, M. D. Glinchuk, A. V. Ragulya and A. Pietraszko, *Ferroelectrics*, 2005, **316**, 31–41.
- 47 L. H. Robins, D. L. Kaiser, L. D. Rotter, P. K. Schenck, G. T. Stauf and D. Rytz, *J. Appl. Phys.*, 1994, **76**, 7487–7498.
- 48 S. Vangchangyia, E. Swatsitang, P. Thongbai, S. Pinitsoontorn, T. Yamwong, S. Maensiri, V. Amornkitbamrung and P. Chindaprasirt, *J. Am. Ceram. Soc.*, 2012, **95**, 1497–1500.
- 49 Y. H. Lin, J. Cai, M. Li, C. W. Nan and J. He, *Appl. Phys. Lett.*, 2006, **88**, 172902.
- 50 P. Thongbai, B. Putasaeng, T. Yamwong and S. Maensiri, *J. Mater. Sci. Mater. Electron.*, 2012, **23**, 795–801.
- 51 S. Y. Chung, I. D. Kim and S. J. L. Kang, *Nat. Mater.*, 2004, **3**, 774–778.
- 52 Q. Zhang, T. Li, Z. Chen, R. Xue and Y. Wang, *Mater. Sci. Eng. B Solid-State Mater. Adv. Technol.*, 2012, **177**, 168–172.
- 53 H. Tang and H. A. Sodano, *Nano Lett.*, 2013, **13**, 1373–1379.

- 54 H. J. Lee, M. H. Park, G. H. Kim, J. Y. Seok, Y. J. Kim, C. S. Hwang and A. Q. Jiang, *J. Appl. Phys.*, 2011, **109**, 114113.
- 55 T. Pandirengan, M. Arumugam and M. Durairaj, *Thin Solid Films*, 2017, **628**, 117–126.
- 56 W. B. Li, D. Zhou, L. X. Pang, R. Xu and H. H. Guo, *J. Mater. Chem. A*, 2017, **5**, 19607–19612.

CHAPTER 4

***STUDIES ON DIELECTRIC
AND ENERGY STORAGE
BEHAVIOR OF
PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$
NANOCOMPOSITE***

4.1 INTRODUCTION

High energy density capacitors with fast charge/discharge feature have drawn considerable interest due to their great potential for application in electrical devices such as used in weapons, sensors, lasers and nuclear accelerator, etc and other pulse power applications¹⁻³. The energy density of a capacitors is calculated by $U = \int E dD$, where U is the total stored energy density, E is the applied electric field and, D is the electric displacement⁴⁻⁶. Therefore, to have a material for high energy density capacitor, it must have a moderate dielectric constant and high breakdown strength. Polymer ceramic nanocomposite based on PVDF have been widely investigated and found to exhibit excellent dielectric, breakdown, and energy storage behavior⁷⁻¹⁰. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is a giant dielectric material ($\sim 10^4$) non-ferroelectric in nature and shows nearly constant dielectric constant over a wide temperature and frequency range^{11,12}. Accordingly, its inclusion in PVDF matrix could incur less energy loss^{11,13}. Dielectric behavior of PVDF-CCTO composite has been investigated by different research groups^{10,14,15}. Thomas *et al.*, investigated the dielectric behavior of PVDF-CCTO composite; where CCTO filler are in 1-7 μm range. Observed dielectric constant has been fitted in various theoretical models like Maxwell's, Clausius-Mossotti, Effective medium theory, logarithmic law and Yamada¹⁶. Yang *et al.* studied the comparative study of effect of micro and nanosize CCTO fillers on the dielectric properties of CCTO-PVDF composite is also carried out. The composite with nanosized CCTO filler exhibits better dielectric properties as compared to micro-sized filler. Better dielectric behavior of nanosized CCTO filler is attributed to formation of conductive interfaces at boundaries in PVDF matrix¹⁷. Effect of coupling agent such as Si69 on dielectric properties of PVDF-CCTO composite has also been investigated. Observed dielectric behavior is assigned to good compatibility of the ethoxy ($-\text{OC}_2\text{H}_5$) group of Si69 and PVDF matrix¹⁰. Arbatti *et al.* has studied dielectric behavior of P(VDF-TrFE)-CCTO composite. They have got a flexible composite having very high dielectric constant ~ 33 at 1kHz; but the loading of CCTO ceramic filler is ~ 50 vol %, which is quite high¹⁵. There has always been a fascination of obtaining a polymer-ceramic nanocomposite of good dielectric and energy storage behavior at low loading of ceramic filler. High loading of ceramic filler compromises with mechanical strength¹⁸. Earlier studies have confirmed that PVDF-CCTO nanocomposite have moderate dielectric constant, low tangent loss and high mechanical strength. Also,

incorporation of CCTO will cause low area hysteresis loop by virtue of its non-ferroelectric nature^{11,13}. The composites with low area hysteresis loop have good energy storage properties¹⁹. This chapter presents the detailed investigation on structural, morphological, dielectric, electrical displacement vs electric field and energy storage behavior of PVDF-CCTO nanocomposite thick films (with different vol % loading of CCTO).

4.2 EXPERIMENTAL

It includes the synthesis of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films and their structural, dielectric and displacement vs electric field studies, which are described in the following subsections.

4.2.1 Synthesis of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films

The nanoparticles of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) are prepared by a sol-gel method. The CCTO is calcined at 900° C for 3 hours. PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films with different vol% loading of CCTO nanoparticles are prepared by solution casting technique (it is mentioned in Sec. 2.2.2). PVDF-CCTO nanocomposite films are prepared at four different vol% (i.e. 4 vol%, 8 vol%, 12vol%, and 15 vol%), which has been nominated as PVDF-4CCTO, PVDF-8CCTO, PVDF-12CCTO and PVDF-15CCTO respectively.

4.2.2 Structural studies of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films

X – ray diffraction (XRD) and scanning electron microscope (SEM) (Sec. 2.3.1) have been used to investigate the phases and surface morphology respectively. Fourier transform infrared spectroscopy (FTIR) is used to find out the bonding of different crystalline phases in PVDF-CCTO nanocomposite films. These techniques are already discussed in the sec. 2.3.1 of chapter 2.

4.2.3 Electrical studies

The dielectric constant, tangent losses, ac conductivity, and energy storage behavior of the PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films at different vol% (4 vol%, 8 vol%, 12 vol% and 15 vol %) measure at room temperature. The energy density and efficiency of the films have also been calculated from displacement vs electric field data. The details of these technique are already described in the Sec. 2.3.4 of Chapter 2.

4.3 RESULT AND DISCUSSION

The result of structural and electrical studies is described in the subsequent sections.

4.3.1 Structural studies

The results of X-ray diffraction (XRD), scanning electron microscope (SEM), and fourier transform infrared spectroscopy (FTIR) are discussed in the subsequent sections.

4.3.1.1 X-ray diffraction

X-ray diffraction (XRD) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles, pure PVDF and PVDF-CCTO nanocomposite films is shown in figure 4.1. Peaks of PVDF and CCTO can be clearly seen in the XRD, which confirms the inclusion of CCTO nanoparticles in the PVDF matrix. Various crystalline phases of PVDF-CCTO nanocomposite films in XRD pattern are observed. The diffraction peaks at $2\theta = 18.4^\circ$, 19.8° , 20.2° and 27.9° corresponding to planes (020), (110), (021) and (111) respectively. These peaks are observed for all PVDF-CCTO nanocomposite films. These planes are the signature of α -phase of PVDF^{20,21}. The peak at $2\theta = 26.8^\circ$ representing the (022) plane corresponds to γ -phase of PVDF²². The minority of γ -phase observed in PVDF-8CCTO and PVDF-12CCTO nanocomposite films, but the γ -phase disappeared in the PVDF-15CCTO nanocomposite film. The presence of β -phase confirmed by the peaks at $2\theta = 20.7^\circ$ and 36.6° are assigned to (200) and, (020) planes in PVDF-8CCTO and PVDF-12CCTO nanocomposite films^{20,23}. The peak corresponding to β -phase in PVDF-8CCTO nanocomposite film is showing less broadening as compared to PVDF-12CCTO nanocomposite film. Therefore, crystallite size of β -phase in PVDF-8CCTO nanocomposite film is smaller as compared to PVDF-12CCTO nanocomposite film.

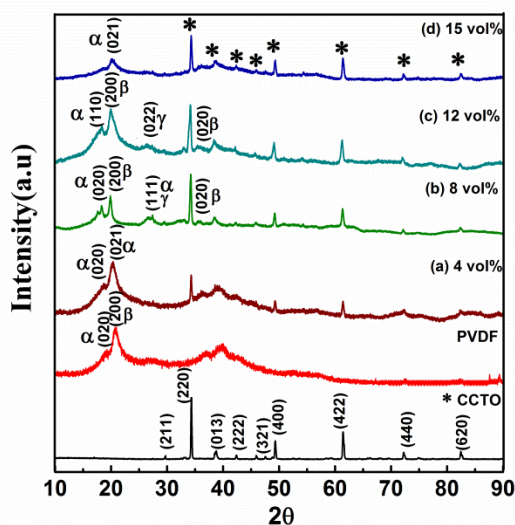


Fig 4.1 X-ray diffraction patterns of CCTO, (a) PVDF- 4CCTO, (b) PVDF- 8CCTO, (c) PVDF- 12CCTO and, (d) PVDF- 15CCTO nanocomposite films.

4.3.1.2 Scanning electron microscope

Fig. 4.2 shows the scanning electron microscope (SEM) images of the PVDF-CCTO nanocomposite films with 4 vol%, 8 vol%, 12 vol%, and 15 vol% loading of CCTO nanoparticles. Homogenous distribution of CCTO nanoparticles in the PVDF matrix is clearly visible, which is achieved by sonification of magnetically stirred solution of PVDF and CCTO in DMF. White portion

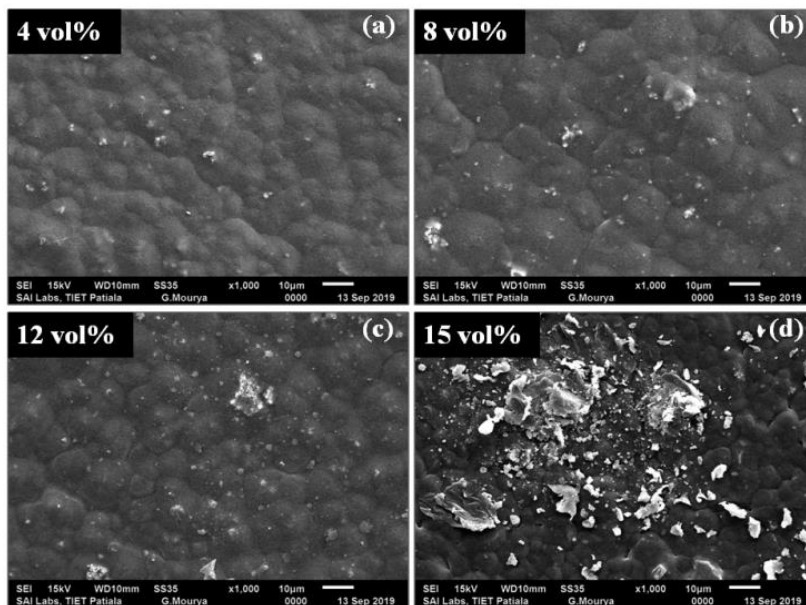


Fig. 4.2 SEM micrographs of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15 CCTO nanocomposite films.

of SEM images are representing CCTO nanoparticles, whereas black spherulite structure is representing PVDF matrix. Slight aggregation of CCTO nanoparticles occurs with increase in the volume fraction of CCTO in PVDF matrix^{17,18}.

4.3.1.3 Fourier transform infrared spectroscopy

Figure 4.3 shows Fourier transform infrared spectroscopy (FTIR) spectra of pure PVDF and PVDF-CCTO nanocomposite films in the range of 500-1500 cm^{-1} . All the PVDF-CCTO nanocomposite film are showing the presence of α , β , and γ -phases. Absorption band present at 490, 615 and 763 cm^{-1} correspond to α -phase of PVDF. Absorption band of 490 cm^{-1} due to the bending and wagging vibration of CF_2 group, whereas 615, 763 cm^{-1} are assigned to the rocking vibration, a mixed mode of CF_2 bending and CCC skeletal vibration^{24,25}. The prominent absorption bands of α -phase i.e. 763, 795, 975, 1214, and 1380 cm^{-1} are only observed in PVDF-8CCTO nanocomposite; which confirms that it consists majority of α -phase.

The absorption bands at 840, 876 and 1167 cm^{-1} attributed to β -phase, whereas the peak at 1231 and 1071 cm^{-1} assigned as γ -phase and it was related to CH_2 group ascribing its wagging and rocking symmetries²⁶. The presence of γ -phase in PVDF-CCTO nanocomposite films consisting 4 vol% and 15 vol% CCTO are not observed in XRD, whereas it appears in FTIR^{26,27}. This might be related with sensitivity of

XRD for γ -crystalline phase in these nanocomposites, whereas FTIR relies on the vibration of bonds. Therefore, the γ -phase is appearing in IR, but it is absent in XRD. But, the γ -phase is also polar phase and this phase normally exhibit high energy density²⁴.

4.3.2 Electrical properties

The electrical studies include dielectric behavior and electrical displacement vs electric field (D-E) studies. The discharging and charging energy density as well as energy efficiency of PVDF-CCTO nanocomposite thick films have been calculated from electrical displacement vs electric field (D-E) data.

4.3.2.1 Studies on dielectric behavior

Figure 4.4 shows the frequency dependence of dielectric constant (ϵ) of the PVDF- CCTO nanocomposite films at room temperature. Trend of variation of dielectric constant for all PVDF-CCTO nanocomposite films are similar. The dielectric constant is found to increase with

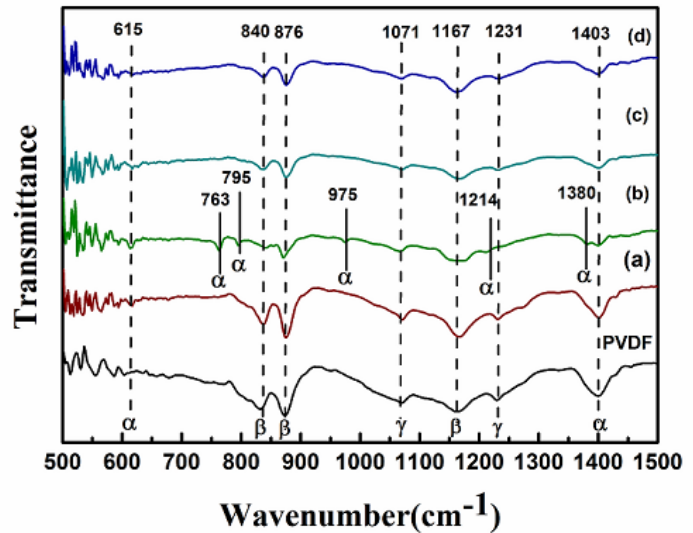


Fig. 4.3 Fourier transform infrared spectra of CCTO, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

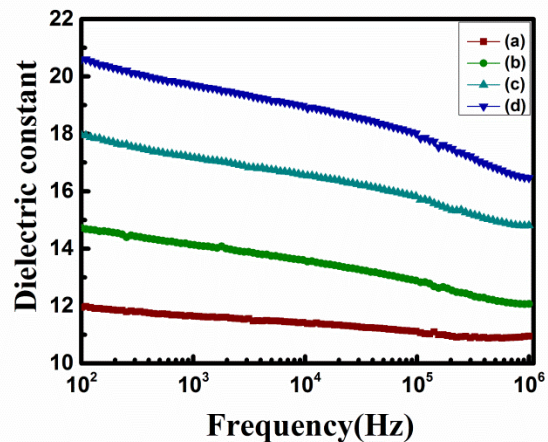


Fig. 4.4 Frequency dependent dielectric constant of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15 CCTO nanocomposite films.

increase of CCTO loading in the PVDF-CCTO nanocomposite films. Dielectric constant of CCTO is very high and hence its inclusion in PVDF creates local internal field²⁸, which tends to increase the dielectric constant. More is loading more is dielectric constant of nanocomposite films. For frequency $> 10^5$ Hz, dielectric constant decreases. Here dielectric behavior originates from the micro-brownian motion of nanocrystalline chain segment (α -relaxation)²⁸ and molecular motion onto amorphous/crystalline interfaces arises among PVDF and between PVDF-CCTO^{29,30}.

Figure 4.5 shows the frequency dependence of tangent loss ($\tan\delta$) of the PVDF-CCTO nanocomposite films at room temperature. Initially tangent loss decreases with frequency and attains minima. At frequency $> 10^5$ Hz; tangent loss starts again increasing. This feature is common to all PVDF-CCTO nanocomposite films. High tangent loss at lower frequencies might be arising due to surface effects; whereas enhancement in tangent loss for frequency $> 10^5$ Hz is resulting due to competing relaxation phenomena among PVDF crystalline phases (i.e. α , β and, γ -phases) and CCTO nanoparticles.

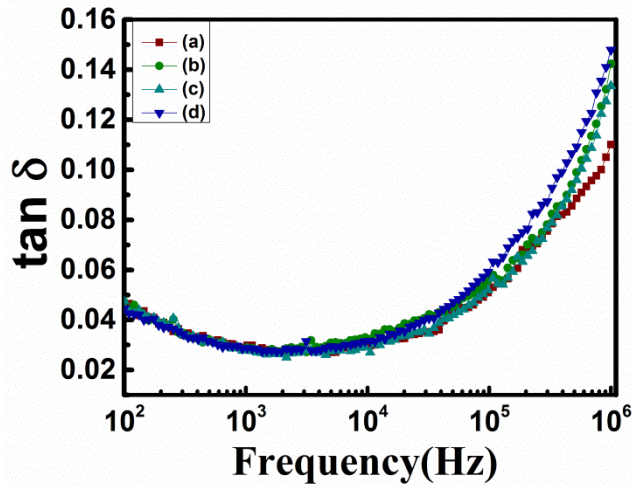


Fig 4.5 Frequency dependent tangent loss of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

AC conductivity also gives information about the relaxation behavior in dielectric materials. The ac conductivity is calculated from dielectric data by using formula:

$$\sigma_{ac} = \omega \tan\delta \varepsilon_0 \varepsilon_r \dots\dots\dots (4.1)$$

Where ω is the angular frequency ($\omega = 2\pi f$), ε_0 is the permittivity of free space, ε_r is the dielectric constant and $\tan\delta$ (tangent loss) of the sample.

Figure 4.6 shows the frequency dependence of ac conductivity (σ) of the PVDF-CCTO nanocomposite films at room temperature. The frequency at which ac conductivity starts increasing (on set frequency) is found to decrease with increase in loading of CCTO in PVDF-CCTO nanocomposite films, which indicates that dipolar relaxation time of CCTO may be greater as compared to relaxation time of PVDF ³¹. Ac conductivity data has also been fitted in Jonscher power law in order to elucidate to conduction mechanism. The hopping of Ti^{3+} ion of CCTO as well as CF^{2-} ions of PVDF might be taking place through oxygen vacancies and amorphous chain of PVDF respectively. Hopping of charge carrier contribute either towards dielectric relaxation or conduction. There is a correlation between conductivity and dielectric relaxation ³². For confirming it, ac conductivity has been fitted in Jonscher power law as represented below:

$$\sigma = \sigma_{dc} + A\omega^n \quad \dots\dots\dots (4.2)$$

Where A is some constant, σ_{dc} is dc conductivity, index 'n' represent the amount of interaction among mobile ions and lattices ³³. The value of $\sigma_{dc} = 1.4 \times 10^{-9}$ S/m and $n = 1.1$, the value $n > 1$ suggest the localized hopping of mobile ions.

The effective dielectric constant of PVDF-CCTO nanocomposite films have also been predicted by using various models [43-45]. Figure 4.7 shows the dielectric constant of the CCTO-PVDF

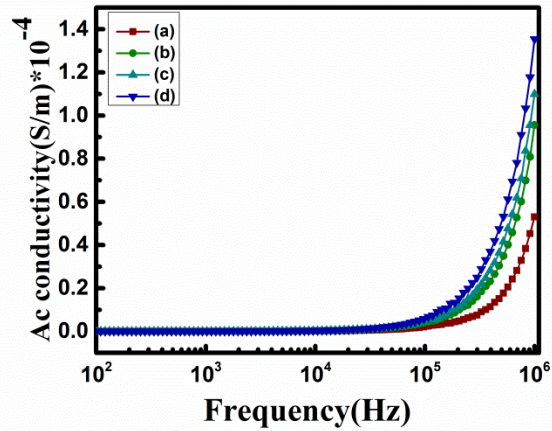


Fig: 4.6 Frequency dependent ac conductivity of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

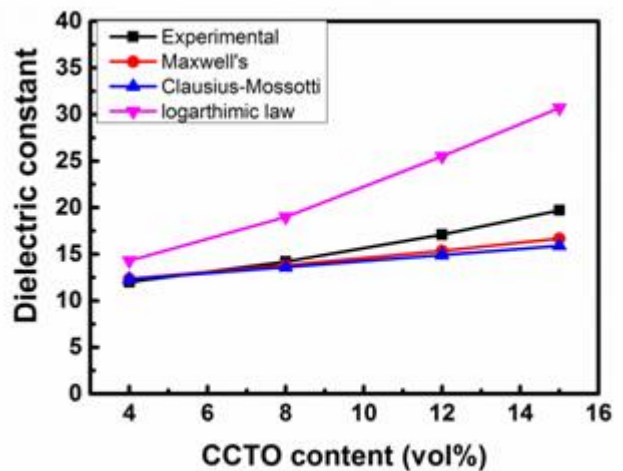


Fig. 4.7 Variation of effective dielectric constant at 1 kHz of PVDF-CCTO nanocomposite films with different vol% of CCTO ceramic in PVDF-CCTO nanocomposite.

nanocomposite films at 1 kHz for different volume fraction of CCTO. Dielectric behaviour of biphasic composite, where high dielectric constant nanoparticles are dispersed in low dielectric constant polymeric matrix is well described by Maxwell's model, which is given by:

$$\varepsilon_r = \left[\frac{\delta_p \varepsilon_p (2/3 + \varepsilon_c/3\varepsilon_p) + \delta_c \varepsilon_c}{\delta_p (2/3 + \varepsilon_c/3\varepsilon_p) + \delta_c} \right] \dots\dots\dots (4.3)$$

Where (δ_c, δ_p) and $(\varepsilon_c, \varepsilon_p)$ are the volume fraction and dielectric constant of CCTO and PVDF respectively. Where $\varepsilon_c = 7968$ and $\varepsilon_p = 11.5$ and these are the dielectric constant of CCTO and PVDF^{12, 26}. Where δ_c and δ_p are the volume fraction of CCTO and PVDF in the composite, respectively. The experimental result deviate from the Maxwell's model with increased loading of CCTO. Because in this model, filler is assumed to be spherical in nature.

Clausius- Mossotti law is used to predict the dielectric constant of a composite having spherical ceramic crystallites dispersed in continuous medium³⁷. The effective dielectric constant according to this law is given by:

$$\varepsilon_r = \varepsilon_p \left[1 + 3\delta_c \left(\frac{\varepsilon_c - \varepsilon_p}{\varepsilon_c + 2\varepsilon_p} \right) \right] \dots\dots\dots (4.4)$$

Logarithmic law is most commonly used dielectric mixture rule proposed by Lichtenecker's which is given by:

$$\log \varepsilon_r = \delta_c \log \varepsilon_c + \delta_p \log \varepsilon_p \dots\dots\dots (4.5)$$

The effective dielectric constant calculated by logarithmic law is close to experimental data at low volume fraction of CCTO in PVDF-CCTO nanocomposite films. Whereas, effective dielectric constant obtained by Maxwell's model and Clausius- Mossotti law are very close to experimental value of dielectric constant of PVDF-CCTO nanocomposite. Slight difference between experimental and theoretical value might be arising due to irregular symmetry of CCTO nanoparticles in PVDF-CCTO nanocomposite films.

4.3.2.2 Studies on electrical displacement and energy storage

Figure 4.8 shows variation of unipolar electric-displacement with electric field curve of PVDF-CCTO nanocomposite films. The electric displacement is given by $D = \varepsilon_0 E + P$, if ε_0

$E \gg P$; the $D \sim P$. The value of maximum polarization ($P_{\max}$) and remnant polarization (P_r) for PVDF-8CCTO nanocomposite film with 8 vol% of CCTO are $1.7 \mu\text{C}/\text{cm}^2$ (at $500 \text{ kV}/\text{cm}$) and $0.6 \mu\text{C}/\text{cm}^2$, which is highest as compared to other nanocomposite films. Occurrence of highest value

of maximum polarization in PVDF-8CCTO nanocomposite film is associated with emergence of β

and γ -phase of PVDF along with α -phase. The β and γ phase of PVDF are also observed in PVDF-12CCTO nanocomposite film; but the value of P_s and P_r is found to be less as compared to PVDF-8CCTO nanocomposite film. If one looks at peaks of XRD of β -phase in PVDF-CCTO nanocomposite films at 20.7° and 36.7° . The broadening in corresponding peak for PVDF-8CCTO nanocomposite film is smaller as compared to those of PVDF-12CCTO nanocomposite film. Therefore, crystallite size of β - phase in PVDF-8CCTO nanocomposite film is larger as compared to PVDF-12CCTO nanocomposite film. Therefore, PVDF-8CCTO nanocomposite film exhibits highest maximum polarization ($P_{\max}$)³⁸. Higher value of (P_r) for PVDF-8CCTO nanocomposite film is

ascribed to irreversibility of large polar crystallite at low field¹⁴. When the vol% of CCTO >12 , the unipolar loop is becoming almost parallel to electric field axis. Moreover, maximum polarization is also very low. This behaviour is ascribed to non-ferroelectric nature of CCTO. The larger crystallite size of β -phase in PVDF-8CCTO nanocomposite film,

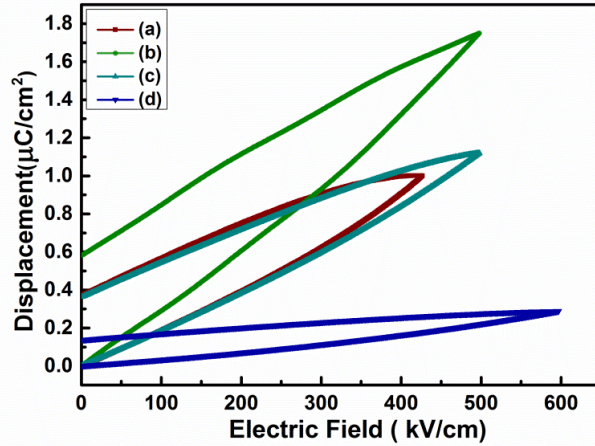


Fig. 4.8 Displacement loops of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO, and (d) PVDF-15 CCTO nanocomposite films.

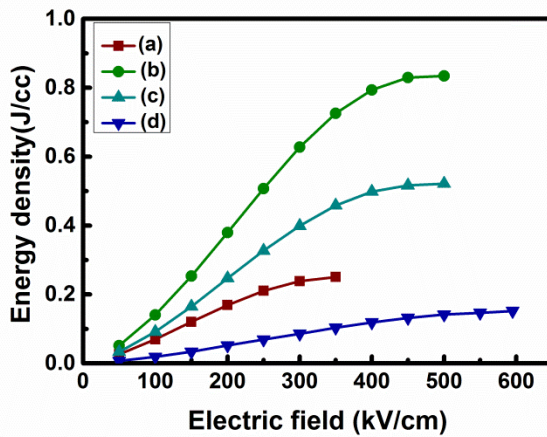


Fig. 4.9 Energy density of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO, and (d) PVDF-15CCTO nanocomposite films.

and the alignment of polymeric chain corresponding to α , β and γ -phases rearranged in PVDF-8CCTO nanocomposite film in such a way that separation between $\text{CH}_2\text{-CF}_2$ dipole is increased which might be increasing the resultant dipole moment and, hence polarization. Energy storage properties of other nanocomposites have also been reported^{39,40}. They show excellent energy storage behavior at very high electric field (~ 4000 kV/cm), and useful for high voltage capacitor. Whereas, PVDF-8CCTO nanocomposite shows 0.8 J/cc at an electric field of ~ 500 kV/cm as shown in fig 4.9; which is higher as compared to previous reports at same electric field^{39,40}. These nanocomposites may be useful for the capacitor operating at moderately high voltage ($\sim$ kV).

Discharge energy density = $\int E \, dD$. Discharge energy density has been found to be maximum for PVDF-8CCTO nanocomposite film i.e. $U_D = 1$ J/cc. Energy efficiency has been calculated by using formula:

$$\eta(\%) = \frac{\text{Discharging energy density}}{\text{Charging energy density}} * 100\% \dots\dots\dots (4.6)$$

The energy efficiency for PVDF- 8CCTO nanocomposite film has also been found to be highest i.e. 65 % at 100 kV/cm as shown fig 4.10. The highest discharge energy density and energy efficiency of PVDF-8CCTO nanocomposite film is ascribed to larger crystallite of β -phase and increased dipole moment due to ordering of α , β and γ - phase of PVDF in PVDF-CCTO nanocomposite films.

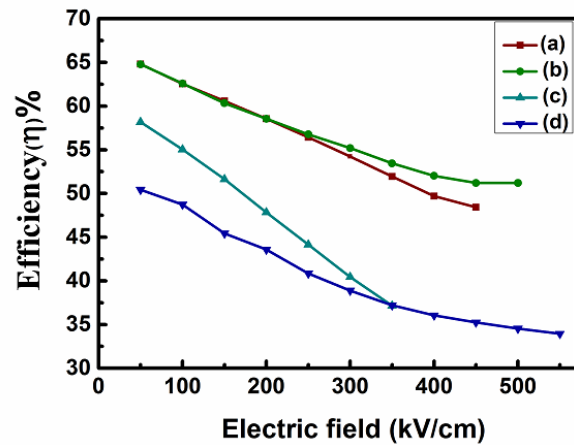


Fig 4.10 Efficiency of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

Mechanism of nucleation of β -phase in

PVDF based nanocomposite has been explained elsewhere^{41,42}. But in our case CCTO is a n-type semiconductor, therefore the surface of CCTO will be treated as negatively charged⁴³. When negatively charged surface of CCTO nanoparticles interact with CH_2 group of PVDF, electroactive β -phase is promoted i.e. TTTT conformation. Small amount of γ - phase i.e. TTTGTTTG' also exist. Force field required for internal chain rotation might be provided by

internal local field of CCTO at interface of PVDF and CCTO. Crystalline size and alignment polymeric chain corresponding to α , β and γ - phase has an effect on dipole moment and hence, on polarization. The polarization behavior affects the energy storage behavior.

4.4 CONCLUSION

PVDF-CCTO nanocomposite films has been synthesized and characterized at different vol% (4, 8, 12 and 15 vol%) loading of CCTO nanoparticles. The dielectric constant of PVDF-CCTO nanocomposite films increases with increase in loading of CCTO nanoparticles. The various models are also fitted, but the effective dielectric constant obtained by Maxwell's model and Clausius- Mossotti law are very close to experimental value of dielectric constant of PVDF-8CCTO nanocomposite film. PVDF-8CCTO nanocomposite films exhibits highest maximum and remnant polarization i.e. $1.7 \mu\text{C}/\text{cm}^2$ at (500 kV/cm) and $0.6 \mu\text{C}/\text{cm}^2$, respectively. It also possesses highest discharge energy density 0.85 J/cc at 500 kV/cm and energy efficiency of $\sim 65 \%$ at 100 kV/cm. Enhanced energy density and polarization are attributed to increase dipole moment due to ordering of α , β , γ -phases of PVDF in PVDF-CCTO nanocomposite films. The reported work is opening the way for further investigation of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ based polymer matrix nanocomposite as a novel material for high energy density capacitors.

References

- 1 H. Tang and H. A. Sodano, *Nano Lett.*, 2013, **13**, 1373–1379.
- 2 J. Li, Q. Meng, W. Li and Z. Zhang, *J. Appl. Polym. Sci.*, 2011, **116**, 2674–2684.
- 3 D. Hernández-Rivera, G. Rodríguez-Roldán, R. Mora-Martínez and E. Suaste-Gómez, *Sensors (Switzerland)*, , DOI:10.3390/s17051009.
- 4 Q. Li, K. Han, M. R. Gadinski, G. Zhang and Q. Wang, *Adv. Mater.*, 2014, **26**, 6244–6249.
- 5 Q. Fan, M. Liu, C. Ma, L. Wang, S. Ren, L. Lu, X. Lou and C. Jia, 2018, 0–20.
- 6 Z. Yao, Z. Song, H. Hao, Z. Yu, M. Cao, S. Zhang, M. T. Lanagan and H. Liu, *Adv. Mater.*, 2017, **29**, 1601727.
- 7 P. Kim, N. M. Doss, J. P. Tillotson, P. J. Hotchkiss, M. J. Pan, S. R. Marder, J. Li, J. P. Calame and J. W. Perry, *ACS Nano*, 2009, **3**, 2581–2592.
- 8 S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai and Z. An, *RSC Adv.*, 2015, **5**, 40692–40699.
- 9 J. Yao, C. Xiong, L. Dong, C. Chen, Y. Lei, L. Chen, R. Li, Q. Zhu and X. Liu, *J. Mater. Chem.*, 2009, **19**, 2817.
- 10 C. Yang, H. S. Song and D. B. Liu, *Compos. Part B Eng.*, 2013, **50**, 180–186.
- 11 M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, *J. Solid State Chem.*, 2000, **151**, 323–325.
- 12 S. Kaur, A. Kumar, A. L. Sharma and D. P. Singh, *Ceram. Int.*, 2019, **45**, 7743–7747.
- 13 S. Jesurani, K. Samikannu and K. Thirunavukarasu, , DOI:10.1007/s10854-011-0468-9.
- 14 P. Thomas, S. Satapathy, K. Dwarakanath and K. B. R. Varma, *Express Polym. Lett.*, 2010, **4**, 632–643.
- 15 M. Arbatti, X. Shan and Z. Cheng, *Adv. Mater.*, 2007, **19**, 1369–1372.
- 16 P. Thomas, K. T. Varughese, K. Dwarakanath and K. B. R. Varma, *Compos. Sci. Technol.*, 2010, **70**, 539–545.
- 17 W. Yang, S. Yu, R. Sun and R. Du, *Acta Mater.*, 2011, **59**, 5593–5602.
- 18 P. Gupta, A. Kumar, M. Tomar, V. Gupta and D. P. Singh, *J. Mater. Sci. Mater. Electron.*, 2017, **28**, 11806–11812.
- 19 H. Tang, Z. Zhou and H. A. Sodano, *ACS Appl. Mater. Interfaces*, 2014, **6**, 5450–5455.
- 20 W. Li, Q. Meng, Y. Zheng, Z. Zhang, W. Xia and Z. Xu, *Appl. Phys. Lett.*, 2010, **96**, 94–97.
- 21 P. Martins, A. C. Lopes and S. Lanceros-Mendez, *Prog. Polym. Sci.*, 2014, **39**, 683–706.
- 22 X. Cai, T. Lei, D. Sun and L. Lin, *RSC Adv.*, 2017, **7**, 15382–15389.
- 23 J. Li, Q. Meng, W. Li and Z. Zhang, *J. Appl. Polym. Sci.*, 2011, **122**, 1659–1668.
- 24 N. Betz, A. Le Moël, E. Balanzat, J. M. Ramillon, J. Lamotte, J. P. Gallas and G. Jaskierowicz, *J. Polym. Sci. Part B Polym. Phys.*, 1994, **32**, 1493–1502.
- 25 Z. Z. and T. C. M. Chung, *Macromolecules*, 2007, **40**, 783–785.

- 26 S. Kaur, A. Kumar, A. L. Sharma and D. P. Singh, *J. Mater. Sci. Mater. Electron.*, 2017, **28**, 8391–8396.
- 27 W. X. and Z. X. Wenjing Li, Qingjie Meng, Yuansuo Zheng, Zhicheng Zhang Zhang, *Appl. Phys. Lett.*, 2010, **96**, 192905.
- 28 V. Sencadas, S. Lanceros-Méndez, V. Sencadas, S. Lanceros-Méndez, R. Sabater Serra, A. Andrio Balado and J. Gómez Ribelles, *Eur. Phys. J. E*, 2012, **35**, 4–5.
- 29 B. Hahn, J. Wendorff and D. Y. Yoon, *Macromolecules*, 1985, **18**, 718–721.
- 30 J. W. Sy and J. Mijovic, *Macromolecules*, 2002, **33**, 933–946.
- 31 C. V. Chanmal and J. P. Jog, *Express Polym. Lett.*, 2008, **2**, 294–301.
- 32 B. Behera, P. Nayak and R. N. P. Choudhary, *Mater. Res. Bull.*, 2008, **43**, 401–410.
- 33 M. De, S. Hajra, R. Tiwari, S. Sahoo, R. N. P. Choudhary and H. S. Tewari, *Ceram. Int.*, 2018, **44**, 11792–11797.
- 34 Maxwell JC, A Treatise on Electricity & Magnetism - Volume 2 : James Clerk Maxwell : Free Download, Borrow, and Streaming : Internet Archive.
- 35 H. Frolich, *Theory of dielectrics dielectric constant and dielectric loss.*, Clarendon Press, Oxford, 1949.
- 36 Nalwa HS, Ferroelectric polymers : chemistry, physics, and applications / [edited by] Hari Singh Nalwa. - Version details - Trove.
- 37 C. P. Wong, T. Marinis, Jianmin Qu and Yang Rao, *IEEE Trans. Components Packag. Technol.*, 2000, **23**, 680–683.
- 38 S. S. Chen, J. Hu, L. Gao, Y. Zhou, S. M. Peng, J. L. He and Z. M. Dang, *RSC Adv.*, 2016, **6**, 33599–33605.
- 39 S. Liu , Z. Jiwei, W. Jinwen, X. Shuangxi, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1533–1540.
- 40 S. Liu, S. Xue, S. Xiu, B. Shen and J. Zhai, *Nat. Publ. Gr.*, 2016, 1–11.
- 41 C. Nio, P. Thakur, A. Kool, A. Hoque, B. Bagchi and S. Roy, *RSC Adv.*, 2016, **6**, 26288–26299.
- 42 P. Thakur, A. Kool, B. Bagchi, S. Das and P. Nandy, *Appl. Clay Sci.*, 2014, **99**, 149–159.
- 43 A. R. Darvishil, R. Bayati, O. S. Bishe, L.D. Wang, W.L.Li J. Sheng and W.D. Fei, *J. Appl. Phys.*, 2015, **117**, 094103.

CHAPTER 5

***STUDIES ON THE EFFECT OF
FUNCTIONALIZATION OF
 $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ NANOPARTICLES
IN PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$
NANOCOMPOSITE ON
DIELECTRIC AND ENERGY
STORAGE BEHAVIOR***

5.1 INTRODUCTION

Polymer ceramic nanocomposites have gained a lot of attention of scientific and engineering community due to their prospective applications for high energy density capacitors, varistors, phase-array antennae, charge storage etc.¹⁻⁵. Ceramic materials having a high dielectric constant such as BaTiO₃ (BT), BaSrTiO₃ (BST), Pb(Zr,Ti)O₃ (PZT), CaCu₃Ti₄O₁₂ (CCTO) etc are used as fillers in the polymer based composites⁶⁻¹². Among all ceramic fillers, calcium copper titanate (CCTO) shows a giant dielectric constant ($\epsilon \sim 10^4 - 10^5$) which is constant over a wide range of frequency ($10^2 - 10^6$ Hz) and temperature (100 K - 600 K)^{13,14}. But its application in various electronic devices is hindered due to its high tangent loss. On the other hand, polyvinylidene fluoride (PVDF) has a relatively low dielectric constant (~ 11) and low tangent loss (~ 0.01)¹⁵. The mechanical strength of PVDF is obviously very high as compared to the ceramic dielectric material such as CCTO. Therefore, PVDF-CCTO nanocomposite thick films could be advantageous with moderate dielectric constant, low tangent loss, and high mechanical strength³; which makes these nanocomposites suitable for various electronic applications¹⁶⁻¹⁸. The high dielectric constant and low tangent loss of PVDF-CCTO nanocomposite is desirable at a smaller volume percentage of loading CCTO in the PVDF matrix. In order to achieve high dielectric constant, large volume percentage loading of CCTO compromises with the mechanical strength of nanocomposite¹⁹. However, dispersion of ceramic fillers in the PVDF matrix is usually non-homogenous due to the low surface energy of the polymer²⁰. The formation of ceramic agglomerate in the nanocomposite increases the dielectric loss. The homogenous distribution of nanoparticles and its better interfacial connectivity with functional groups of polymers have become a fascinating subject since it may lead to better dielectric behavior and mechanical strength²¹⁻²⁵. The interfacial modification among the interfaces of polymer ceramic nanocomposite has been achieved by adopting different processing ways such as sonification, quenching and, functionalization etc.²⁶⁻²⁸ Among them, surface functionalization of ceramic nanoparticles with different functional groups (such as -OH, -NH₂, -SO₃H etc.) before incorporating it into the polymer matrix affects the dielectric and energy storage properties significantly. Tang *et al*⁷ have functionalized the surface of Ba_{0.2}Sr_{0.8}TiO₃ nanofibers functionalized with amine group by using ethylenediamine and prepared the PVDF-BST nanocomposite films. Amine

groups are well known to provide strong interaction with PVDF matrix, which improves dispersion and the charge uniformity at the ceramic/polymer interface. It shows ultra high energy density of 14.86 J/cc at 450 MV/m and provide microsecond discharged time. Shaohui *et al* ²⁴ have functionalized the surface of Ba_{0.6}Sr_{0.4}TiO₃ nanofibers at a low volume fraction with a hydroxyl group (-OH group) before making its composite with PVDF. This nanocomposite exhibits enhanced dielectric constant, reduced loss, and improved breakdown strength. The energy density is found to be 6.4 J/cm³ at loading of 2.5 wt% of functionalized Ba_{0.6}Sr_{0.4}TiO₃ nanofibers in the PVDF based nanocomposites. The improved properties are attributed to improved surface modification and crystallinity. Li *et al* ²⁹ studied the effect of functionalization of the BaTiO₃ nanoparticles by amine group on dielectric and energy storage behavior of P(VDF-CTFE) based nanocomposite. Presence of organic surface layer on the particles show better compatibility between polymer matrix and filler, which in turn improves the dielectric constant and energy storage behavior.

The incorporation of functionalized CCTO nanoparticles in PVDF-CCTO nanocomposite and its effect on dielectric and energy storage behavior is of immense importance to the scientific and technological community. This kind of investigation have not been carried out till date. The earlier study (discussed in chapter 4) on PVDF-CCTO nanocomposite films have shown that the nanocomposite film loaded with 8 vol% CCTO nanoparticles (i.e. PVDF-8CCTO) exhibited excellent polarization and energy storage behavior³⁰. This optimization, i.e. 8 vol% CCTO nanoparticles loading in the PVDF-CCTO nanocomposite is used to investigate the effect of incorporation of functionalized CCTO nanoparticles in PVDF-CCTO nanocomposite, on its dielectric and energy storage behavior. The amine functional group has been chosen to functionalize the CCTO nanoparticles as it is well known that it provide very good compatibility with PVDF matrix ^{5,7}. This chapter provides a comparative study of functionalized and non-functionalized 8 vol% CCTO nanoparticles incorporated in PVDF matrix. The nanocomposite consisting of functionalized and non-functionalized CCTO nanoparticles are abbreviated as PDVF-8FCCTO and PVDF-8CCTO respectively. The comparative study covers structural, morphological, dielectric, and energy storage behavior of these nanocomposites.

5.2 EXPERIMENTAL

It includes the synthesis of functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles and PVDF-CCTO nanocomposite films and their structural, dielectric, and displacement vs electric field studies, which are described in the following subsections.

5.2.1 Synthesis of functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ powder of 5 grams is prepared by sol-gel method is dispersed in 500 ml N, N-Dimethylformamide (DMF) through sonication for 15 minutes. This solution is stirred with magnetic stirrer at room temperature for one hour and, 500 ml ethylenediamine (EDA) is added in the stirred solution. The resulting solution is subjected to heating at 60°C along with continuous stirring further for 6 hours. This solution is allowed to cool down to room temperature. Cooled solution is subjected to centrifugation at 9000 rpm for 10 min. The centrifuged product is dried at 60°C for 12 hours in oven, which result in functionalized CCTO nanoparticles with amine ($-\text{NH}_2$) group.

5.2.2 Synthesis of functionalised $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles in polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films

PVDF-CCTO nanocomposite thick film ($\sim 50 \mu\text{m}$) with loading of 8 vol % functionalized CCTO nanoparticles (FCCTO) are prepared by solution casting technique. The nanocomposite thick films consisting of functionalized and non-functionalized CCTO nanoparticles are abbreviated as PDVF-8FCCTO and PVDF-8CCTO respectively.

5.2.3 Structural studies

X-ray diffraction (XRD), scanning electron microscope (SEM), and fourier transform infrared spectroscopy (FTIR) have been used to detect the phases and surface morphology. These techniques are already discussed in sec.2.3.1 of chapter 2.

5.2.4 Electrical studies

The dielectric constant, tangent losses, and energy storage behavior of the functionalized CCTO nanoparticles (FCCTO) based nanocomposite has been investigated at room temperature. The energy density and efficiency has also been calculated.

5.3 RESULT AND DISCUSSION

The results of structural and electrical studies are described in subsequent sections.

5.3.1 Structural studies

The results of X-ray diffraction (XRD), scanning electron microscope (SEM), and fourier transform infrared spectroscopy (FTIR) are discussed in subsequent sections.

5.3.1.1 X-ray diffraction

Figure 5.1 shows the X-ray diffraction of CCTO powder, pure PVDF, PVDF-8CCTO and PVDF-8FCCTO nanocomposite thick films. The pure CCTO and pure PVDF peaks can clearly seen in the XRD^{15,31}. The diffraction peak at $2\theta = 18.4^\circ$ corresponds (020) plane of α -phase of PVDF is common in both the nanocomposite films. The diffraction peaks at $2\theta = 20.7^\circ$ and 36.6° are assigned to (200) and, (020) planes of β -phase of PVDF which can be clearly seen in the PVDF-8CCTO nanocomposite film^{32,33}. In functionalized nanocomposite film the peak present at $2\theta = 20.1^\circ$ belong to (110) plane of the γ -phase and a small peak to α -phase³². The rest of peaks in both nanocomposite films belongs to crystalline phase of CCTO nanoparticles, which confirms incorporation of CCTO nanoparticles into the PVDF matrix.

5.3.1.2 Scanning electron microscope

Figure 5.2 shows the scanning electron microscope (SEM) micrographs of non-functionalized and functionalized CCTO

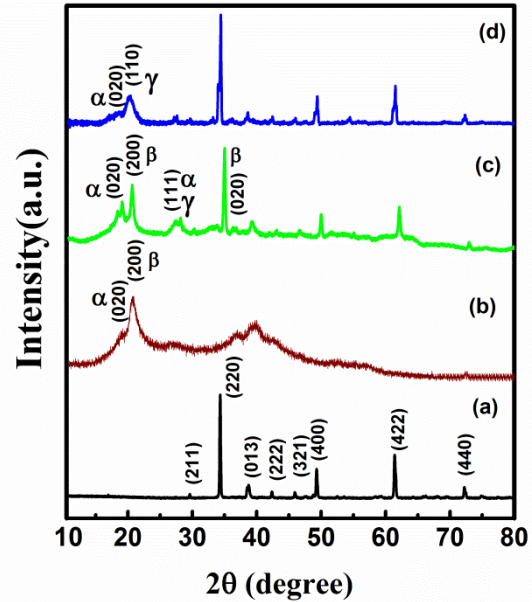


Fig. 5.1 X-ray diffraction of the (a) $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, (b) pure PVDF, (c) PVDF-8CCTO and, (d) PVDF-8FCCTO nanocomposite film.

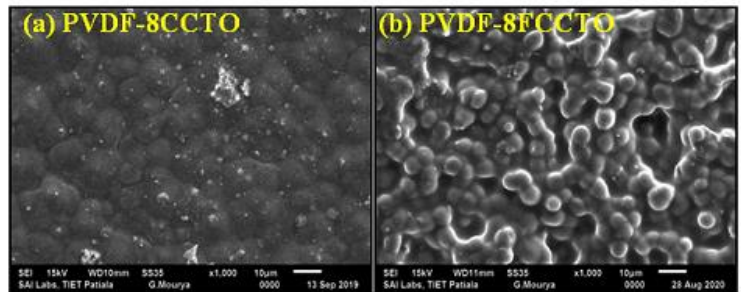


Fig. 5.2 Scanning electron microscope images of (a) PVDF-8CCTO and, (b) PVDF-8FCCTO nanocomposite films

nanocomposite films. PVDF-8CCTO nanocomposite film exhibit well separated spherulite structure and homogenous dispersion of CCTO nanoparticles in PVDF clearly visible with very less agglomeration³⁰. The functionalization of CCTO nanoparticles in the PVDF-8FCCTO nanocomposite leads to more homogeneous dispersion of functionalized CCTO nanoparticles [Fig 5.2 (b)]. The uniform spherical structures are clearly visible, which might be arising due to encapsulation of functionalized CCTO nanoparticles by PVDF. This might be happening by improved interfacial forces between PVDF and amine group functionalized CCTO nanoparticles due to better compatibility and charge uniformity at polymer/ceramic interface^{5,7}

5.3.1.3 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is used to confirm the surface functionalization of CCTO nanoparticles with amine $-NH_2$ groups. Figure 5.3 shows the comparative study of FTIR spectra of CCTO and functionalized CCTO nanoparticles with ethylenediamine. The absorption bands appear at 1450 cm^{-1} and 3350 cm^{-1} in the functionalized CCTO shows the presence of $-NH_2$ (amine) group, which confirms the functionalization of the CCTO nanoparticles by amine group [7,20]. The absorption bands

present at 571, 525 and 465 cm^{-1} attributed to Ca-O, Cu-O and Ti-O-Ti stretching vibrations respectively³⁴.

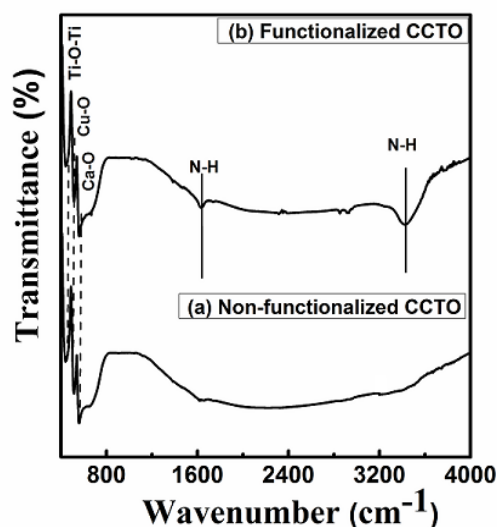


Fig. 5.3 Fourier transform infrared spectra of (a) non-functionalized and, (b) functionalized $CaCu_3Ti_4O_{12}$ powder.

Figure 5.4 shows FTIR spectra of pure PVDF, PVDF-8CCTO and PVDF-8FCCTO nanocomposite films in the range of $500\text{--}1500\text{ cm}^{-1}$. Pure PVDF and PVDF-8CCTO nanocomposite film shows the presence of α , β , and γ -phases. The absorption bands present at 615, 763, 795, 975, 1214 and 1380 cm^{-1} correspond to α -phase. The majority of α -phase is present in PVDF-8CCTO nanocomposite film. The absorption band at 840, 876 and 1176 cm^{-1} is confirmed the presence of β -phase. In fig 5.4 (c), PVDF-8FCCTO nanocomposite

film does not show the bands corresponding to β -phase, but the bands corresponding to γ -phase are observed at $\sim 776 \text{ cm}^{-1}$ and $\sim 1071 \text{ cm}^{-1}$. Therefore, incorporation of amine group functionalized CCTO nanoparticles in PVDF matrix also leads to change of crystallinity of PVDF i.e. γ -phase is developed along with α - phase. Similar kind of observation have been reported for some other nanocomposites ⁷.

5.3.2 Electrical studies

The electrical studies include dielectric behavior and electrical displacement vs electric field (D-E) studies. The discharging energy density as well as energy efficiency of PVDF-8CCTO and PVDF-8FCCTO nanocomposite thick films have been calculated from electrical displacement vs electric field data. The results of these studies are discussed in the following subsections.

5.3.2.1 Studies on dielectric behavior

Figure 5.5 shows the comparison in the dielectric constant of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films. The dielectric constant of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films at 1 kHz are found to be ~ 14 and ~ 19 respectively, which means the incorporation of functionalized CCTO nanoparticles in the PVDF matrix enhances the dielectric constant

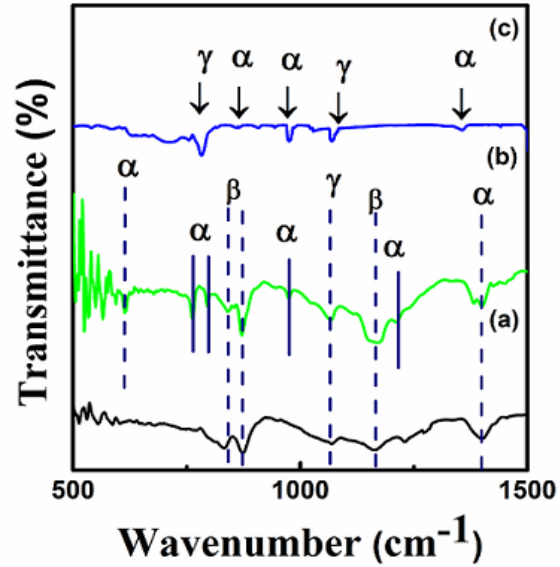


Fig. 5.4 Fourier transform infrared spectra of (a) PVDF, (b) PVDF-8CCTO and, (c) PVDF-8FCCTO nanocomposite films.

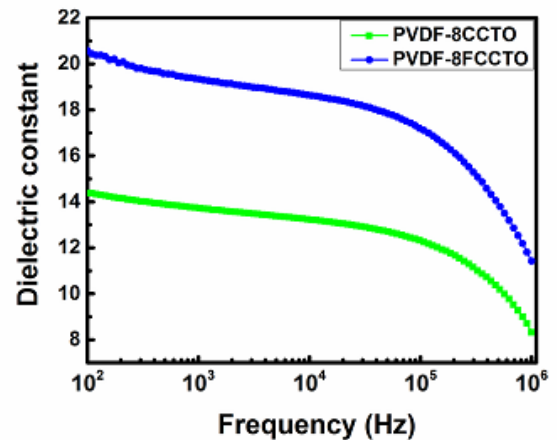


Fig. 5.5 Frequency dependent dielectric constant of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

by 35 %. The trend of the dielectric constant is found to be similar except the frequency at which dielectric constant starts showing decreasing trend, which is slightly lower in PVDF-8FCCTO as compared to PVDF-8CCTO nanocomposite thick film. This observed trend is ascribed to decrease in the relaxation time on incorporation of functionalized CCTO nanoparticles in PVDF matrix ³⁵. This can be further corroborated from the variation of ac conductivity with frequency (Fig. 5.7) the onset frequency (at which ac conductivity starts increasing) is lower for PVDF-8FCCTO as compared to that of PVDF-8CCTO nanocomposite thick film. Dielectric constant decreases above ($> 10^5$) frequency range due to lack of response of dipoles of nanocomposite film with respect to the applied field ²⁹. FTIR and XRD studies shows that PVDF-8FCCTO nanocomposite film is dominated by γ -phase of PVDF, which is less polar as compared to the β -phase dominant in the PVDF-8CCTO nanocomposite films. But still, 35% enhancement in the dielectric constant of PVDF-8FCCTO nanocomposite thick film has been observed. This might be ascribed to creation of additional dipoles due to interfacial modification by incorporation of amine group functionalized CCTO nanoparticles in the PVDF matrix. The causes of evolution of additional dipole moments are as follows.

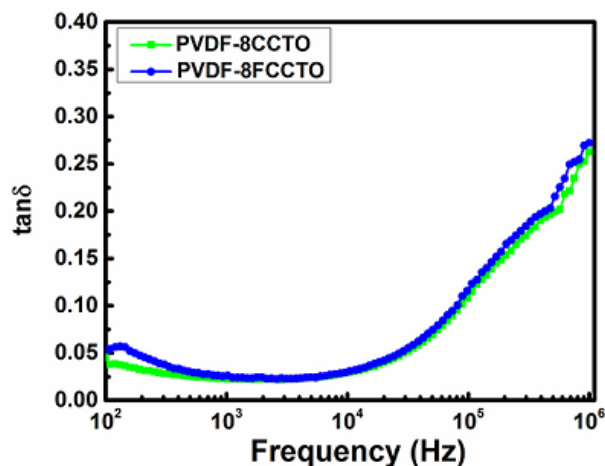


Fig. 5.6 Frequency dependent tangent loss of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

1. The surface of amine group functionalized nanoparticles are uniformly charged in PVDF-8FCCTO nanocomposite thick films. These charges may interact with some opposite charges in polymeric chain and creating additional dipoles, which is contributing to increased dielectric constant ³⁶.
2. The $-NH_2$ group attached with CCTO nanoparticles might be increasing the covalent polar character at PVDF/FCCTO interface ⁴. The interaction of $-NH_2$ group with CH_2 and CF_2 dipoles is more intense as evidenced by SEM studies, where PVDF is encapsulating in the functionalized CCTO nanoparticles. These interactions might be leading towards

creation of more dipoles, which is contributing to net dipole moment and increasing the dielectric constant.

Figure 5.6 shows the comparison between tangent loss of PVDF-8CCTO and PVDF-8FCCTO nanocomposite films.

Tangent loss is mainly arising due to the combined effect of dc conductivity, interfacial polarization, and dipolar relaxation³⁷. At 1 kHz the losses for both the films is found to be nearly same ~ 0.027 . The formation of large number of interfaces in the PVDF-8FCCTO nanocomposite thick films may leads to additional dipolar relaxation, which may increase the tangent loss. But the value of tangent

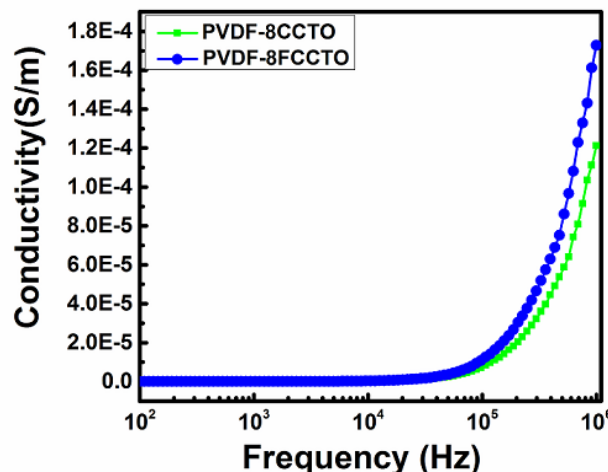


Fig. 5.7 Ac conductivity of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

loss remain unchanged, which is ascribed to the evolution γ -phase, that overcome the dielectric losses occurring due to the relaxation of dipoles at the interfaces. The γ -phase of PVDF has reduced loss as compared to β and α - phases^{7,10}. At higher frequency, the losses are increases due to competing relaxation phenomena between crystalline phases of PVDF and CCTO nanoparticles³⁰.

5.3.2.2 Studies on electrical displacement and energy storage behavior

Figure 5.8 shows the unipolar displacement vs electric field loops of PVDF-8CCTO and PVDF-8FCCTO nanocomposite film. The value of maximum polarization ($P_{\max}$) for PVDF-8FCCTO nanocomposite film is $\sim 2.1 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm), which is significantly higher as compared to its

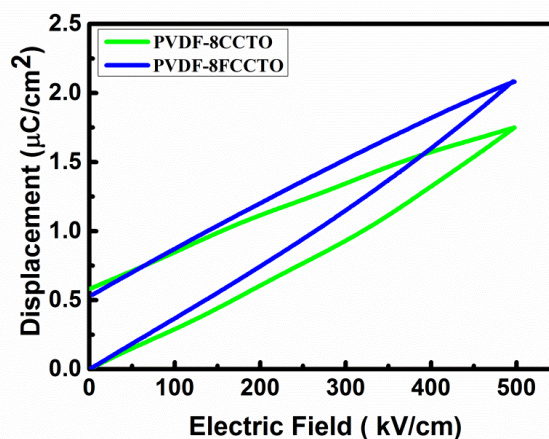


Fig 5.8 Unipolar D-E loop of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

value for PVDF-8CCTO nanocomposite film is $\sim 1.7 \mu\text{C}/\text{cm}^2$ (at $500 \text{ kV}/\text{cm}$) (already discussed in Chapter 4). The value of remnant polarization of PVDF-8FCCTO nanocomposite thick films is found to be slightly less as compared to PVDF-8CCTO nanocomposite thick films. Their respective value are $\sim 0.54 \mu\text{C}/\text{cm}^2$ and $\sim 0.58 \mu\text{C}/\text{cm}^2$. The observation of maximum

polarization and low remnant polarization in PVDF -8FCCTO nanocomposite film will ultimately provide increased energy density and efficiency.

Figure 5.9 shows the discharge energy density PVDF-8CCTO and PVDF-8FCCTO nanocomposite films calculated from D-E loops. The method of calculation is already mentioned in Sec. 2.3.2.1 of chapter 2. PVDF-8FCCTO nanocomposite at $500 \text{ kV}/\text{cm}$, the stored energy density is $\sim 1.2 \text{ J}/\text{cm}^3$, whereas it is $\sim 0.8 \text{ J}/\text{cm}^3$ for PVDF-8CCTO nanocomposite^{21,30}. The

incorporation of amine group functionalized CCTO nanoparticles in PVDF matrix enhance the discharge energy density by 50 %.

Figure 5.10 shows the energy efficiency of PVDF-8CCTO and PVDF-8FCCTO under various applied field. It can be seen that, PVDF-8FCCTO nanocomposite exhibits high energy efficiency as compared to that of PVDF-8CCTO nanocomposite film. The respective values of energy efficiency for

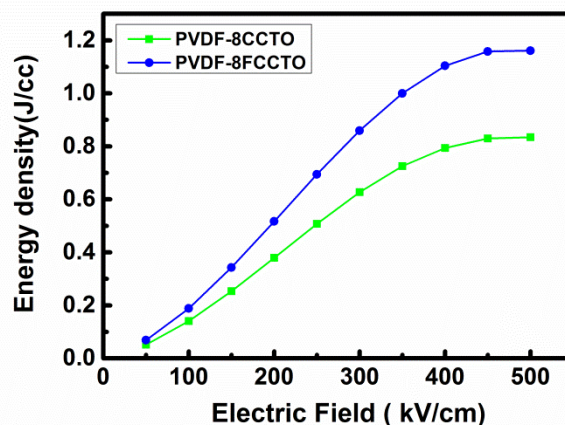


Fig. 5.9 Energy density of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

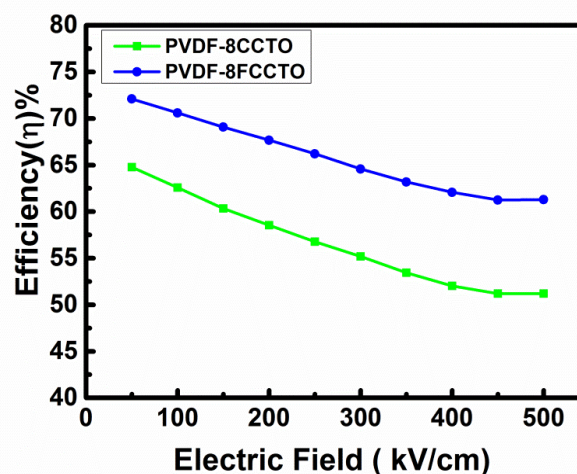


Fig. 5.10 Energy efficiency under the applied electric field of PVDF-8CCTO and, PVDF-8FCCTO nanocomposite films.

PVDF-8FCCTO and PVDF-8CCTO nanocomposite thick films are $\sim 70.5\%$ and $\sim 62.5\%$ at 100 kV/cm. The observed behavior of PVDF-8FCCTO nanocomposite thick film such as a maximum polarization, lower remnant polarization, increased discharge energy density, and energy efficiency is attributed to evolution of γ -phase in PVDF-8FCCTO nanocomposite which is responsible for high energy density and efficiency^{7,10,21,38}. The creation of large number of dipoles at the interfaces, increases the resultant net polarization, which increase the discharge energy density and efficiency.

5.4 CONCLUSION

The incorporation of amine group functionalized CCTO nanoparticles in PVDF matrix is found to affect the dielectric and energy storage behavior significantly. At 1 kHz the dielectric constant of the PVDF-8CCTO and PVDF-8FCCTO nanocomposite film are found to be ~ 14 and ~ 19 respectively. The dielectric constant is enhanced by 35 % without compromising with tangent loss, whereas tangent loss is found to be ~ 0.027 at 1 kHz for both the films. Discharging energy density for PVDF-8CCTO and PVDF-8FCCTO nanocomposite films are found to be ~ 0.8 J/cc and ~ 1.2 J/cc (at 500 kV/cm) respectively. The discharge energy density of PVDF-8FCCTO nanocomposite films is increased by 50%. The energy efficiency of PVDF-8FCCTO is significantly higher as PVDF-8CCTO nanocomposite thick films. The enhancement in the dielectric constant, energy density, and energy efficiency of PVDF-8FCCTO nanocomposite film is attributed to evolution of γ -phase in PVDF and, enhanced dipole moment by virtue of interfacial interaction in PVDF/FCCTO interfaces.

References

- 1 M. Arbatti, X. Shan and Z. Cheng, *Adv. Mater.*, 2007, **19**, 1369–1372.
- 2 S. Kumar, S. Supriya and M. Kar, *Compos. Sci. Technol.*, 2018, **157**, 48–56.
- 3 A. Srivastava, K. K. Jana, P. Maiti, D. Kumar and O. Parkash, *J. Eng.*, 2015, **2015**, 9.
- 4 W. Xia and Z. Zhang, *IET Nanodielectr*, 2018, **1**, 17–31.
- 5 O. S. Yakovenko, L. Y. Matzui and L. L. Vovchenko, *J. Mater. Sci.*, 2017, **52**, 5345–5358.
- 6 P. Hu, W. Sun, M. Fan, J. Qian, J. Jiang, Z. Dan, Y. Lin, C. W. Nan, M. Li and Y. Shen, *Appl. Surf. Sci.*, 2018, **458**, 743–750.
- 7 H. Tang and H. A. Sodano, *Nano Lett.*, 2013, **13**, 1373–1379.
- 8 T. Liu, M. Wallace, S. Trolier-McKinstry and T. N. Jackson, *J. Appl. Phys.*, 2017, **122**, 164103.
- 9 D. L. Sun, A. Y. Wu and S. T. Yin, *J. Am. Ceram. Soc.*, 2008, **91**, 169–173.
- 10 N. Phromviyo, P. Thongbai and S. Maensiri, *Appl. Surf. Sci.*, 2018, **446**, 236–242.
- 11 N. J. Joshi, G. S. Grewal, V. Shrinet, T. P. Govindan and E. Road, 2012, **19**, 83–90.
- 12 A. V Trukhanov, V. O. Turchenko, I. A. Bobrikov, S. V Trukhanov, I. S. Kazakevich and A. M. Balagurov, *J. Magn. Magn. Mater.*, 2015, **393**, 253–259.
- 13 M. A. Subramanian, D. Li, N. Duan, B. A. Reisner and A. W. Sleight, *J. Solid State Chem.*, 2000, **151**, 323–325.
- 14 A. P. Ramirez, M. A. Subramanian, M. Gardel, G. Blumberg, D. Li, T. Vogt and S. M. Shapiro, *Solid State Commun.*, 2000, **115**, 217–220.
- 15 S. Satapathy, S. Pawar, P. K. Gupta and K. B. R. Varma, *Bull. Mater. Sci.*, 2011, **34**, 727–733.

- 16 C. V. Chanmal and J. P. Jog, *Express Polym. Lett.*, 2008, **2**, 294–301.
- 17 Y. Wang, P. He and F. Li, .
- 18 W. Yang, S. Yu, R. Sun and R. Du, *Acta Mater.*, 2011, **59**, 5593–5602.
- 19 S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai and Z. An, *RSC Adv.*, 2015, **5**, 40692–40699.
- 20 J. Zhang, J. Ma, L. Zhang, C. Zong, A. Xu, Y. Zhang, B. Geng and S. Zhang, *RSC Adv.*, 2020, **10**, 7065–7072.
- 21 S. Liu, S. Xue, S. Xiu, B. Shen and J. Zhai, *Nat. Publ. Gr.*, 2016, 1–11.
- 22 L. Gao, J. He, J. Hu and Y. Li, *J. Phys. Chem. C*, 2014, **118**, 831–838.
- 23 J. Fu, Y. Hou, M. Zheng, Q. Wei, M. Zhu and H. Yan, *ACS Appl. Mater. Interfaces*, 2015, **44**, 24480–24491.
- 24 and Z. W. Liu Shaohui, Zhai Jiwei, Wang Jinwen, Xue Shuangxi, *ACS Appl. Mater. Interfaces*, 2014, **6**, 1533–1540.
- 25 S. Liu and J. Zhai, *J. Mater. Chem. A*, 2015, **3**, 1511–1517.
- 26 F. Shi, J. Ma, P. Wang and Y. Ma, *J. Taiwan Inst. Chem. Eng.*, 2012, **43**, 980–988.
- 27 L. Tshwenya and O. A. Arotiba, *RSC Adv.*, 2017, **7**, 34226–34235.
- 28 L. Xie, X. Huang, C. Wu and P. Jiang, *J. Mater. Chem.*, 2011, **21**, 5897–5906.
- 29 J. Li, J. Claude, L. E. Norena-Franco, S. Il Seok and Q. Wang, *Chem. Mater.*, 2008, **20**, 6304–6306.
- 30 S. Kaur and D. P. Singh, *Mater. Chem. Phys.*, 2020, **239**, 122301.
- 31 S. Kaur, A. Kumar, A. L. Sharma and D. P. Singh, *Ceram. Int.*, 2019, **45**, 7743–7747.
- 32 J. Li, Q. Meng, W. Li and Z. Zhang, *J. Appl. Polym. Sci.*, 2011, **116**, 2674–2684.
- 33 P. Martins, A. C. Lopes and S. Lanceros-Mendez, *Prog. Polym. Sci.*, 2014, **39**, 683–706.

- 34 C. Yang, H. S. Song and D. B. Liu, *Compos. Part B Eng.*, 2013, **50**, 180–186.
- 35 P. Gupta, A. Kumar, M. Tomar, V. Gupta and D. P. Singh, *J. Mater. Sci. Mater. Electron.*, 2017, **28**, 11806–11812.
- 36 S. L. Zhong, Z. M. Dang, W. Y. Zhou and H. W. Cai, *IET Nanodielectrics*, 2018, **1**, 41–47.
- 37 Y. Li, X. Huang, Z. Hu, P. Jiang, S. Li and T. Tanaka, *ACS Appl. Mater. Interfaces*, 2011, **3**, 4396–4403.
- 38 K. W. Wagner, *Arch. für Elektrotechnik*, 1914, **2**, 371–387.

CHAPTER 6
SUMMARY
AND
FUTURE SCOPE

6.1 INTRODUCTION

Polymer ceramic nanocomposite has been widely investigated due to its prospective applications in high energy density capacitor, and embedded electronics. Polymer provides mechanical and dielectric strength to the composite, whereas ceramic fillers have high dielectric constant. The polymer ceramic nanocomposites have moderate dielectric constant along with high mechanical and dielectric strength, which make them suitable candidate for energy storage applications. It is always desirable to have a ceramic dielectric filler in polymeric matrix which have high dielectric constant, which is constant in a broad frequency and temperature range. The calcium copper titanate (CCTO) ceramic has found to have very high dielectric constant ($\sim 10^4$) which is invariant over wide range of frequency (10^2 - 10^6 Hz) and temperature (100 K - 600 K). Among all dielectric polymers the polyvinylidene fluoride (PVDF) has low dielectric constant (~ 10), but it is very versatile in nature because of different crystalline phases (*viz* α , β , γ , δ and ϵ) along with different dielectric and polarization behaviour.

The nanocomposite of CCTO with PVDF could be of special interest in order to understand the underlying physics as well as its possibility for energy storage capacitor such as high energy density capacitor. Therefore, in the present work dielectric and energy storage properties of polyvinylidene fluoride - calcium copper titanate (PVDF-CCTO) nanocomposites have been investigated.

6.2 COMPONENT OF STUDY

The dielectric and energy storage behaviour of polyvinylidene fluoride - calcium copper titanate (PVDF-CCTO) nanocomposites has been studied. The different component involved in these studies are discussed in the subsequent sections.

6.2.1 Synthesis of materials

Polyvinylidene fluoride (PVDF) and PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films are synthesized for studying the dielectric and energy storage behavior. CCTO nanoparticles incorporated in PVDF matrix have also been synthesized in order to optimize its particle size and dielectric behavior.

6.2.1.1 Synthesis of polyvinylidene fluoride thick films and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

Polyvinylidene-fluoride (PVDF) thick films have been synthesized by solution casting technique. These thick films have been annealed at 50°C, 90°C, 100°C, 110°C and 130°C respectively for 5 hours in air. The details of study have been given in sec.3. 2.1, chapter 3.

Calcium copper titanate nanoparticles has been synthesized by sol-gel method in order to optimize the particles size in the nanometre range, which is discussed in sec. 3.3.1, chapter 3.

6.2.1.2 Synthesis of polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films

Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (PVDF-CCTO) nanocomposite films have been prepared by solution casting technique. These nanocomposite films have been synthesized at different loading of CCTO nanoparticles. The details have been given in sec. 4.2.1, chapter 4.

6.2.1.3 Synthesis of polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films incorporated with functionalized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles prepared by sol-gel method has been functionalized with amine group (---NH_2) in order to investigate its effect on dielectric and energy storage behaviour. The details have been given in Sec. 5.2.1, Chapter 5.

6.2.2 Structural and morphological studies

X-ray diffraction (XRD) and scanning electron microscope (SEM) have been carried out to determine the crystal structure and surface morphology of the nanoparticles and the nanocomposite thick films (Sec. 2.3.1), whereas high resolution transmission electron microscopy (HRTEM) has been carried out to determine particle size & morphology of the $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles. Fourier transform infrared spectroscopy (FTIR) has been employed to investigate different polymorph in the nanocomposite films.

6.2.3 Electrical Studies

The electrical studies have been done in two sections. Dielectric constant (permittivity), dielectric loss (tangent loss), and I-V (current-voltage) measurements have been carried out at low field (Sec. 2.3.2.1). Displacement vs electric field measurements have been carried out at high electric field (Sec. 2.3.2.2).

6.3 RESULTS

The results of structural, dielectric and energy storage of CCTO as well as PVDF-CCTO nanocomposite are briefly summarized in the following sections.

6.3.1 Polyvinyl fluoride thick films and $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

The results of PVDF thick films and CCTO ceramic nanoparticles are briefly summarized in the subsequent subsections.

6.3.1.1 Structural studies

X-ray diffractions (XRD) of PVDF thick films confirms that PVDF polymer is semi-crystalline in nature (Sec.3.2.2.1.1, Chapter 3) whereas CCTO has a perovskite type structure and the pure phase of CCTO powder is obtained at 900°C sintering temperature (Sec 3.3.2.1.1, Chapter 3). Scanning electron microscope (SEM) and fourier

transform infrared spectroscopy (FTIR) has been performed in order to study the crystallographic structure, surface morphology (Sec. 3.2.2.1.2, Chapter 3) and groups present in PVDF thick films (Sec. 3.2.2.1.3, Chapter 3). Transmission electron micrograph (TEM) is carried out to determine the size of the nanoparticles (Sec. 3.3.2.1.2, Chapter 3).

6.3.1.2 Dielectric studies

The dielectric constant measurements have been carried out at room temperature with frequency. PVDF thick films annealed at 100°C has been found higher dielectric constant (~ 11), whereas for CCTO ceramic dielectric constant has been found to be ~ 7990 at 1 kHz.

6.3.1.3 Displacement vs Electric field studies

The displacement vs electric field has been carried out for the PVDF films annealed at different temperatures such as 50°C, 90°C, 100°C, 110°C and 130°C for 5 hours. The maximum polarization ($P_{\max} \sim 1.27 \mu\text{C}/\text{cm}^2$) as well as remnant polarization ($P_r \sim 0.38 \mu\text{C}/\text{cm}^2$) is found to be highest for the film annealed at 100°C.

6.3.1.4 Current-voltage studies

The current-voltage measurement has given the nonlinearity and breakdown voltage of CCTO pellet as ~ 6.3 and $\sim 4400 \text{ V}/\text{cm}$ respectively. The discharging and charging behaviour of capacitor structure formed by CCTO pellet has given discharging time and energy density $\sim 0.34 \text{ ms}$ and $\sim 7 \text{ J}/\text{cc}$ respectively.

6.3.2 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films

Results of structural, morphological, and electrical studies of polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (PVDF-CCTO) nanocomposite thick films are briefly summarized as follows.

6.3.2.1 Structural studies

X-ray diffraction (XRD) of PVDF-CCTO nanocomposite films confirms the inclusion of CCTO nanoparticles in the PVDF matrix. Transmission electron microscope (TEM) shows the CCTO nanoparticles have a semi spherical shape with very less agglomeration and the average particle size comes in $\sim 60 \text{ nm}$. Scanning electron microscope (SEM) shows the homogenous distribution of the CCTO nanoparticles in the PVDF matrix. Fourier spectra shows the presence of α , β and γ phases in the PVDF-CCTO nanocomposite films.

6.3.2.2 Dielectric studies

The trend of frequency dependent dielectric constant in PVDF-CCTO nanocomposite thick films found to be similar in all compositions. The dielectric constant is increases with increase in the loading of CCTO nanoparticles (i.e. loading at 4 vol%, 8 vol%, 12vol%, and 15 vol%). CCTO nanoparticles has high dielectric constant its inclusion in PVDF matrix

creates local internal field, which also increased the dielectric constant in PVDF-CCTO nanocomposite films. The tangent loss found to be less at 1 kHz in PVDF-CCTO nanocomposite thick films and it starts increase at higher frequency $>10^5$ Hz its due to competing relaxation phenomena among PVDF crystalline phases (i.e. α , β and γ) and CCTO nanoparticles.

6.3.2.3 Displacement vs Electric field loop

The displacement vs electric field studies have been carried out for PVDF-CCTO nanocomposite films. The value of maximum polarization ($P_{\max}$) and remnant polarization (P_r) for PVDF-8CCTO nanocomposite film with 8 vol% of CCTO are found $\sim 1.7 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm) and $0.6 \mu\text{C}/\text{cm}^2$, which is highest as compared to other nanocomposite films.

6.3.3 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films incorporated with functionalised $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

The results of the functionalized CCTO nanoparticles with amine group, and PVDF-functionalised CCTO (PVDF-FCCTO) nanocomposites are summarized as follows:

6.3.3.1 Structural and morphological studies

X-ray diffraction (XRD) of functionalized CCTO nanoparticles confirms the crystalline phase of CCTO. Scanning electron microscope (SEM) shows the homogeneous dispersion of functionalized CCTO nanoparticles in the PVDF matrix and uniform spherical structures are clearly visible. Fourier transform infrared spectroscopy (FTIR) confirms the surface functionalization of CCTO nanoparticles with amine ($-\text{NH}_2$) groups.

6.3.3.2 Dielectric studies

The frequency dependent dielectric measurement has been carried out for PVDF-8CCTO and PVDF-8FCCTO nanocomposite films at room temperature, which have respective dielectric constant at 1 kHz are found to be ~ 14 and ~ 19 . The tangent losses at 1 kHz found to be nearly same ~ 0.027 for both the films.

6.3.2.2 Displacement vs Electric field loop

The unipolar displacement vs electric field loops have been measured for PVDF-8CCTO and PVDF-8FCCTO nanocomposite films. The value of maximum polarization ($P_{\max}$) for PVDF-8FCCTO nanocomposite film is $\sim 2.1 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm), which is significantly higher as compared to its value $\sim 1.7 \mu\text{C}/\text{cm}^2$ for PVDF-8CCTO nanocomposite film (at ~ 500 kV/cm).

6.4 CONCLUSION

The important conclusions drawn from the present investigations have been briefly summarized in the following subsections.

6.4.1 Polyvinylidene fluoride thick films

Polyvinylidene fluoride (PVDF) thick films have been synthesized by solution casting technique. The PVDF fabricated film is subjected to annealing at 50°C, 90°C, 100°C, 110°C and 130°C for 5 hours in air. The effect of annealing temperature on structural, dielectric and polarization behavior have been investigated. The XRD and FTIR results shows that β -phase has almost disappeared above 100°C. Coexistence of polar β -phase along with α -phase is observed upto an annealing temperature of 100°C. Films annealed at temperature > 100°C completely converts into α -phase.

The film annealed at 100°C exhibits highest dielectric constant and maximum polarization, which are ~ 11 (at 1 kHz) and $\sim 1.27 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm) respectively. The enhanced dielectric constant and maximum polarization might be attributed to increased dipolar contribution at α/β interfaces as well as amorphous crystalline interface.

6.4.2 Calcium copper titanate nanoparticles

Nanoparticles of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has been synthesized by sol- gel method. The X-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) have respectively been used to determine the phase purity and particle size of CCTO nanoparticles. The average size of CCTO particles is lying in the range 50–60 nm. The dielectric constant and tangent loss of CCTO pellet at 1 kHz are found to be ~ 7790 and ~ 0.096 respectively. The breakdown electric field and non-linear coefficient are obtained as $\sim 4400 \text{ V}/\text{cm}$ and ~ 6.3 respectively. The capacitor structure formed by CCTO exhibits very good discharging energy density and decay response. Discharging time and discharged energy density are found to be $\sim 0.34 \text{ ms}$ and $\sim 7 \text{ J}/\text{cc}$ respectively. Therefore, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits high dielectric constant, high breakdown electric field, along with very good capacitive behaviour.

6.4.3 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite thick films

Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (PVDF-CCTO) nanocomposite films have been fabricated by solution casting method, where $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanoparticles are incorporated at different vol% (4, 8, 12 and 15 vol%) in PVDF polymer matrix. According to loading volume % of CCTO, the nanocomposite film is denoted PVDF-4CCTO, PVDF-8CCTO, PVDF-12CCTO and PVDF-15CCTO respectively. X-ray diffraction (XRD) studies have confirmed the phase purity as well as the inclusion of the CCTO nanoparticles in the PVDF matrix. The scanning electron microscope (SEM) micrograph shows slight aggregation of CCTO nanoparticles due to increase in the loading of CCTO nanoparticles in PVDF matrix.

The dielectric constant of PVDF-CCTO nanocomposite films increases with increase in

loading of CCTO nanoparticles. Initially tangent loss decreases with frequency and attains minima. At frequency $> 10^5$ Hz; tangent loss starts again increasing. This feature is common to all PVDF-CCTO nanocomposite films. High tangent loss at lower frequencies might be arising due to surface effects; whereas enhancement in tangent loss for frequency $> 10^5$ Hz is resulting due to competing relaxation phenomena among PVDF crystalline phases (i.e. α , β and, γ -phases) and CCTO nanoparticles. PVDF-8CCTO nanocomposite films show maximum polarization and remnant polarization i.e. $\sim 1.7 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm) and $\sim 0.6 \mu\text{C}/\text{cm}^2$ respectively. It also possesses highest discharge energy density $\sim 0.85 \text{ J/cc}$ at 500 kV/cm and energy efficiency of $\sim 65 \%$ at 100 kV/cm. Enhanced energy density and polarization are attributed to increase dipole moment due to ordering of α , β , γ -phases of PVDF in PVDF-CCTO nanocomposite films. This work is taking a lead for more investigation of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ based polymer nanocomposite as a unique material for high energy density capacitors.

6.4.4 Polyvinylidene fluoride - $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films incorporated with functionalised $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles

The conclusion drawn in chapter 4 of the present thesis has shown that PVDF-CCTO nanocomposite films loaded with 8 vol% CCTO nanoparticles (i.e. PVDF-8CCTO) exhibited excellent polarization and energy storage behavior. Therefore, the effect of functionalization of CCTO nanoparticles on dielectric and energy storage have been carried out only for this composition. The nanocomposite consisting of functionalized and non-functionalized CCTO nanoparticles are abbreviated as PVDF-8FCCTO and PVDF-8CCTO respectively.

The incorporation of amine group functionalized CCTO nanoparticles in PVDF matrix is found to affect the dielectric and energy storage behaviour significantly. At 1 kHz the dielectric constant of the PVDF-8CCTO and PVDF-8FCCTO nanocomposite films are found to be ~ 14 and ~ 19 respectively. The dielectric constant is enhanced by 35 % without compromising with tangent loss, whereas tangent loss is found to be ~ 0.027 at 1 kHz for both the films. PVDF-8FCCTO nanocomposite films exhibits maximum polarization is $\sim 2.1 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm) than PVDF-8CCTO nanocomposite film whereas remnant polarization is found to be same $0.5 \mu\text{C}/\text{cm}^2$ (at 500 kV/cm). Discharging energy density for PVDF-8CCTO and PVDF-8FCCTO nanocomposite films are found to be $\sim 0.8 \text{ J/cc}$ and $\sim 1.2 \text{ J/cc}$ (at 500 kV/cm) respectively. The discharge energy density of PVDF-8FCCTO nanocomposite films is increased by 50%. The energy efficiency of PVDF-8FCCTO is significantly higher as PVDF-8CCTO nanocomposite thick films. The enhancement in the dielectric constant, energy density, and energy efficiency of PVDF-8FCCTO nanocomposite

film is attributed to evolution of γ -phase in PVDF and, enhanced dipole moment by virtue of interfacial interaction in PVDF/FCCTO interfaces.

6.5 FUTURE SCOPE OF THESIS

The investigations in present work on PVDF-CCTO nanocomposite may form the basis for

its relevance towards further applications in the microelectronics and energy storage capacitors. The work carried out in this thesis is mainly focused on studies of the dielectric and energy storage behaviour of PVDF-CCTO nanocomposites, which could be useful for high energy density capacitors. But further investigation related with modification of processing condition and its effect on dielectric and energy storage behaviour, are still required. Keeping this in point of view, some interesting and novel investigations will be as follows;

1. The composite of CCTO nanoparticles with other dielectric polymers such as polyvinylidene difluoride–trifluoroethylene (PVDF-TrFE), biaxially oriented polypropylene (BOPP) need to be investigated on the front of their dielectric and energy storage behaviour.
2. The functionalization of nanoparticles in polymer-based composites is found to affect its dielectric and energy storage behaviour. The effect of functionalization of CCTO nanoparticles functionalized with other functionalized groups e.g. -OH, -SO₃H and, its composite with various dielectric polymers would also be an interesting investigation.
3. The losses of CCTO ceramic is higher, which could be suppressed by making core-shell nanoparticles. The incorporation of core shell nanoparticles in polymeric matrix can also improve dielectric and energy storage behaviour.

Influence of annealing on dielectric and polarization behavior of PVDF thick films

Shobhneek Kaur¹ · Ashok Kumar² · Amit L. Sharma³ · Dwijendra P. Singh¹ 

Received: 17 November 2016 / Accepted: 7 February 2017 / Published online: 18 February 2017
© Springer Science+Business Media New York 2017

Abstract The polyvinylidene fluoride (PVDF) thick film has been fabricated by a solution casting method. The fabricated film is subjected to annealing at 50, 90, 100, 110 and 130 °C for 5 h. The effect of annealing on structural, crystalline, dielectric and polarization behavior is investigated. The β -phase PVDF is found to coexist with α -phase for annealing temperature upto 100 °C, after that β -phase is converted to α -phase. The film annealed at 100 °C, exhibits enhanced permittivity, reduced tangent loss and enhanced polarization. The dielectric permittivity and tangent loss of film annealed at 100 °C are ~ 11 and ~ 0.025 respectively for the frequency range of 10^3 – 10^5 Hz. The saturation polarization for this film is ~ 1.27 $\mu\text{C}/\text{cm}^2$. The enhanced dielectric permittivity and polarization for the film annealed at 100 °C might be attributed to increase in crystalline α and β -phase interface as well as crystalline amorphous interface. The thick film of PVDF with improved dielectric and polarization behavior could be useful for high power electronics application.

1 Introduction

High energy density capacitors have drawn considerable interest due to their great potential of application in electric vehicles and other pulse power applications [1–4]. Dielectric permittivity and polarization behavior of material are

one of the important parameter for high energy density [5–7]. A flexible semi-crystalline polymer such as polyvinylidene fluoride (PVDF) is flexible and, has high dielectric breakdown strength but low intrinsic permittivity [7]. PVDF is typically crystalline with five distinct crystalline structure named as α , β , γ , δ and ϵ phases [8, 9]. Among them, ϵ and δ phases are rarely studied due to their poor stability [10]. The β crystalline form possesses strong polarization, which has a zigzag (all -trans) confirmation (TTTT) of the polymer chain. The development of β -phase content has always attracted great interest; because electro active properties depend on β -phase content. The β form in PVDF could be obtained by stretching, quenching and polling under high electric field [11]. PVDF film formed from dimethylformamide (DMF) solution casting has been reported to have stable β -phase at low temperature (~ 50 °C), where porosity of film is very high, preventing it from electrical applications [12, 13]. Effect of annealing temperature on phase transition in poly(vinylidene fluoride) film has been widely studied by different research groups [14–16]. Satapathy et al. [14] have observed the changes in phase content in the PVDF film formed by using dimethyl sulfoxide (DMSO) at different annealing temperature that affects the polarization behavior. The crystalline phase transformation and dielectric properties of α and β -phase have also been investigated [17, 18]. The γ -phase of the PVDF can be obtained from existing α and β -phase, by annealing induced phase transition caused by slow melting and recrystallization process [17]. Guan et al. [18] have studied the effect of crystalline phase orientation on dielectric and energy storage behavior in PVDF based copolymer. Most of the research reports are focused on effect of annealing temperature on microstructure and crystallinity of PVDF thick films. The effect of crystalline phase on dielectric and energy storage has also been investigated for

✉ Dwijendra P. Singh
dpsingh@thapar.edu

¹ School of Physics & Materials Science, Thapar University, Patiala 147004, India

² CSIR- National Physical Laboratory, Delhi 110012, India

³ Thin Film Group, CSIR- CSIO, Chandigarh 160030, India

the PVDF based PVDF or PVDF-TrFE copolymer [19, 20]. The existing literature is still devoid of detailed investigation on the effect of annealing temperature of PVDF thick film on dielectric and polarization behavior. These investigations will provide a way for monitoring the phase stability and its effect on dipolar behavior of PVDF thick film. Here, we report the effect of annealing temperature on the dielectric and polarization behavior of PVDF thick film.

2 Experimental

PVDF thick films were prepared by solution casting method. 2 gm. PVDF powder was dissolved in 100 ml of N-N Dimethylformamide (DMF), [Sigma Aldrich]. This solution was magnetically stirred at 50 °C. When the solution becomes thick, it was poured into the petridish. This solution was dried at 160 °C in a vacuum oven in order to evaporate the DMF. PVDF thick film of thickness of 20–30 μm was separated out from petridish. These films have been annealed at 50, 90, 100, 110 and 130 °C respectively for 5 h in air. X-ray diffraction (XRD) was used to investigate the crystal structure of annealed PVDF films. Diffractograms were recorded by using PANalytical

diffractometer by using Cu K α radiation. Fourier Transform Infrared spectroscopy (FTIR) (Agilent Resolution Pro Cary 660) was employed to investigate the bonding and different polymorph present in the annealed films. The PVDF thick film was of rectangular shape. The gold electrodes of area (0.25 cm²) were sputtered on both sides of films by using Auto fine coater-JEOL, JEC-3000FC. The dielectric properties of the electroded films were measured by Solatron 1260 gain/phase analyzer. The P-E loops were measured by using premier Radiant-II ferroelectric tester by applying an triangular wave of frequency of 10 Hz. Differential Scanning Calorimetry (DSC) was carried out by using a METSCIT STA449C instrument under nitrogen atmosphere at the heating /cooling at rate of 5 °C/min.

3 Results and discussion

Figure 1 shows the X-ray diffractogram of PVDF thick films annealed at different temperatures. Two peaks appearing at $2\theta = 18.4^\circ$ and 20° corresponds to α -phase of PVDF and are corresponding to (0 2 0) and (1 1 0) planes respectively [21]. The peaks of γ -crystalline phase appears at $2\theta = 18.5^\circ$ (0 2 0) and 20.1° (1 1 0); whereas the presence

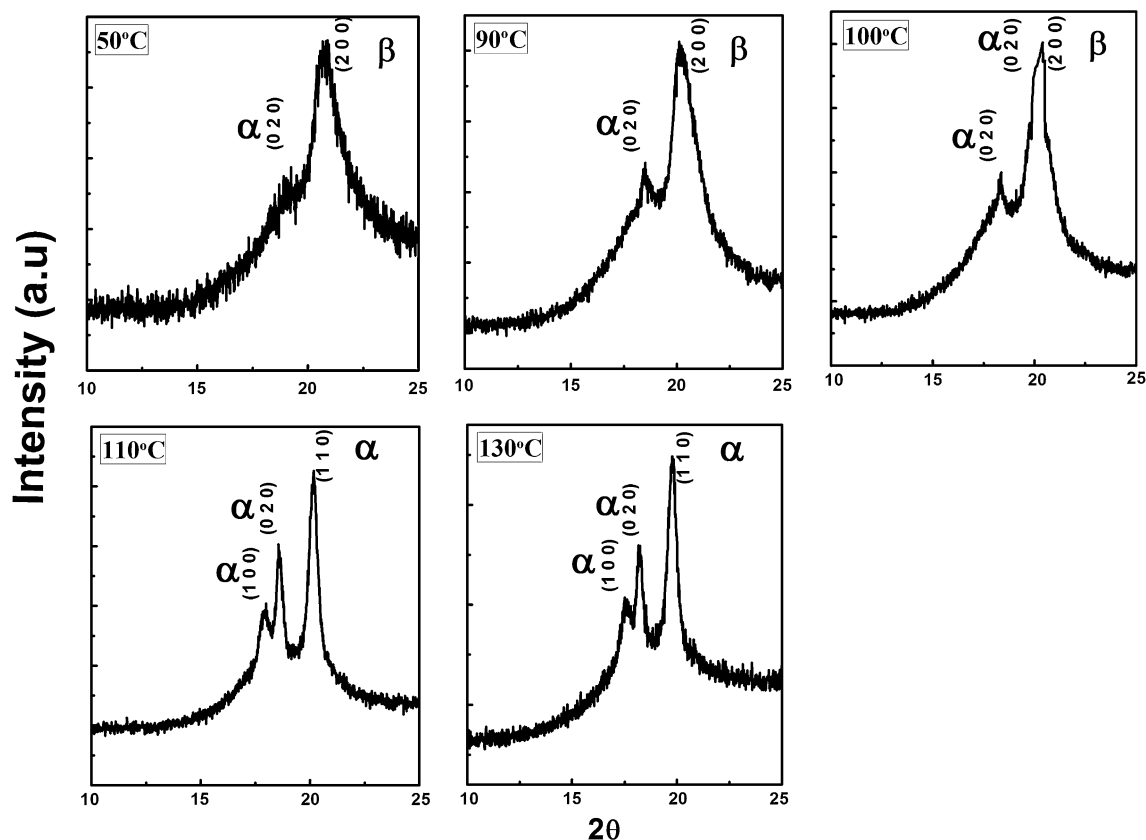


Fig. 1 X-ray diffractogram of PVDF thick films annealed at different temperatures

of β -phase is confirmed by peaks at 20.7° (2 0 0) and 20.8° (1 1 0) [4, 14, 22]. In our case, the PVDF film annealed at 90°C shows prominent peak corresponding to β -phase at $2\theta=20.7^\circ$ (2 0 0) and weak peak at $2\theta=19.1^\circ$ (1 1 0) corresponds to α -phase. When the annealing temperature is increased, the peak of α -phase ($2\theta=19.1^\circ$) is becoming prominent along with β -phase. The increase in annealing temperature usually promotes the growth of crystallite size. The broadening in the peak of β -phase for the film annealed at 90°C is smaller than the film annealed at 50°C ; which confirms that crystalline size of β -phase for the film annealed at 90°C is larger than the film annealed at 50°C . But for the film annealed at 100°C , no intense peak of β -phase of PVDF has been observed. Two peaks of α -phase are occurring along with β -phase for the film annealed at 100°C ; which indicates that α -phase is growing at the cost of β -phase. The conversion of β -phase into α -phase may be arising due to thermally induced chain reorientation [21]. When the annealing temperature is increased upto 110°C , the peak of β -phase PVDF i.e. $2\theta=20.7^\circ$ (2 0 0) completely disappeared. The XRD studies have made it clear that α and β -phase of PVDF are in coexistence for the film annealed upto 100°C ; but β -phase completely disappears for the film annealed at temperature greater or equal to 110°C .

Fourier transform infrared spectroscopy is carried out for investigating the phase transformation and chain orientation in PVDF film annealed at different temperatures. The absorbance band at 490, 530, 615, 766, 795, 974, 1149, 1210, 1383, 1402 and 1455 cm^{-1} are related to α -phase [23]. The bands at 613 and 765 cm^{-1} are the bending and wagging vibration of CF_2 and rocking vibration of PVDF chain respectively. The bands at 840, 878, 1171 and 1232 cm^{-1} corresponds to β -phase of PVDF. The absorption band at 872 cm^{-1} was assigned to CH_2 and CF_2 group generated from the CH_2 rocking and CF_2 stretching; while the band at 1171 and 1234 cm^{-1} were related to CH_2 group ascribing its wagging and rocking [24]. The band at 1402 cm^{-1} is related with in plane bending or scissoring of CH_2 group; whereas the band at 1070 cm^{-1} attributed to the bending of C-C-C [25].

The absorption band in the range $1230\text{--}1240\text{ cm}^{-1}$ may either be related to β or γ -phase of PVDF, whereas absorption band in the range $1275\text{--}1280\text{ cm}^{-1}$ confirmly corresponds to β -phase of PVDF [26, 27]. Figure 2 shows the FTIR spectra of PVDF film annealed at different temperature. The absorption band corresponds to β -phase of PVDF ($840, 878, 1171, 1234$ and 1279 cm^{-1}) predominantly appears for the film annealed at $50, 90, 100^\circ\text{C}$ respectively. For film annealed at 100°C the intensity of the peak corresponding β -phase at 840 and 878 cm^{-1} has been decreased; whereas two peaks of α -phase at 766 and 976 cm^{-1} of PVDF has appeared. The prominent occurrence of α -phase of PVDF has also been observed in X-ray diffraction at

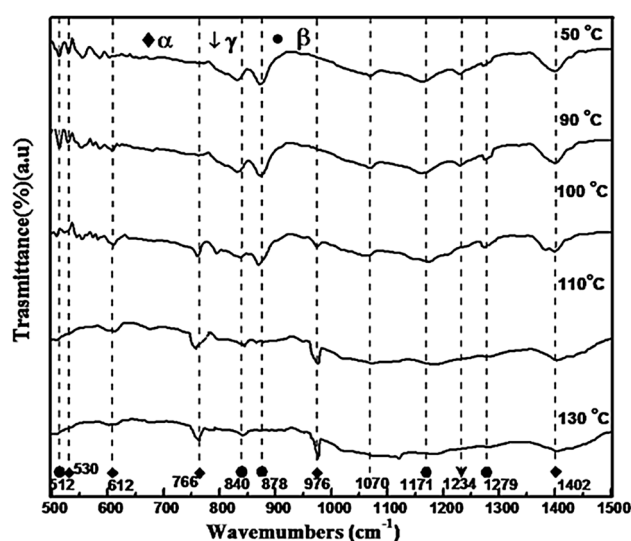


Fig. 2 IR spectra of PVDF thick films annealed at different temperatures

annealing temperature greater than 100°C . The FTIR results also shows the peak of β -phase has almost disappeared; whereas the prominent peaks of α -phase are still present for film annealed at 110°C . The results observed by XRD and FTIR are supporting each other. All the absorption band of β -phase of PVDF except at 840 cm^{-1} , disappears for the film annealed at 110 and 130°C .

Figure 3 shows the differential scanning calorimetry (DSC) thermograph of PVDF thick films annealed at different temperatures. The melting temperature for the film annealed at $50, 90, 100, 110$ and 130°C are found to be $\sim 162, 161, 161, 158$ and 158°C respectively. The film annealed at 90°C exhibits double melting peak. The low temperature melting peak is due to formation of α crystalline phase, where high temperature peak is due to the β -phase [28, 29]. The film annealed at temperature other than 90°C do not show double melting peak; which indicate that PVDF film predominantly crystallizes in single phase [30]. Observed DSC data supports the outcome of XRD and FTIR. For the film annealed upto 100°C the melting temperature is observed in the range $161\text{--}162^\circ\text{C}$, whereas it decreases to $\sim 158^\circ\text{C}$ for the film annealed at 110 and 130°C . These studies indicate that β -phase is dominant for the film annealed upto 100°C and it converts into α -phase for films annealed at 110 to 130°C . The thermal and structural analysis have confirmed that β -phase coexist along with α -phase for annealing temperature upto 100°C . It will be more interesting to observe the effect of annealing on dielectric and polarization behavior of PVDF thick film.

Figure 4a shows the variation of dielectric permittivity of PVDF film annealed at different temperature. IR, XRD and DSC studies have confirmed that β -phase exists along with

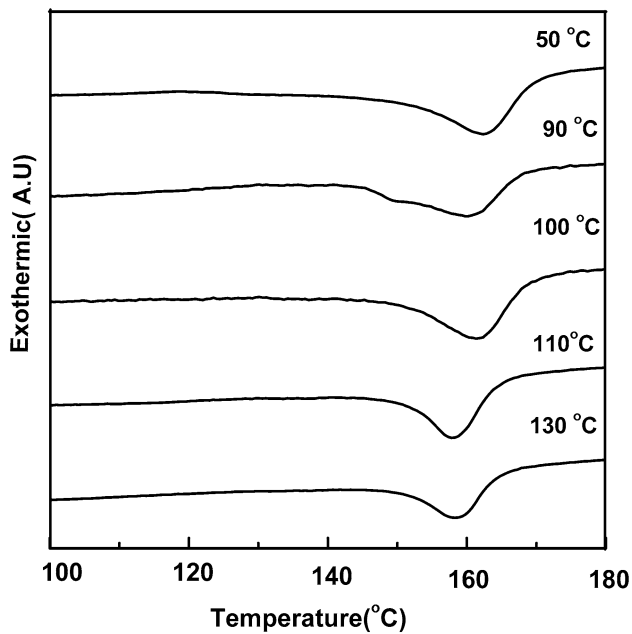


Fig. 3 Melting DSC curves for PVDF thick films annealed at different temperatures

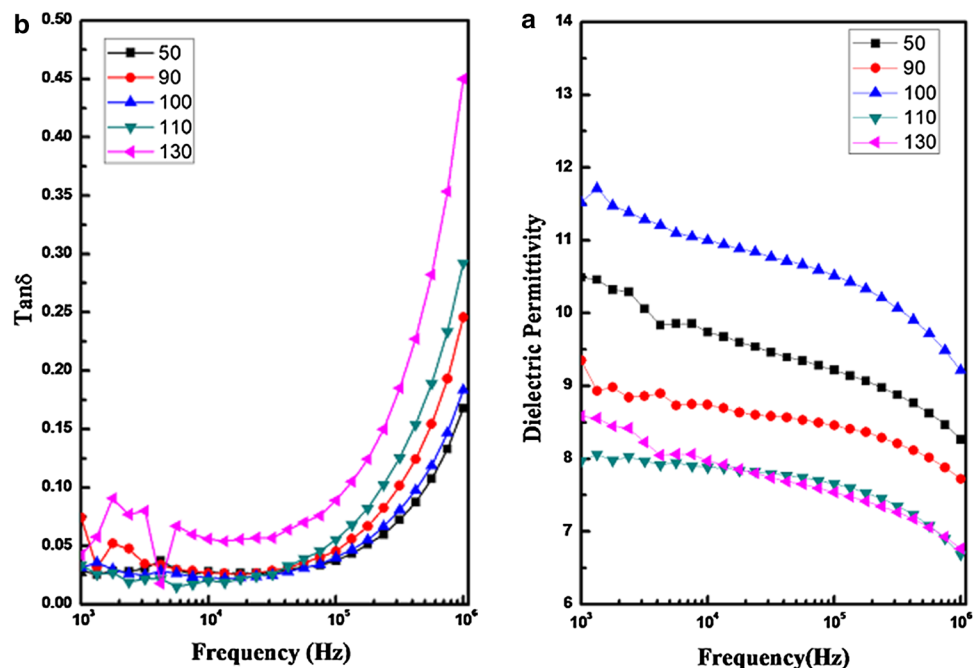
α -phase of PVDF upto annealing temperature of 100 °C. The overall variation of dielectric permittivity is similar to earlier reports in literature [14, 21, 22]. The dielectric permittivity in the lower frequency range is found to be large than the higher frequencies for all films. It is almost constant in frequency range 10^3 – 10^5 Hz. The value of dielectric permittivity for the film annealed at 100 °C is found to

be highest. Dielectric permittivity for all films is decreasing for the frequency $\geq 10^6$ Hz; which is assigned to α_c relaxation of PVDF thick film. Dielectric permittivity is mostly governed by two factors (a) interface between α and β crystalline phase, (b) interface between crystalline/ amorphous region. The dielectric permittivity for the film annealed at 100 °C is ~ 11 in frequency range of 10^3 – 10^5 Hz. The interface between α -phase and β -phase increases the effective dipole moment; which in turn increases the local electric field. Hence, large number of polar/ nonpolar interface might be increasing the dielectric permittivity. The interface between polar β -phase and amorphous region might also be contributing to the enhanced dielectric permittivity.

Figure 4b tangent loss of PVDF thick film annealed at different temperature. The tangent loss corresponding to PVDF film annealed at 90 and 100 °C is lowest in whole frequency range (10^2 – 10^6 Hz). The loss tangent for the film annealed at 100 °C is 0.025 in frequency range 10^3 to 10^5 Hz. The loss tangent is almost constant in frequency range 10^3 to 10^5 Hz and increases towards a peak value at frequency $\geq 10^6$ Hz; which is typical feature of α_c relaxation of PVDF [31, 32]. The total tangent loss is the result of conduction of electron, interfacial polarization and dipolar relaxation [33]. The conduction electron and interfacial polarization are dominant only upto frequency $\sim 10^5$ Hz. The losses due to dipolar relaxation i.e. (CH_2 and CF_2 dipoles of PVDF) are dominant at higher frequency.

Figure 5 makes it clear that annealing temperature affects the polarization behavior under the same electric field 250 kV/cm. The saturation polarization (P_s) as well as remnant polarization (P_r) is found to be highest for the

Fig. 4 **a** Variation of dielectric permittivity with frequency for PVDF thick films annealed at different temperatures. **b** Tangent loss of PVDF thick films annealed at different temperatures



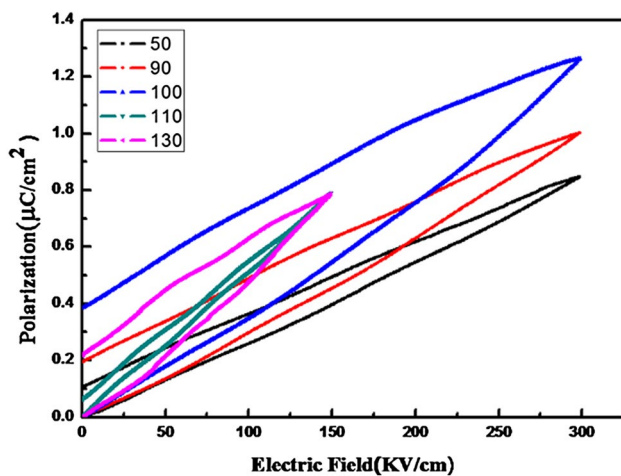


Fig. 5 Unipolar P-E loop of PVDF thick films annealed at different temperatures

Table 1 Remnant and saturation polarization of PVDF thick films annealed at different temperatures

S.No	Annealing Tem.(°C)	P_r	P_s
1	50	0.106	0.846
2	90	0.194	1
3	100	0.386	1.27
4	110	0.062	0.79
5	130	0.217	0.78

P_r remnant polarization; P_s saturation polarization; result obtained from a unipolar P-E loop graph

film annealed at 100 °C. The values of saturation polarization (P_s) and remnant polarization (P_r) for the PVDF thick film annealed at different temperature are given in Table 1. The annealing temperature might be increasing the crystallite size as well as crystallinity. The β -phase crystallite of PVDF are increasing in size with increase of annealing temperature from 50 to 90 °C; thereby increasing the dipole moment. The increased dipole moment enhances the saturation polarization. The α -phase starts growing at the cost of β -phase for the film annealed at 100 °C, where the vector sum of dipole moments of CH_2 and CF_2 dipoles at α/β interface as well as crystalline amorphous interface is contributing for more increase in dipole moment as compared to film annealed at 90 °C. The increase in dipole moment may be attributed to highest saturation polarization for this film. When annealing temperature becomes greater >100 °C, the β -phase PVDF film convert into α -phase thereby exhibiting smallest value of polarization. The remnant polarization for 100 °C is also highest ($\sim 0.39 \mu\text{C}/\text{cm}^2$); which is approximately $\sim 30\%$ of saturation polarization ($\sim 1.27 \mu\text{C}/\text{cm}^2$). The small crystallite and amorphous dipoles are polarized

by low electric field, whose contents are very low. Most of these dipoles are reversible due to their small size. The high electric field improves the polarization dramatically by orienting large polar crystallite. However, most of oriented crystals could not be disoriented due to lack of sufficient free space between crystallite grains. Hence, remnant polarization for the film annealed at ~ 100 °C is quite high [34]. The observed polarization behavior is found to be in agreement with dielectric and structural observation. The film annealed at temperature >100 °C, completely converts into α -phase thereby exhibiting low values of saturation and remnant polarization. The structural observations i.e. XRD and FTIR results are also supported by dielectric and P-E data for the PVDF film annealed at different temperatures. One important point that must be noted, film annealed at 100 °C shows better interconnectivity and mechanical strength as compared to film annealed at lower temperature [34]. The observation of improved dielectric and polarization behavior of the film annealed at 100 °C may be useful for high power electronics application.

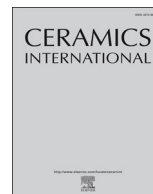
4 Conclusion

The polyvinylidene fluoride (PVDF) thick film has been fabricated by solution casting method. The fabricated film is subjected to annealing at 50, 90, 100, 110 and 130 °C for 5 h in air. The effect of annealing temperature on structural, dielectric and polarization behavior has been investigated. Coexistence of polar β -phase along with α -phase is observed upto annealing temperature of 100 °C. Films annealed at temperature >100 °C completely converts into α -phase. The dielectric permittivity (~ 11 at 1 kHz) and polarization ($\sim 1.27 \mu\text{C}/\text{cm}^2$) is found to be highest for the film annealed at 100 °C, which might be attributed to increased dipolar contribution at α/β interfaces as well as amorphous crystalline interface. The vector sum of dipole moments of CH_2 and CF_2 dipoles is increasing at these interfaces, and improving the dielectric and polarization behavior of the PVDF thick film. The films annealed at 100 °C with improved dielectric and polarization behavior may be useful for high power electronic applications.

References

1. P. Barber, S. Balasubramanian, Y. Anguchamy, S. Gong, A. Wibowo, H. Gao, H.J. Ploehn, H.C. Zur Loye, *Mater.* **2**(4), 1697–1733 (2009)
2. H. Tang, H.A. Sodano, *Nano Lett.* **13**(4), 1373–1379 (2013)
3. H. Tang, Y. Lin, H.A. Sodano, *Adv. Energy Mater.* **3**(4), 451–456 (2013)
4. J. Li, Q. Meng, W. Li, Z. Zhang, *J. Appl. Polym. Sci.* **122**(3), 1659–1668 (2011)

5. Z.C. Zhang, Q.J. Meng, T.C.M. Chung, *Polym.* **50**(2), 707–715 (2009)
6. N. Ortega, A. Kumar, J.F. Scott, D.B. Chrisey, M. Tomazawa, S. Kumari, D.G.B. Diestra, R.S. Katiyar, *J. Phys. Condens. Matter* **24**(44), 445901 (2008)
7. R.X. Han, J.Z. Jin, P. Khanchaitit, J.K. Wang, Q. Wang, *Polym.* **53**(6), 1277–1281 (2012)
8. H.S. Nalwa, *Ferroelectric polymers: Chemistry, physics and applications*. (Marcel Dekker, New York, 1995) Chap. 3 and 4, 183–260
9. A.J. Lovinger, *Developments in crystalline polymers*. D.C. Bassett, (Springer, Netherlands, 1982), Chap. 5
10. A.J. Lovinger, *Macromol.* **15**(1), 40–44 (1982)
11. M.M. Nasef, H. Saidi, K.Z.M. Dahlan, *J. Polym. Degrad. Stab.* **75**(1), 85–92 (2002)
12. X. He, K. Yao, *Appl. Phys. Lett.* **89**(11), 112909 (2006)
13. S. Chen, K. Yao, F.E.H. Tay, C.L. Liow, *J. Appl. Phys.* **102**(10), 104108 (2007)
14. S. Satapathy, S. Pawar, P.K. Gupta, K.B.R. Varma, *Bull. Mater. Sci.* **34**(4), 727–733 (2011)
15. W.M. Prest, D.J. Luca, *J. Appl. Phys.* **46**(10), 4136–4143 (1975)
16. V. Tiwari, G. Srivastava, *J. Polym. Res.* **21**(11), 587 (2014)
17. W.M. Prest, D.J. Luca, *J. Appl. Phys.* **49**(10), 5042–5047 (1978)
18. F. Guan, J. Pan, J. Wang, Q. Wang, L. Zhu, *Macromol.* **43**(1), 384–392 (2010)
19. Q. Meng, W. Li, Y. Zheng, Z. Zheng, Z. Zhang, *J. Appl. Polym. Sci.* **116**(5), 2674–2684 (2010)
20. Y. Zhao, W. Yang, Y. Zhou, Y. Chen, X. Cao, Y. Yang, J. Xu, Y. Jiang, *J. Mater. Sci: Mater. Electron* **27**(7), 7280–7286 (2016)
21. R.G. Jr, *J. Appl. Polym. Sci.* **100**(4), 3272–3279 (2006)
22. R.G. Jr, *J. Mater. Sci.* **34**(18), 4489–4500 (1999)
23. P. Martins, A.C. Lopes, S.L. Mendez, *Prog. Polym. Sci.* **39**(4), 683–706 (2014)
24. B. Luo, X. Wang, Y. Wang, L. Li, *J. Mater. Chem. A* **2**(3), 510–519 (2010)
25. S. Lanceros-Mendez, J.F. Mano, A.M. Costa, V.H. Schmidt, *J. Macromol. Sci. Part B* **40**(3–4), 517–527 (2001)
26. Y. Bromashenko, R. Pogreb, O. Stanevsky, E. Bormashenko, *Polym. Test.* **23**(7), 791–796 (2004)
27. H.C. Yang, Q.Y. Wu, H.Q. Liang, L. Wan, Z. Xu, *J. Poly. Sci. Part B: Poly. Phys.* **51**(19), 1438–1447 (2013)
28. C. Marega, A. Marigo, *Eur. Polym. J.* **39**(8), 1713–1720 (2003)
29. Y.L. Madorskaya, N.N. Loginova, L.P. Kastorski, O.V. Kuzmichov, V.L. Maksimov, A.M. Lobanov, *Polym. Sci. USSR* **28**(6), 1433–1440 (1996)
30. K.P. Parmoda, A. Mohamed, I.Y. Phang, T. Liu, *Polym. Int.* **54**(1), 226–232 (2005)
31. Z. Zhang, T.C.M. Chung, *Macromol.* **40**(4), 783–785 (2007)
32. Z. Zhang, T.C.M. Chung, *Macromol.* **40**(33), 9391–9397 (2007)
33. Y. Li, X. Huang, Z. Hu, P. Jiang, S. Li, T. Tanaka, *Appl. Mater. Interfaces* **3**(11), 4396–4403 (2011)
34. C.V. Chanmal, J.P. Jog, *Express. Polym. Lett.* **2**(4), 294–301 (2008)



Dielectric and energy storage behavior of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles for capacitor application

Shobhneek Kaur^a, Ashok Kumar^b, Amit L. Sharma^c, Dwijendra P. Singh^{a,*}

^a School of Physics & Materials Science, Thapar Institute of Engineering & Technology, Patiala 147004, India

^b CSIR-National Physical Laboratory, New Delhi 110012, India

^c Thin Film Group, CSIR-CSIO, Chandigarh 160030, India

ARTICLE INFO

Keywords:

Nanoparticles

HRTEM

Dielectric

Energy density

Discharging behavior of capacitor

ABSTRACT

Nanoparticles of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has been synthesized by using sol-gel method. The X-ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) have respectively been used to confirm phase purity and determination of CCTO nanoparticles. The size of most of CCTO particles is lying in the range 50–60 nm. The dielectric constant and tangent loss of CCTO at 1 kHz has been found to be ~ 7790 and ~ 0.096 respectively. The breakdown electric field and nonlinear coefficient are found as ~ 4400 V/cm and ~ 6.3 respectively. High value of breakdown electric field and dielectric constant are respectively attributed to: (i) formation of large number of energy bands in grain boundary that traps the electrons at grain/grain boundary interface and, (ii) grain boundary inter barrier layer capacitance (IBLC). High dielectric constant and high breakdown electric field materials are very good for the pulsed power application. Discharge energy density and discharging time are obtained as ~ 7 J/cc and ~ 0.34 ms respectively. Therefore, CCTO exhibits high dielectric constant and high breakdown electric field along with very good capacitive behavior.

1. Introduction

Nanosized ceramic materials with high dielectric constant and low dielectric loss are required for the various electronic applications such as high energy density capacitors, embedded capacitors, varistor etc [1,2]. These materials are also useful as ceramic filler in polymer ceramic composites [3]. The smaller size of ceramic particle will not affect the breakdown and mechanical strength of composite appreciably [4]. Though, there are different dielectric ceramic materials (such as BaTiO_3 , $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, and PbTiO_3 etc.) having a high dielectric constant and low dielectric loss: but their applications are limited by virtue of variation in dielectric behavior with temperature [5,6]. On the other hand, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is recently discovered dielectric material which possess very high dielectric constant ($\sim 10^4$) over a wide temperature range (100–600 K) and frequency range (100 Hz–1 MHz) [7,8]. The giant dielectric constant material calcium copper titanate has been synthesized by various methods, i.e. like solid state method, sol-gel method, combustion method and co-precipitation method etc. [9–12]. Nanoparticle of giant dielectric material CCTO has also been synthesized by sol gel technique, where the size of nanoparticle is found to be in the range of 80–120 nm [13,14]. The dielectric behavior of CCTO ceramic prepared by different technique has been widely studied [15–18]. Vangchangyia et al., achieved excellent dielectric and nonlinear current-

voltage behavior of pure CCTO ceramic prepared by sol-gel route. At 1 kHz, room temperature dielectric constant and tangent loss has been reported as 9516 and 0.02 respectively [19]. But in this report CCTO has been sintered at a temperature of 1100 °C for 6 h, whereas the calcinations temperature of CCTO precursor is 900 °C. The sintering at higher temperature will lead to grain growth, which will obviously provide the high dielectric constant.

The objective of this work is to synthesize $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles so that it could be very good ceramic filler for making polymer ceramic nanocomposite; which is of immense importance for high energy density capacitor [19,20]. We report the particle size, dielectric, breakdown and nonlinear behavior of CCTO nanoparticles having size in the range of 50–60 nm. The high dielectric constant material is mainly useful for capacitor applications. The discharging time, discharge behavior and energy density of the capacitor formed by CCTO ceramic has also been investigated.

2. Experimental

2.1. Materials and synthesis of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

$\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles were prepared by using sol-gel technique. Calcium nitrate tetrahydrate ($\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$), Copper nitrate trihydrate

* Corresponding author.

E-mail address: dpsingh@thapar.edu (D.P. Singh).

<https://doi.org/10.1016/j.ceramint.2019.01.077>

Received 8 October 2018; Received in revised form 6 November 2018; Accepted 9 January 2019

Available online 11 January 2019

0272-8842/ © 2019 Published by Elsevier Ltd.

($\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$) and Titanium (IV) Isopropoxide ($\text{C}_{12}\text{H}_{28}\text{O}_4\text{Ti}$) from sigma aldrich were used as raw materials. A stoichiometric ratios of calcium nitrate tetrahydrate and copper nitrate trihydrate were dissolved in ethanol separately. When both the solutions become homogenous, they were mixed and labeled as solution I. A second solution of titanium isopropoxide in acetylacetone was prepared and labeled as solution II. Solutions I and II were mixed together at room temperature and a sol was formed by heating the mixture at 90 °C. Then, diluted ethanol was added drop-wise in the above solution to obtain a gel type solution. The formed gel was dried at 140 °C for 5 h to get the precursor of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, which is grinded in an agate mortar to get a fine powder. The obtained precursor powder was then calcined at 900 °C for 3 h to get brown coloured $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. The calcined CCTO was pelletized, compressed and sintered at 900 °C for 3 h for densification of pellet. Time and temperature for calcination and sintering were same in order to avoid the crystalline growth of CCTO.

2.2. Characterization of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$

X – Ray Diffraction (XRD) was used to investigate the crystal structure of CCTO powder. Diffractograms were recorded by PANalytical diffractometer by using Cu K_α radiation. Energy Dispersive X-ray Spectroscopy (EDS) of CCTO powder was also carried out for detecting the chemical composition (Agilent Resolution Pro Cary 660). The particle size of CCTO was confirmed from high resolution transmission electron microscopy (HRTEM) Tecnai G2, F30. The sample for TEM was prepared by adding a small amount of ethanol in CCTO powder and dropping the sample solution onto carbon coated copper grids. The Raman spectroscopy was carried out by Renishaw spectrometer; where the sample was excited with polarized light of Ar^+ laser ($\lambda = 514.5 \text{ nm}$) and analyzed by using an Jobin Yvon spectrometer. The gold electrodes were coated on both sides of pellet of diameter 6 mm by using AUTO fine coater-JEOL, JEC-3000FC, same method is adopted in other report for studying the dielectric behavior of the nanoferrite [21]. The thickness of pellets was $\sim 2 \text{ mm}$. Dielectric properties of CCTO pellet were measured with an applied voltage of 1.0 V in frequency range of 10^2 – 10^6 Hz by using Hioki 353250, LCR meter. The current – voltage (I-V) characteristics and discharged behavior were measured by using Keithley 2410 Source Measuring unit. The current voltage data were recorded at a rise rate of 1.5 V/sec. The values of the breakdown electric field (E_b) and nonlinear coefficient (α) were determined at current density in the range of 1–10 mA/cm^2 .

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the X-ray diffraction (XRD) pattern of CCTO powder. The CCTO powder has observed to exhibit cubic crystal structure with lattice parameter, $a = 7.38 \text{ \AA}$. Broadening in peak profile is used to determine the crystalline size. The crystalline size can be directly evaluated by using Scherrer formula [22].

The plot of $W_{hkl} \cos \theta$ versus $4 \sin \theta$ is popularly called as W-H plot [23]. The inset of Fig. 1 shows the W-H plot for CCTO powder. The slope and intercept along y-axis has been determined from the linear fit of the scattered results. The crystalline size is estimated from the intercept along y-axis, and the strain is determined from the slope of the fit. The crystalline size of CCTO is found to be $\sim 53 \text{ nm}$ with corresponding strain value of 0.813×10^{-3} .

Fig. 2a shows high resolution transmission electron microscopy [HRTEM] image of CCTO nanoparticles. The HRTEM image reveals the microstructure of CCTO nanopowder; where the curved edges cylindrical particles are present. The particles are also showing very weak agglomeration. The size of particle has been measured by considering the distribution in HRTEM images: which has been shown in Fig. 2b. The particle sizes are in the range of 20–120 nm, but majority of particles are lying in the range of 50–60 nm. The average particle size

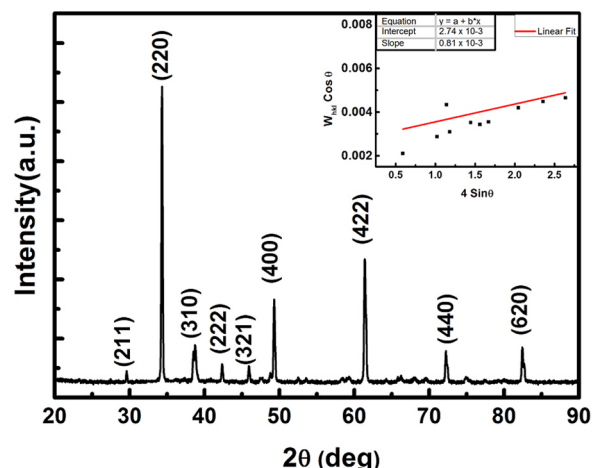


Fig. 1. X-ray diffraction of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanopowder synthesized by calcination for 3 h at 900 °C (inset is showing Williamson & Hall plot).

obtained from HRTEM, are in good agreement with the crystallite size determined from XRD. The SAED pattern in inset of Fig. 2c shows the crystalline feature of CCTO particles; HRTEM images exhibit very good (clear) lattice fringes (shown in Fig. 2c) with interplanar spacing $\sim 3.7 \text{ \AA}$ which corresponds to $[200]$ plane of CCTO. The fringes are not exhibiting any interconnecting zone as it has been observed in other research reports [15,24]. Fig. 2d shows the energy dispersive spectroscopy (EDS) analysis of CCTO nanopowder synthesized by modified sol-gel route. The atomic percentage of Ca, Cu, Ti are found to be 4.39, 17.66 and 17.57 with respective percentage error of 1, 2.21 and 2.4. The ratio of $\text{Ca}/\text{Cu} + \text{Ti}$ resembles with its ratio in standard $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$. Any impurity peak has not been observed in EDS spectra. EDS studies confirm the elemental stoichiometry in synthesized sample. Sintering of CCTO pellet at 900 °C for 3 h (same as that of calcinations) leads to a homogeneous morphological structure shown in Fig. 3. The average grain size has been found to be $\sim 220 \text{ nm}$. The grains and grain boundaries are clearly visible in sintered CCTO ceramic pellet.

3.2. Raman analysis

Fig. 4 shows the Raman spectra of synthesized CCTO nanopowder. The optical branches of CCTO split two A, two E and four F Raman active modes [25,26]. The peak of Raman spectra at 451 cm^{-1} , 516 cm^{-1} are assigned to A_g symmetry; where atomic motion is related to rotation like TiO_6 octahedra. The peak at 579 cm^{-1} related to F_g symmetry where antistretching between O-Ti-O takes place. Strongly damped mode between wave number 200–300 cm^{-1} (i.e. 216, 229 and 251 cm^{-1}) are also observed [27,28]. These modes might be a result of interference between Raman scattering from two vibration modes. The interference arises from an anharmonic coupling between A and F - symmetries [29]. Where the Raman mode appearing in wave number 186–270 cm^{-1} are assigned to interference between Raman scattering from A-type of symmetries via anharmonic interactions. Therefore, Raman spectra is also confirming the formation of CCTO nanopowders.

3.3. Dielectric properties

Fig. 5 shows the room temperature; frequency dependent dielectric behavior of CCTO pellets. The CCTO nanopowder has pelletized and sintered at 900 °C for 3 h. The temperature and time has been kept same as of calcination in order to prevent the increase in size of CCTO crystallites in pellet. The value of dielectric constant and tangent loss at 1 kHz, has been found to be ~ 7990 and ~ 0.096 respectively. The value of dielectric constant has been found to be in agreement with earlier reports in literature [19,30,31]. The occurrence of high

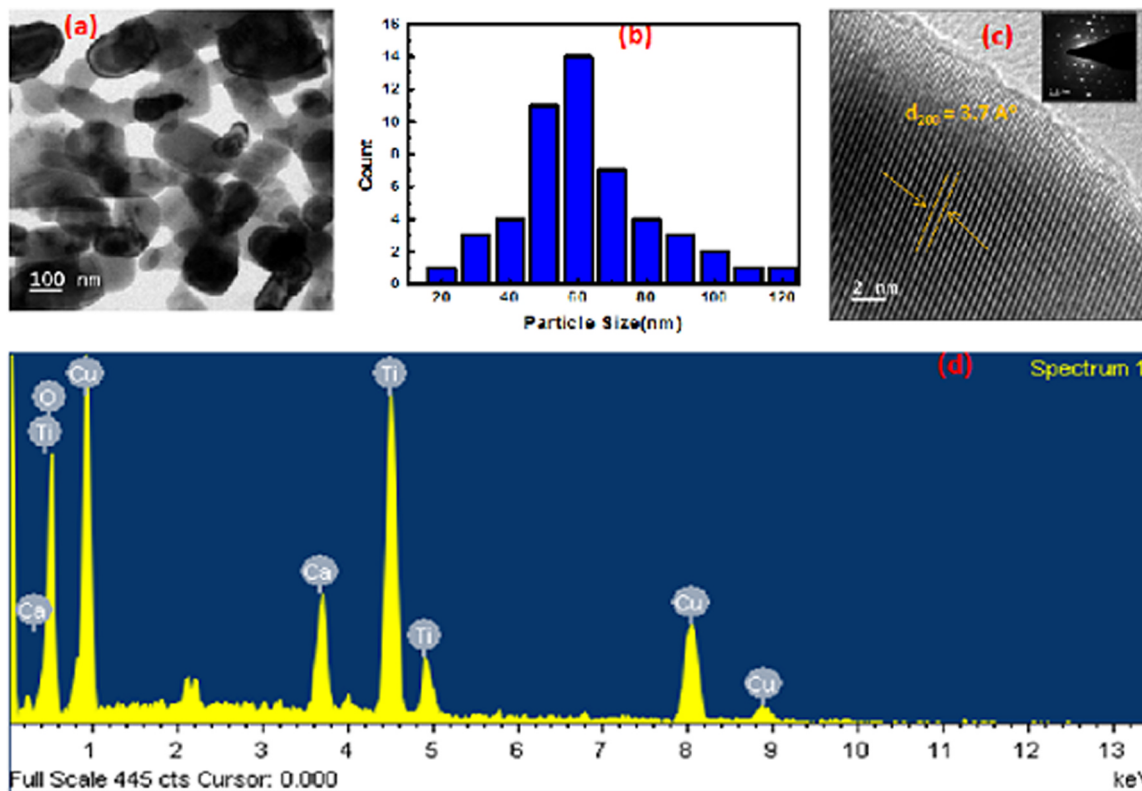


Fig. 2. (a) High Resolution Transmission Electron Microscopic (HRTEM) image, (b) Particle size distribution, (c) High resolution fringes and Selected Area Electron Diffraction (SAED) pattern, (d) Energy Dispersive Spectroscopy (EDS) spectrum, of synthesized $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanoparticles.

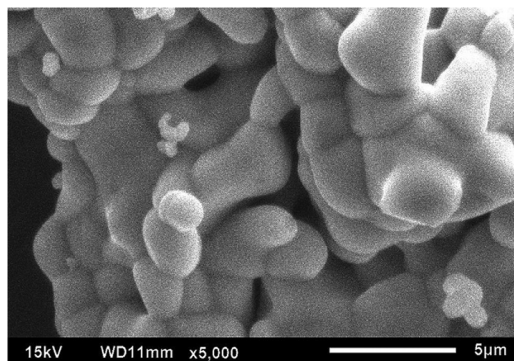


Fig. 3. Scanning micrograph of sintered CCTO pellet at 900 °C for 3 h.

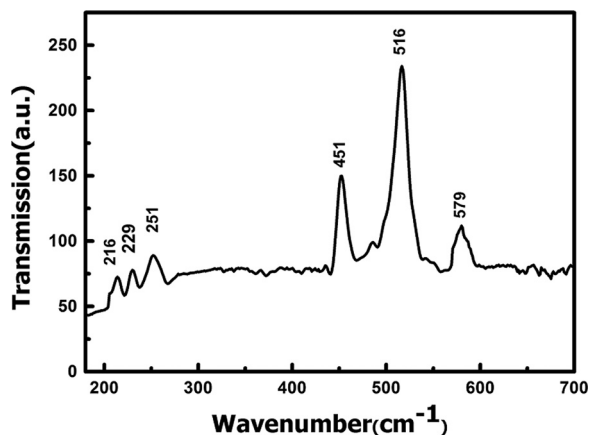


Fig. 4. Raman Spectra of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano powder at room temperature.

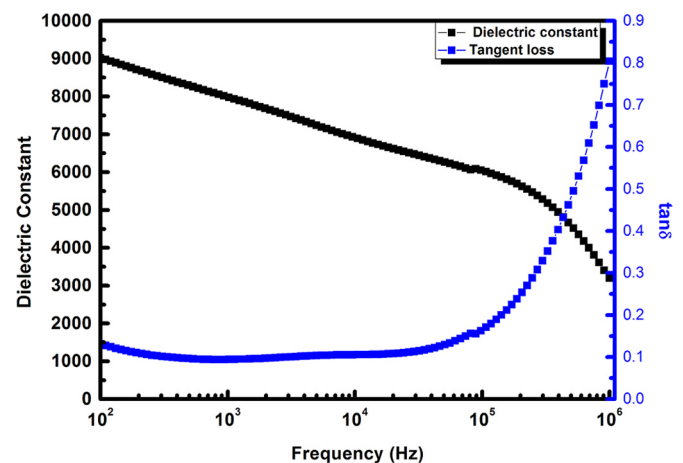


Fig. 5. Variation in dielectric constant (ϵ_r) and tangent loss ($\tan \delta$) with frequency of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at room temperature.

dielectric constant in polycrystalline CCTO is not associated with intrinsic property of crystal [10,32]: but it is attributed to the creation grain boundary inter barrier layer capacitance (IBLC). According to this model the dielectric constant of a material can be expressed as [33]

$$\epsilon = \frac{d\epsilon_g}{t} \quad (1)$$

where "d" is the grain size and "t" is the thickness of grain boundary and ϵ_g is the dielectric constant of the grain boundary layer. The dielectric permittivity in our case is not a high as reported elsewhere [10,19]: but tangent loss of (~ 0.096) at 1 kHz is moderately small. In reports, where high dielectric constant has been found, CCTO is sintered at high temperature ($\sim 1100^\circ\text{C}$) for long duration ≥ 6 h. But in our case sintering temperature and time is same as that of synthesis temperature of

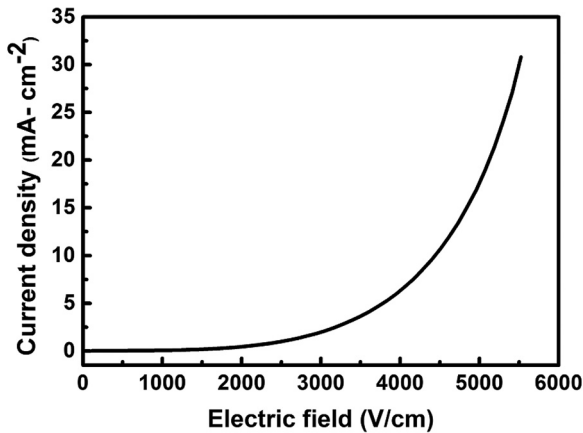


Fig. 6. Current density vs electric field curve of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ at room temperature.

CCTO nanopowder in order to avoid the crystalline growth. The smaller grain in ceramic lead to larger number of thin grain boundary. According to above formula (1), the combination of small grain size and thin grain boundary might be leading to moderate dielectric constant ~ 7990 and low tangent loss (~ 0.096) at 1 kHz.

3.4. Current density vs electric field

Fig. 6 shows the current density vs electric field curve at room temperature synthesized CCTO pellets. The nonlinear current - voltage behavior indicates the non-Ohmic transport in CCTO; which is represented below in Eq. (2) [33]:

$$I = KV^\alpha \quad (2)$$

where "K" is proportionality constant, and " α " is nonlinear coefficient. The nonlinear coefficient is calculated by using equation:

$$\alpha = \frac{\partial(\ln I)}{\partial(\ln V)} \quad (3)$$

The value of the nonlinear coefficient calculated from current, voltage characteristics is found to be ~ 6.30 . The values of breakdown electric field (E_b) is recorded from current density vs electric field curve at 10 mA/cm^2 (Fig. 6). The breakdown electric field has been found to be $\sim 4400 \text{ V/cm}$. This value of breakdown field is highest to the best of our knowledge [10,34–37]. Existence of electron energy band structure across an insulating grain boundary is reported in CCTO ceramic [37], which is equivalent to n-i-n structure with acceptor like interface

trapping of the electron in the grain boundary region. The high value of breakdown electric field and nonlinear coefficient might be arising due to formation of large number of energy bands in grain boundary that traps the electrons at grain/grain boundary interface.

3.5. Discharging current & energy density studies

The Metal-CCTO-Metal capacitor structure is fabricated. The capacitance and energy storage behavior of capacitor formed by CCTO has also been investigated. The discharge behavior of capacitor is one of the important parameter for its application. The discharge speed and discharge energy density is measured by using; capacitor discharge circuit reported in literature [38,39]. A pulse of 500 V is applied across the capacitor formed by CCTO, and decay of discharging current with time has been measured. The data of discharging current vs time is shown in Fig. 7a. The curve has been fitted in expression $I = I_0 \exp(-t/\tau)$. The value of time constant (τ) has been found to be $\sim 0.339 \text{ ms}$. In this circuit current is discharged through a load resistance $R_L \sim 50 \text{ k}\Omega$ in series with CCTO sample.

The stored energy density in a capacitor is given by using formula (4):

$$U_D = \frac{1}{2} \epsilon_0 \epsilon_r E_b^2 \quad (4)$$

By taking $\epsilon_r = 9000$, value of dielectric constant at 100 Hz; and $E_b = 4396.7 \text{ V/cm}$ is value of breakdown strength recorded from current density vs electric field data. The energy density has been found to be $\sim 7 \text{ J/cc}$. Energy density can also be calculated from polarization vs electric field curve by using formula of energy density $E_d = \int E dP$, where "E" is electric field strength and "P" is polarization. But the polarization of pure CCTO does not depend on electric field [Ref 40]. Alternate way of calculating the energy density can be performed from charging /discharging current vs time at fixed voltage (electric field) as follows. The power is calculated by using:

$$P = i^2(R_L + R) \quad (5)$$

where R_L is load resistance and R is resistance of CCTO pellet. The discharge energy density is calculated by using:

$$E_d = \frac{1}{V} \int P dt \quad (6)$$

The value of E_d is calculated from discharging current vs time curve, where V is volume and P is power.

Discharge energy density vs time curve has been shown in Fig. 7b. The experimental energy discharge time, i.e. $\tau_{0.9}$ is defined as time for discharge energy density in load to reach 90% of its maximum value. The energy discharging time has been found to $\sim 0.34 \text{ ms}$; which is

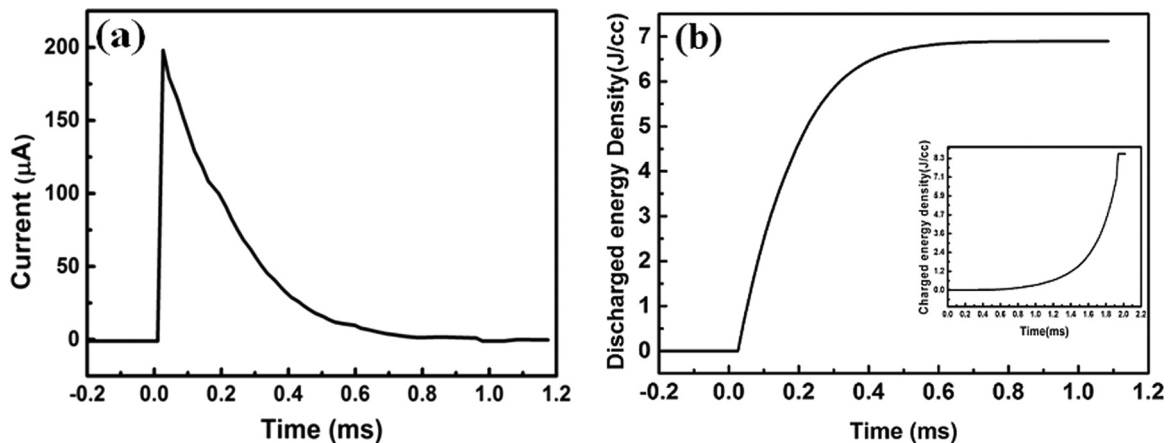


Fig. 7. (a) Discharging current response with time, (b) discharged energy density with time of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ capacitor with an inset of charged energy density with time at an applied electric field 3000 (V/cm).

smaller even as compared to PVDF- SrTiO₃ composites [41]. The discharging time is dependent on capacitance by $\tau = R_L C$ (where $R_L = 50 \text{ k}\Omega$, $C = 8 \text{ nF}$); which gives $\tau \sim 0.40 \text{ ms}$, this value is approximately similar to that obtained from the discharging curve (Fig. 7a). The maximum value of energy density measured from the discharge curve (Fig. 7b) is 6.8 J/cc , which is consistent with the energy density determined by using the formula (4). The energy density of CCTO based capacitor is found to be much higher as compared to energy density of BaTiO₃ based capacitor [42]. The inset of Fig. 7b shows the charging density vs time curve. the maximum value of charging energy density has been found to be $\sim 8.3 \text{ J/cc}$. Therefore the efficiency can be calculated by using formula:

$$\eta = \frac{\text{Discharging energy density}}{\text{Charging energy density}}$$

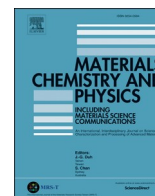
Which comes $\sim 82\%$ at an electric field of 3000 V/cm .

4. Conclusion

The nanoparticles of giant dielectric material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) has been synthesized. HRTEM and XRD studies have confirmed that a large number of the particles are having their sizes in the range of $50\text{--}60 \text{ nm}$. The dielectric behavior and current - voltage characteristics of CCTO pellet has been investigated. This pellet is sintered at synthesizing temperature, i.e. 900°C for 3 h to avoid the growth of crystallites. The dielectric constant and tangent loss of CCTO at 1 kHz are ~ 7790 and ~ 0.096 respectively. The breakdown electric field and non-linear coefficient are found to be $\sim 4400 \text{ V/cm}$ and ~ 6.3 respectively. The high value of breakdown electric field and dielectric constant are respectively attributed to (i) formation of a large number of energy bands in grain boundary that traps the electrons at grain/grain boundary interface and, (ii) grain boundary inter barrier layer capacitance (IBLC). High dielectric constant along with high breakdown electric field are useful for pulsed power application. The capacitor formed by CCTO exhibits very good discharging current and discharge energy decay response. Discharging time and discharged energy density are found to be $\sim 0.34 \text{ ms}$ and $\sim 7 \text{ J/cc}$ respectively. Therefore, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ exhibits high dielectric constant, high breakdown electric field, along with very good capacitive behavior.

References

- [1] H. Chen, T.N. Cong, W. Yang, C. Tang, Y. Li, Y. Ding, Progress in electrical energy storage system: a critical review, *Prog. Nat. Sci.* 19 (2009) 291–312.
- [2] P.Y. Raval, A.R. Makadiya, P.R. Pansara, P.U. Sharma, N.H. Vasoya, J.A. Bhalodia, S. Kumar, S.N. Dolia, K.B. Modi, Effect of the thermal history on structural, microstructural properties and J-E characteristics of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ polycrystalline ceramic, *Mater. Chem. Phys.* 212 (2018) 343–350.
- [3] S. kaur, A. Kumar, A.L. Sharma, D.P. Singh, Influence of annealing on dielectric and polarization behavior of PVDF thick films, *J. Mater. Sci.: Mater. Electron* 28 (2017) 8391–8396.
- [4] S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai, Z. An, Poly(vinylidene fluoride) nanocomposite capacitors with a significantly enhanced dielectric constant and energy density by filling with surface-fluorinated $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$ nanofibers, *RSC Adv.* 5 (2015) 40692–40699.
- [5] X. Chou, J. Zhai, H. Jiang, X. Yao, Dielectric properties and relaxor behavior of rare-earth (La, Sm, Eu, Dy, Y) substituted barium zirconium titanate ceramics, *J. Appl. Phys.* 102 (2007) 084106–084112.
- [6] P. Gupta, A. Kumar, M. Tomar, V. Gupta, D.P. Singh, Enhanced dielectric properties and suppressed leakage current density of PVDF composites flexible film through small loading of submicron $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ Crystallites, *J. Mater. Sci.: Mater. Electron* 28 (2017) 11806–11812.
- [7] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, High dielectric constant in $\text{ACu}_3\text{Ti}_4\text{O}_{12}$ and $\text{ACu}_3\text{Ti}_3\text{FeO}_{12}$ phases, *J. Solid State Chem.* 151 (2000) 323–325.
- [8] C.C. Homes, T. Vogt, S.M. Shapiro, S. Wakimoto, A.P. Ramirez, Optical response of high-dielectric-constant perovskite-related oxide, *Science* 293 (2001) 673–676.
- [9] R. Jia, X. Zhao, J. Li, X. Tang, Colossal breakdown electric field and dielectric response of Al doped $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *Mater. Sci. Eng. B* 185 (2014) 79–85.
- [10] D.L. Sun, A.Y. Wu, S.T. Yin, Structure, properties and impedance spectroscopy of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by sol-gel process, *J. Am. Ceram. Soc.* 91 (2008) 169–173.
- [11] C. Kumar, Dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ prepared by sol-gel combustion technique, *J. Mater. Sci.: Mater. Electron* 22 (2011) 579–582.
- [12] B. Barbier, C. Combettes, S. Guillemet-Fritsch, T. Chartier, F. Rossignol, A. Rumeau, T. Lebey, E. Duttrade, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics from co-precipitation method: dielectric properties of pellets and thick films, *J. Eur. Ceram. Soc.* 29 (2009) 731–735.
- [13] S. Jesurani, S. Kanagesan, R. Velmurugan, C. Thirupathi, M. Sivakumar, T. Kalaivani, Nanoparticles of giant dielectric material, calcium copper titanate from a sol-gel technique, *Mater. Lett.* 65 (2011) 3305–3308.
- [14] X. Ouyang, P. Cao, W. Zhang, Z. Liu, Z. Huang, W. Geo, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ - PVDF polymeric composites with enhanced capacitive energy density, *Int. J. Mod. Phys. B* 29 (2015) 1540003.
- [15] E. Swatsitang, A. Niyompan, T. Putjuso, Giant dielectric, low dielectric loss, and non-ohmic properties of nanocrystalline $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, *J. Mater. Sci.: Mater. Electron* 24 (2014) 3514–3520.
- [16] P. Thomas, K. Dwarakanath, K.B.R. Varma, T.R.N. Kutty, Nanoparticles of the giant dielectric material $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ from a precursor route, *J. Phys. Chem.* 69 (2008) 2594–2604.
- [17] B.A. Bender, M.J. Pan, The effect of processing on the giant dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, *Mater. Sci. Eng. B* 117 (2005) 339–347.
- [18] L. Singh, U.S. Rai, K.D. Mandal, B.C. Sin, H. Lee, H. Chung, Y. Lee, Comparative dielectric studies of nanostructured BaTiO_3 , $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ and 0.5BaTiO_3 : $0.5\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nano-composites synthesized by modified sol-gel and solid state methods, *Mater. Charact.* 96 (2014) 54–62.
- [19] S. Vangchangyia, E. Swatsitang, P. Thongbai, S. Pinitsoontorn, T. Yamwong, S. Maensiri, V. Amornkitbamrung, P. Chindaprasirt, Very low loss tangent and high dielectric permittivity in pure- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by a modified sol-gel process, *J. Am. Ceram. Soc.* 95 (2012) 97–1500.
- [20] M. Ahmadipour, M.F. Ain, Z.A. Ahmad, A short review on Copper Calcium Titanate (CCTO) electroceramic: synthesis, dielectric properties, film deposition, and sensing application, *Nano-Micro Lett.* 8 (2016) 291–311.
- [21] N. Lenin, R.R. Kanna, K. Sakthipandi, A.S. Kumar, Structural, electrical and magnetic properties of $\text{NiLa}_x\text{Fe}_{2-x}$ nanoferrites, *Mater. Chem. Phys.* 212 (2018) 385–393.
- [22] B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, Boston, 1956.
- [23] G.K. Williamson, W.H. Hall, X-Ray Line broadening from filled aluminium and wolfram, *Acta Metall.* 1 (1953) 22–31.
- [24] Y. Tian, X. Zhang, Y. Yang, Z. Liu, X. Huang, Sol-gel synthesis and sensing study of perovskite $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanopowders, *Integr. Ferroelectr.* 129 (2011) 188–195.
- [25] N. Kolve, R.P. Bontchev, A.J. Jacobson, V.N. Popov, V.G. Hadjiev, A.P. Litvinchuk, M.N. Lliev, Raman spectroscopy of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$, *Phys. Rev. B* 66 (2002) 132102–1–132102-4.
- [26] A.F.L. Almeida, P.B.A. Fechine, M.P.F. Graca, M.A. Valente, A.S.B. Sombra, Structural and electrical study of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) obtained in a new ceramic procedure, *J. Mater. Sci.: Mater. Electron* 20 (2009) 163–170.
- [27] L.H. Robins, D.L. Kaiser, L.D. Rotter, P.K. Schenk, G.T. Stauff, D. Rytz, Investigation of the structure of barium titanate thin films by Raman spectroscopy, *J. Appl. Phys.* 76 (1994) 7487–7498.
- [28] B. Hlilzer, J. Kulek, M. Polomska, M.D. Glinchuk, A.V. Rangulya, A. Pietraszko, Dielectric and pyroelectric response of BaTiO_3 - PVDF nanocomposites, *Ferroelectrics* 316 (2005) 31–41.
- [29] H.R. Lawrence, L.K. Debra, D.R. Lawrence, K.S. Peter, T.S. Gregory, R. Daniel, Investigation of the structure of barium titanate thin films by Raman spectroscopy, *J. Appl. Phys.* 76 (1994) 7487–7498.
- [30] S. Jesurani, S. Kanagesan, R. Velmurugan, T. Kalaivani, Phase formation and high dielectric constant of calcium copper titanate using sol-gel route, *J. Mater. Sci.: Mater. Electron* 23 (2012) 668–674.
- [31] X. Ouyang, P. Cao, S. Huang, W. Zhang, Z. Huang, W. Gao, Microwave - assisted synthesis of high dielectric constant $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ from sol-gel precursor, *J. Electron Mater.* 44 (2015) 2243–2249.
- [32] D.C. Sinclair, T.B. Adams, F.D. Morrison, A.R. West, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$: one - step internal barrier layer capacitor, *Appl. Phys. Lett.* 80 (2002) 2153–2155.
- [33] Y.H. Lin, J. Cai, M. Li, C.W. Nan, High dielectric and nonlinear electrical behaviors in TiO_2 -rich $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics, *Appl. Phys. Lett.* 88 (2006) 172902.
- [34] P. Thongbai, B. Putaseang, T. Yamwong, S. Maensiri, Current - voltage nonlinear and dielectric properties of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ ceramics prepared by a simple thermal decomposition method, *J. Mater. Sci.: Mater. Electron* 23 (2012) 795–801.
- [35] Z. Tang, Y. Huang, K. Wu, J. Li, Significantly enhanced breakdown field in $\text{Ca}_{1-x}\text{Sr}_x\text{Cu}_3\text{Ti}_4\text{O}_{12}$ ceramics by tailoring donor densities, *J. Eur. Ceram. Soc.* 38 (2018) 1569–1575.
- [36] Q. Zhang, T. Li, Z. Chen, R. Xue, Y. Wang, The non-ohmic and dielectric behavior evolution of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ after heat treatments in oxygen-rich atmosphere, *Mater. Sci. Eng. B* 177 (2012) 168–172.
- [37] S.Y. Chung, I.D. Kim, S.J.L. Kang, Strong nonlinear current-voltage behavior in perovskite - derivative calcium copper titanate, *Nat. Mater.* 3 (2004) 774–777.
- [38] H. Tang, H.A. Sodano, Ultra high energy density nanocomposite capacitors with fast discharge using $\text{Ba}_{0.2}\text{Sr}_{0.8}\text{TiO}_3$ nanowires, *Nano Lett.* 13 (2013) 1373–1379.
- [39] H.J. Lee, M.H. Park, G.H. Kim, J.Y. Seok, Y.J. Kim, C.S. Hwang, A.Q. Jiang, Polarization switching and discharging behaviors in serially connected ferroelectric Pt/Pb (Zr, Ti)O₃/Pt and paraelectric capacitors, *J. Appl. Phys.* 109 (2011) 114113.
- [40] T. Pandirengan, M. Arumugam, M. Durairaj, Development of high dielectric dual phase $[\text{Bi}_2\text{TiO}_{12}]_x[\text{CaCu}_3\text{Ti}_4\text{O}_{12}]_{1-x}$ nanocomposite thin films for modern micro-electronic device application, *Thin Solid Films* 628 (2017) 117–126.
- [41] S. Liu, J. Zhai, Improving the dielectric constant and energy density of poly(vinylidene fluoride) composites induced by surface-modified SrTiO_3 nanofibers by polyvinylpyrrolidone, *J. Mater. Chem. A* 3 (2015) 1511–1517.
- [42] W.B. Li, L.X. Pang, R. Xu, H.H. Guo, Novel barium titanate based capacitors with high energy density and fast discharge performance, *J. Mater. Chem. A* 5 (2017) 19607–19612.



On the structural, dielectric and energy storage behaviour of PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films

Shobhneek Kaur, Dwijendra P. Singh^{*}

School of Physics & Materials Science, Thapar Institute of Engineering & Technology, Patiala, 147004, India

HIGHLIGHTS

- PVDF-CCTO nanocomposite films by solution casting method.
- Nanocomposite film with 8 vol% loading of CCTO exhibits highest saturation and remanant polarization.
- It also possesses highest discharge energy density and energy efficiency.

ARTICLE INFO

Keywords:

Ceramic
Polymer matrix nanocomposite
Electrical properties
High energy density capacitors

ABSTRACT

Polyvinylidene fluoride- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (PVDF-CCTO) nanocomposite films have been fabricated by solution casting method, where $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) nanopowder is incorporated in PVDF polymer matrix. Synthesized films have been structurally, morphologically, and electrically characterized. Dielectric constant of PVDF-CCTO nanocomposite is found to increase with increase in loading of CCTO nanopowder in the frequency range 100 Hz - 1 MHz. Obtained dielectric constant of composites has also been fitted in various theoretical models. Unlike dielectric behaviour, polarization does not show the ordered variation with the loading of CCTO nanopowder. PVDF-CCTO nanocomposite with 8 vol% of CCTO exhibits highest saturation and remnant polarization $1.7 \mu\text{C}/\text{cm}^2$ at 500 kV/cm and $0.6 \mu\text{C}/\text{cm}^2$, respectively. It also possesses highest discharge energy density $0.85 \text{ J}/\text{cc}$ at 500 kV/cm and energy efficiency of $\sim 65\%$ at 100 kV/cm. Enhanced energy density and polarization are attributed to increase dipole moment due to ordering of α , β , γ -phases of PVDF in PVDF-CCTO nanocomposite films.

1. Introduction

Polymer-ceramic dielectric nanocomposite has drawn a lot of attention of scientific community due to its prospect of application in high energy density capacitor, and embedded electronics [1–3]. The energy density of a capacitors is calculated by $U = \int E dD$, where U is the total stored energy density, E is the applied electric field and, D is the electric displacement [4–6]. Therefore, in order to have a material for high energy density capacitor, it must have a moderate dielectric constant and high breakdown strength. The materials which can be used as dielectric ceramic fillers in the composite are BaTiO_3 (BT), BaSrTiO_3 (BST), $\text{Pb}(\text{Zr}, \text{Ti})\text{O}_3$ (PZT), $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) etc [7–9,12]. These materials possess a high dielectric constant, but very low breakdown strength. On the other hand, a wide variety of polymers can be used as a matrix for synthesizing such nanocomposite [10,11], which have a low dielectric constant, but very high breakdown strength. Among these

polymers, polyvinylidene fluoride (PVDF) has low dielectric constant (~ 11) and very high breakdown strength ($\sim 500 \text{ MV}/\text{m}$) [13].

Polymer ceramic nanocomposite based on PVDF have been widely investigated and found to exhibit excellent dielectric and energy storage behaviour [14–17]. But, $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) is a giant dielectric material ($\sim 10^4$) and shows nearly constant dielectric constant over a wide temperature and frequency range [18,19]. $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ is non-ferroelectric in nature. Therefore, its inclusion in PVDF matrix could incur less energy loss [18,20]. Dielectric behaviour of PVDF-CCTO composite has been investigated by different research groups [17,21,22]. Thomas et al. investigated the dielectric behaviour of PVDF-CCTO composite; where CCTO filler are in 1–7 μm range. Observed dielectric constant has been fitted in various theoretical models like Maxwell's, Clausius-Mossotti, Effective medium theory, logarithmic law and Yamada [21]. Yang et al. studied the comparative study of effect of micro and nanosize CCTO fillers on the dielectric properties of

^{*} Corresponding author.

E-mail address: dpsingh@thapar.edu (D.P. Singh).

<https://doi.org/10.1016/j.matchemphys.2019.122301>

Received 17 July 2019; Received in revised form 5 October 2019; Accepted 10 October 2019

Available online 13 October 2019

0254-0584/© 2019 Elsevier B.V. All rights reserved.

CCTO-PVDF composite is also carried out. The composite with nano-sized CCTO filler exhibits better dielectric properties as compared to micro-sized filler. Better dielectric behaviour of nanosized CCTO filler is attributed to formation of conductive interfaces at boundaries in PVDF matrix [9]. Effect of coupling agent such as Si69 on dielectric properties of PVDF-CCTO composite has also been investigated. Observed dielectric behaviour is assigned to good compatibility of the ethoxy ($-\text{OC}_2\text{H}_5$) group of Si69 and PVDF matrix [17]. Arbatti et al. has studied dielectric behaviour of P(VDF-TrFE)-CCTO composite. They have got a flexible composite having very high dielectric constant ~ 33 at 1 kHz; but the loading of CCTO ceramic filler is ~ 50 vol %, which is quite high [22]. There have always been a fascination of obtaining a polymer-ceramic nanocomposite of good dielectric and energy storage behaviour at low loading of ceramic filler. High loading of ceramic filler compromises with mechanical strength [23]. Earlier studies have confirmed that PVDF-CCTO nanocomposites have moderate dielectric constant, low tangent loss and high mechanical strength. Also, incorporation of CCTO will cause less area hysteresis loop by virtue of its non-ferroelectric nature [18,20]. The composites with less hysteresis have good energy storage properties [24].

In this paper we report dielectric, polarization and energy storage behaviour of PVDF-CCTO nanocomposite films. The CCTO filler are nanosized powder in the range of 50–60 nm. Moreover, the loading volume percentage of CCTO nanosized filler in PVDF is very low as compared to previous reports.

2. Experimental details

2.1. Synthesis of PVDF-CCTO nanocomposite films

The nanosized powder of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ (CCTO) was prepared by a sol-gel method. The CCTO powder was calcined at 900°C for 3 h. PVDF- $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanocomposite films with different vol% loading of CCTO were prepared by solution casting technique. First the polymer poly(vinylidene fluoride) (PVDF) powder was dissolved in *N,N*-Dimethylformamide (DMF) and stirred solution for 2 h at room temperature by using magnetic stirrer. The different volume fraction of CCTO nanopowder (4, 8, 12, and 15 vol %) were added in PVDF solvent. After the addition of CCTO powder, the solutions were sonicated for 1 h for ensuring the dispersion of CCTO particles in PVDF matrix. The sonicated solution was stirred for 3–4 h at 60°C for ensuring the homogenous mixing of CCTO nanopowder in PVDF matrix. This process makes the solution viscous, which was poured into petridish. This solution was dried at 160°C in a vacuum oven in order to evaporate DMF. The dried nanocomposite films were easily peeled off from the petridish at room temperature. PVDF-CCTO nanocomposite films are prepared by adding 4 vol %, 8 vol %, 12 vol % and 15 vol % (loading) of CCTO nanopowder; in PVDF polymer matrix which has been nominated as PVDF-4CCTO, PVDF-8CCTO, PVDF-12CCTO and PVDF-15CCTO respectively.

2.2. Characterization techniques

X-ray Diffraction (XRD) was used to investigate the CCTO and PVDF-CCTO nanocomposite films, which were recorded by PANalytical diffractometer by using Cu K_α radiation ($\lambda = 1.54 \text{ \AA}$). The particle size of CCTO was confirmed from high resolution transmission electron microscopy [HRTEM] Tecnai G2, F30. The sample for TEM was prepared by adding a small amount of ethanol in CCTO powder and dropping the sample solution onto carbon coated copper grids. Scanning electron microscopy (SEM), JEOL JSM-6610LV was analyzed the microstructure of PVDF-CCTO nanocomposite films. Fourier transform infrared spectroscopy (FTIR), Agilent Resolution Pro Cary 660 was employed to investigate the bonding and different polymorph present in the PVDF-CCTO nanocomposite films. The electric properties, frequency-dependent dielectric constant and tangent loss were measured using Hioki 353250 LCR meter in the frequency range from 100 Hz to 1 MHz at room

temperature. Electric displacement-electric field loops were measured by using premier Radiant-II ferroelectric tester by applying a triangular wave of frequency of 10 Hz. The gold electrodes of 6 mm diameter were sputtered on both sides of the nanocomposite films surface by using Auto fine coater- JEOL, JEC-3000FC.

3. Result and discussions

Fig. 1 shows the X-ray Diffraction (XRD) of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ nanopowder, pure PVDF and PVDF-CCTO nanocomposites films. PVDF-CCTO nanocomposite films contain loading of 4 vol%, 8 vol%, 12 vol% and 15 vol% of CCTO nanopowder. Peaks of PVDF and CCTO can be clearly seen in XRD, which confirms the inclusion of CCTO nanopowder in PVDF matrix. Various crystalline phases of PVDF-CCTO nanocomposite films in XRD pattern are observed. The diffraction peaks at $2\theta = 18.4^\circ$, 19.8° , 20.2° and 27.9° corresponding to planes (020), (110), (021) and (111) respectively. These peaks are observed for all PVDF-CCTO nanocomposite films. These planes are the signature of α -phase of PVDF [25, 26]. The peak at $2\theta = 26.8^\circ$ representing the (022) plane corresponds to γ -phase of PVDF [27]. The minority of γ -phase observed in PVDF-8CCTO and PVDF-12CCTO nanocomposite films, but the γ -phase disappeared in PVDF-15CCTO nanocomposite film. The presence of β -phase confirmed by the peaks at $2\theta = 20.7^\circ$ and 36.6° are assigned to (200) and, (020) planes in PVDF- 8CCTO and PVDF-12CCTO nanocomposite films [25, 28]. The peak corresponding to β -phase in PVDF-8CCTO nanocomposite film is showing less broadening as compared to PVDF-12CCTO nanocomposite film. Therefore, crystallite size of β -phase in PVDF-8CCTO nanocomposite film is smaller as compared to PVDF-12CCTO nanocomposite film.

Fig. 2 shows the HRTEM and fringes of CCTO nanopowder. The CCTO particles are semi-spherical shape with very weak agglomeration [19]. The average particle size of the CCTO comes in the range of 50–60 nm. The lattice fringes are clear and match with the [0 1 3] plane of the CCTO.

Fig. 3 shows the SEM images of the PVDF-CCTO nanocomposite films with 4 vol%, 8 vol%, 12 vol% and 15 vol% loading of CCTO nanopowder. Homogenous distribution of CCTO nanopowder in PVDF matrix is clearly visible, which is achieved by sonification of magnetically stirred solution of PVDF and CCTO in DMF. White portion of SEM images are representing CCTO nanopowder, whereas black spherulite structure is representing PVDF matrix. Slight aggregation of CCTO nanopowder occurs with increase in the volume fraction of CCTO in PVDF matrix [9,

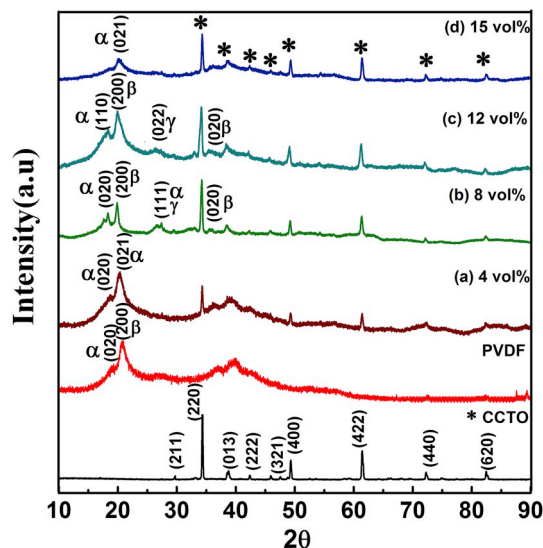


Fig. 1. XRD patterns of CCTO, (a) PVDF- 4CCTO, (b) PVDF- 8CCTO, (c) PVDF- 12CCTO and, (d) PVDF- 15CCTO nanocomposite films.

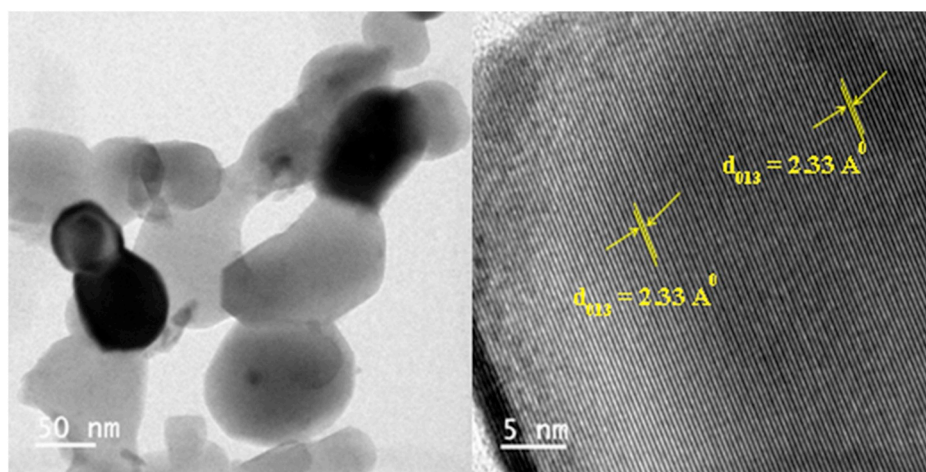


Fig. 2. High resolution transmission electron microscopy (HRTEM) image, and lattice fringes of CCTO nanopowder.

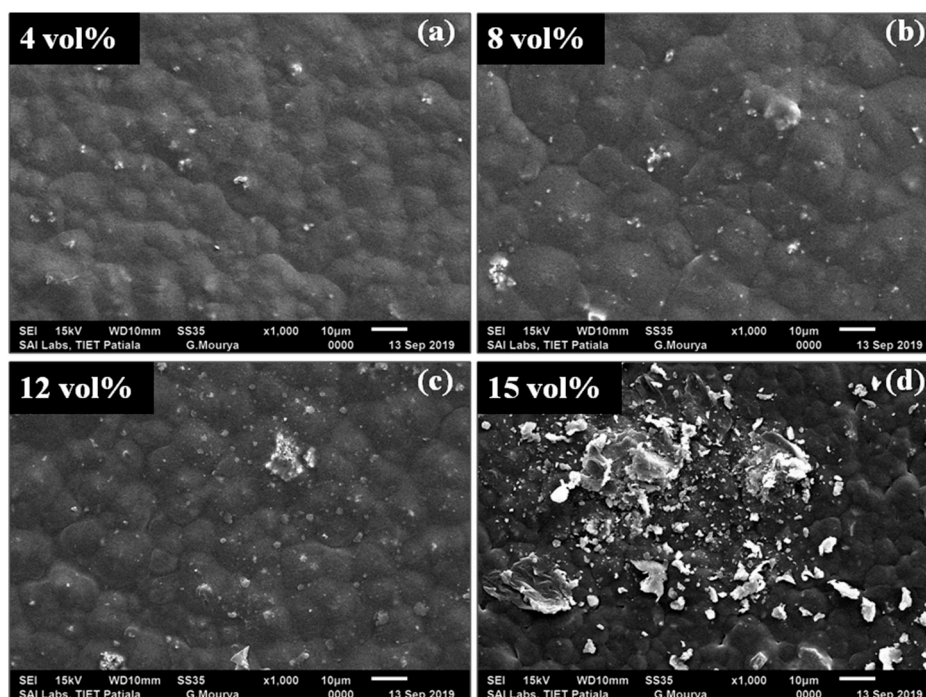


Fig. 3. Scanning electron microscopy (SEM) micrographs of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

23].

Fig. 4 shows FTIR spectra of pure PVDF and PVDF-CCTO nanocomposite films in the range of $500\text{--}1500\text{ cm}^{-1}$. All the PVDF-CCTO nanocomposite film are showing the presence of α , β and γ -phases. Absorption band present at 490 , 615 and 763 cm^{-1} corresponds to α -phase of PVDF. Absorption band of 490 cm^{-1} due to the bending and wagging vibration of CF_2 group, whereas 615 , 763 cm^{-1} are assigned to the rocking vibration, a mixed mode of CF_2 bending and CCC skeletal vibration [29,30]. The prominent absorption bands of α -phase i.e. 763 , 795 , 975 , 1214 , and 1380 cm^{-1} are only observed in PVDF-8CCTO nanocomposite; which confirms that it consist majority of α -phase. The absorption bands at 840 , 876 and 1167 cm^{-1} attributed to β -phase, whereas the peak at 1231 and 1071 cm^{-1} assigned as γ -phase and it was related to CH_2 group ascribing its wagging and rocking symmetries [31]. The presence of γ -phase in PVDF-CCTO nanocomposite films consisting 4 vol% and 15 vol% CCTO are not observed in XRD, whereas it appears in FTIR [31,32]. This might be related with sensitivity of XRD for

γ -crystalline phase in these nanocomposite, whereas FTIR relies on the vibration of bonds. Therefore, the γ -phase is appearing in IR but it is absent in XRD. But, the γ -phase is also polar phase and this phase normally exhibit high energy density [29]. Similar kind of observations are reported by other research groups [32–35].

Despite of having very high dielectric constant of CCTO, its high tangent loss prevent its use in electrical and electronic applications. It's composite with PVDF can provide a material having moderate dielectric constant and low tangent loss, which can be applied for practical purposes. Fig. 5 (i-iii) show the frequency dependence of dielectric constant (ϵ), tangent loss ($\tan \delta$) and, ac conductivity respectively, of the PVDF-CCTO nanocomposite films at room temperature. Trend of variation of dielectric constant for all PVDF-CCTO nanocomposite films are similar. The dielectric constant is found to increase with increase of CCTO loading in PVDF-CCTO nanocomposite films. Dielectric constant of CCTO is very high and hence its inclusion in PVDF creates local internal field [36], which tends to increase the dielectric constant. More is

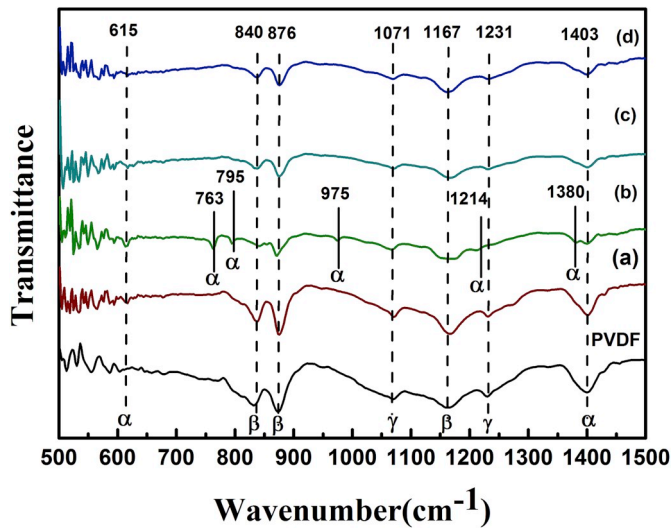


Fig. 4. Fourier Transform Infrared spectroscopy (FTIR) of, (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

loading more is dielectric constant of nanocomposite films. For frequency $> 10^5$ Hz, dielectric constant decreases. Here dielectric behaviour originates from the micro-brownian motion of nanocrystalline chain segment (α -relaxation) [36] and molecular motion onto amorphous/crystalline interfaces arises among PVDF and between PVDF-CCTO [37,38]. Fig. 4 (ii) shows the tangent loss with frequency at room temperature. Initially tangent loss decreases with frequency and attains minima. At frequency $> 10^5$ Hz; tangent loss start again increasing. This feature is common to all PVDF-CCTO nanocomposite films. High tangent loss at lower frequencies might be arising due to surface effects; whereas enhancement in tangent loss for frequency $> 10^5$ Hz is resulting due to competing relaxation phenomena among PVDF crystalline phases (i.e. α , β and γ -phases) and CCTO nanopowder. Further, confirmation of this kind of relaxation has been done by studying the variation of ac conductivity with frequency. The frequency at which ac conductivity starts increasing (on set frequency) is found to decrease with increase in loading of CCTO in PVDF-CCTO nanocomposite films, which indicates that dipolar relaxation time of CCTO may be greater as compared to relaxation time of PVDF [39]. Ac conductivity data has also been fitted in Jonscher power law in order to elucidate to conduction mechanism. The hopping of Ti^{3+} ion of CCTO as well as CF_2^- ions of PVDF might be taking place through oxygen vacancies and amorphous chain of PVDF respectively. Hopping of charge carrier contribute either towards dielectric relaxation or conduction. There is a correlation between conductivity and dielectric relaxation [40]. For confirming it, ac conductivity has been fitted in Jonscher power law $\sigma_{ac} = \sigma_{dc} + A\omega^n$, where A is some constant, σ_{dc} is dc conductivity, index ' n ' represent the amount of interaction among mobile ions and lattices [41]. The value of $\sigma_{dc} = 1.4 \times 10^{-9}$ S/m and $n = 1.1$, the value $n > 1$ suggest the localized hopping of mobile ions.

The effective dielectric constant of PVDF-CCTO nanocomposite films have also been predicted by using various models [42–44]. Fig. 6 shows the dielectric constant of the CCTO-PVDF nanocomposite films at 1 kHz for different volume fraction of CCTO. Dielectric behaviour of biphasic composite, where high dielectric constant nanoparticles are dispersed in low dielectric constant polymeric matrix is well described by Maxwell's model, which is given following equation:

$$\epsilon_r = \left[\frac{\delta_p \epsilon_p (2/3 + \epsilon_c/3\epsilon_p) + \delta_c \epsilon_c}{\delta_p (2/3 + \epsilon_c/3\epsilon_p) + \delta_c} \right]$$

where (δ_c, δ_p) and (ϵ_c, ϵ_p) are the volume fraction and dielectric con-

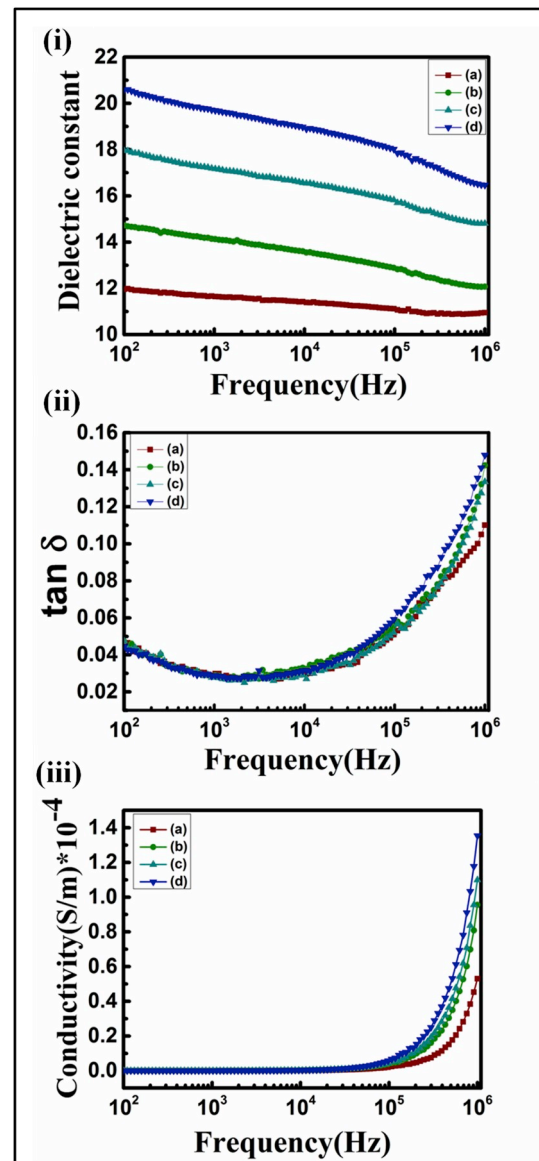


Fig. 5. Frequency dependent (i) dielectric constant, (ii) tangent loss and, (iii) ac conductivity of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15 CCTO nanocomposite films.

stant of CCTO and PVDF respectively. Where $\epsilon_c = 7968$ and $\epsilon_p = 11.5$ and these are the dielectric constant of CCTO and PVDF [19,31]. Where δ_c and δ_p are the volume fraction of CCTO and PVDF in the composite, respectively. The experimental result deviate from the Maxwell's model with increased loading of CCTO. Because in this model, filler is assumed to be spherical in nature.

Clausius-Mossotti law is used to predict the dielectric constant of a composite having spherical ceramic crystallites dispersed in continuous medium [45]. The effective dielectric constant according to this law is given by:

$$\epsilon_r = \epsilon_p \left[1 + 3\delta_c \left(\frac{\epsilon_c - \epsilon_p}{\epsilon_c + 2\epsilon_p} \right) \right]$$

Logarithmic law is most commonly used dielectric mixture rule proposed by Lichtenecker's which is given by:

$$\log \epsilon_r = \delta_c \log \epsilon_c + \delta_p \log \epsilon_p$$

The effective dielectric constant calculated by logarithmic law is close to experimental data at low volume fraction of CCTO in PVDF-

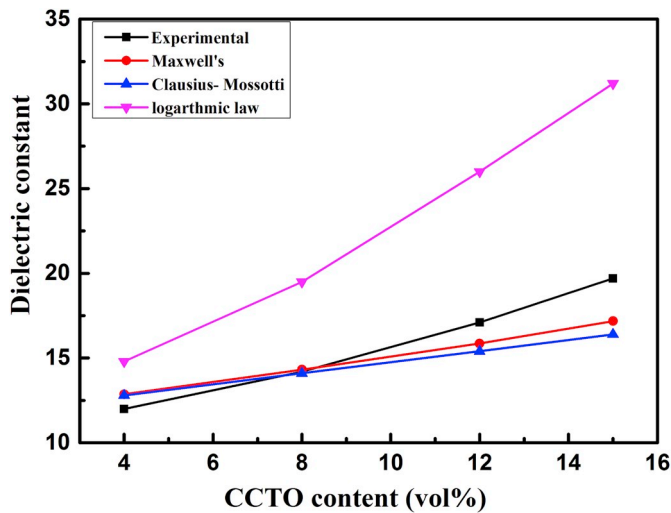


Fig. 6. Variation of effective dielectric constant at 1 kHz of PVDF-CCTO nanocomposite films with different vol% of CCTO ceramic in PVDF-CCTO nanocomposite.

CCTO nanocomposite films. Whereas, effective dielectric constant obtained by Maxwell's model and Clausius-Mossotti law are very close to experimental value of dielectric constant of PVDF-CCTO nanocomposites. Slight difference between experimental and theoretical value might be arising due to irregular symmetry of CCTO nanoparticle in PVDF-CCTO nanocomposite films.

Fig. 7 shows variation of unipolar electric-displacement with electric field curve of PVDF-CCTO nanocomposite films. The electric displacement is given by $D = \epsilon_0 E + P$, if $\epsilon_0 E \gg P$; the $D \sim P$. The value of saturation polarization (P_s) and remnant polarization (P_r) for PVDF-8CCTO nanocomposite film with 8 vol% of CCTO are $1.7 \mu\text{C}/\text{cm}^2$ (at $500 \text{ kV}/\text{cm}$) and $0.6 \mu\text{C}/\text{cm}^2$, which is highest as compared to other nanocomposite films. Occurrence of highest value of saturation polarization in PVDF-8CCTO nanocomposite film is associated with emergence of β and γ -phase of PVDF along with α -phase. The β and γ -phase of PVDF are also observed in PVDF-12CCTO nanocomposite film; but the value of P_s and P_r is found to be less as compared to PVDF-8CCTO nanocomposite film. If one looks at peaks of XRD of β -phase in PVDF-CCTO nanocomposite films at 20.7° and 36.7° . The broadening in corresponding peak for PVDF-8CCTO nanocomposite film is smaller as compared to those of PVDF-12CCTO nanocomposite film. Therefore, crystallite size of β -phase in PVDF-8CCTO nanocomposite film is larger as compared to PVDF-12CCTO nanocomposite film. Therefore, PVDF-8CCTO nanocomposite film exhibits highest saturation polarization (P_s) [13]. Higher value of (P_r) for PVDF-8CCTO nanocomposite film is ascribed to irreversibility of large polar crystallite at low field [21]. When the vol% of CCTO > 12 , the unipolar loop is becoming almost parallel to electric field axis. Moreover, saturation polarization is also very low. This behaviour is ascribed to non-ferroelectric nature of CCTO. The larger crystallite size of β -phase in PVDF-8CCTO nanocomposite film, and the alignment of polymeric chain corresponding to α , β and γ -phases rearranged in PVDF-8CCTO nanocomposite film in such a way that separation between $\text{CH}_2\text{-CF}_2$ dipole is increased which might be increasing the resultant dipole moment and, hence polarization.

Energy storage properties of other nanocomposites have also been reported [46,47]. They show excellent energy storage behaviour at very high electric field ($\sim 4000 \text{ kV}/\text{cm}$), and useful for high voltage capacitor. Whereas, PVDF-8CCTO nanocomposite shows $0.8 \text{ J}/\text{cc}$ at an electric field of $\sim 500 \text{ kV}/\text{cm}$; which is higher as compared to previous reports at same electric field [46,47]. These nanocomposites may be useful for the capacitor operating at moderately high voltage ($\sim \text{kV}$).

Discharge energy density $= \int E dD$. Discharge energy density has been found to be maximum for PVDF-8CCTO nanocomposite film i.e.

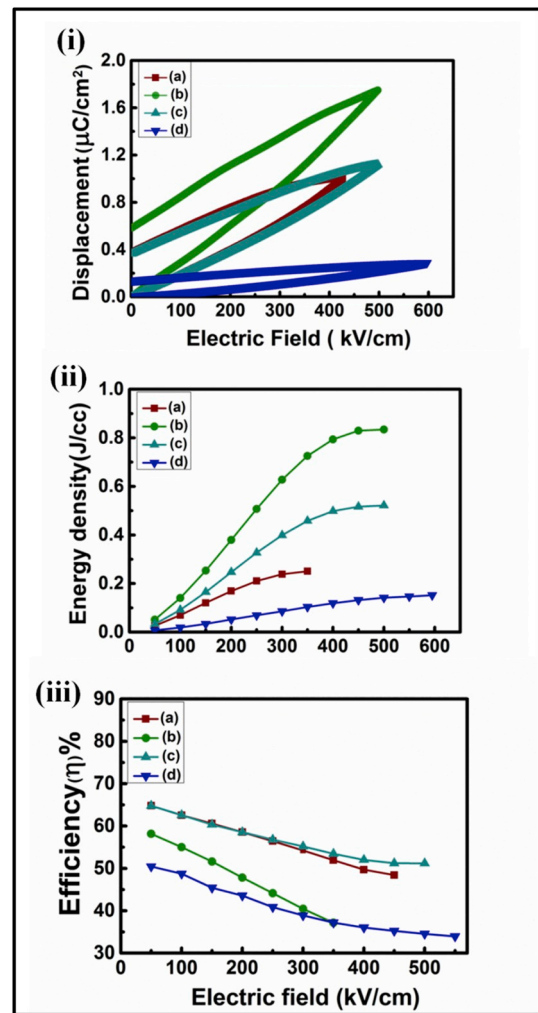


Fig. 7. (i) Unipolar D-E loop (ii) Discharge energy density (iii) Energy efficiency under applied electric field of (a) PVDF-4CCTO, (b) PVDF-8CCTO, (c) PVDF-12CCTO and, (d) PVDF-15CCTO nanocomposite films.

$U_D = 1 \text{ J}/\text{cc}$. Energy efficiency has been calculated by using formula:

$$\eta(\%) = \frac{\text{Discharging energy density}}{\text{Charging energy density}} \times 100\%$$

The energy efficiency for PVDF-8CCTO nanocomposite film has also been found to be highest i.e. 65% at $100 \text{ kV}/\text{cm}$. The highest discharge energy density and energy efficiency of PVDF-8CCTO nanocomposite film is ascribed to larger crystallite of β -phase and increased dipole moment due to ordering of α , β and γ -phase of PVDF in PVDF-CCTO nanocomposite films.

Mechanism of nucleation of β -phase in PVDF based nanocomposite has been explained elsewhere [32,34]. But in our case CCTO is a n-type semiconductor, therefore the surface of CCTO will be treated as negatively charged [48]. When negatively charged surface of CCTO nanoparticles interact with CH_2 group of PVDF, electroactive β -phase is promoted i.e. TTTT conformation. Small amount of γ -phase i.e. TTTGTTTG' also exist due to gauge effect produced by local internal chain rotation. Force field required for internal chain rotation might be provided by internal local field of CCTO at interface of PVDF and CCTO. Crystalline size and alignment polymeric chain corresponding to α , β and γ -phase has an effect on dipole moment and hence, on polarization. The polarization behaviour affects the energy storage behaviour.

4. Conclusions

PVDF-CCTO nanocomposite films has been synthesized and characterized at different vol% (4, 8, 12 and 15 vol%) loading of CCTO nanopowder. The dielectric constant of PVDF-CCTO nanocomposite films increases with increase in loading of CCTO nanopowder. The various models are also fitted, but the effective dielectric constant obtained by Maxwell's model and Clausius-Mossotti law are very close to experimental value of dielectric constant of PVDF-CCTO nanocomposites. PVDF-8CCTO nanocomposite films exhibits highest saturation and remnant polarization i.e. $1.7 \mu\text{C}/\text{cm}^2$ at $(500 \text{ kV}/\text{cm})$ and $0.6 \mu\text{C}/\text{cm}^2$, respectively. It also possesses highest discharge energy density $0.85 \text{ J}/\text{cc}$ at $500 \text{ kV}/\text{cm}$ and energy efficiency of $\sim 65\%$ at $100 \text{ kV}/\text{cm}$. Enhanced energy density and polarization are attributed to increase dipole moment due to ordering of α , β , γ -phases of PVDF in PVDF-CCTO nanocomposite films. The reported work is opening the way for further investigation of $\text{CaCu}_3\text{Ti}_4\text{O}_{12}$ based polymer matrix nanocomposites as a novel material for high energy density capacitors.

Declaration of competing interest

The authors declare that they have no conflict of interest.

Acknowledgments

The authors gratefully acknowledge the help and support of Dr Amit lochan Sharma (CSIO-CSIR, Chandigarh) and Dr Ashok Kumar from (National Physical Laboratory, Delhi).

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.matchemphys.2019.122301>.

References

- [1] S. Kumar, S. Supriya, M. Kar, Enhancement of dielectric constant in polymer-ceramic nanocomposite for flexible electronics and energy storage applications, *Compos. Sci. Technol.* 157 (2018) 48–56, <https://doi.org/10.1016/j.compscitech.2018.01.025>.
- [2] K. Yang, X. Huang, Y. Huang, L. Xie, P. Jiang, Fluoro-Polymer@BaTiO₃ hybrid nanoparticles prepared via RAFT polymerization: toward ferroelectric polymer nanocomposites with high dielectric constant and low dielectric loss for energy storage application, *Chem. Mater.* 25 (2013) 2327–2338, <https://doi.org/10.1021/cm4010486>.
- [3] Z.H. Dai, T. Li, Y. Gao, J. Xu, J. He, Y. Weng, B.H. Guo, Achieving high dielectric permittivity, high breakdown strength and high efficiency by cross-linking of poly(vinylidene fluoride)/BaTiO₃ nanocomposites, *Compos. Sci. Technol.* 169 (2019) 142–150, <https://doi.org/10.1016/j.compscitech.2018.10.014>.
- [4] Q. Li, K. Han, M.R. Gadinski, G. Zhang, Q. Wang, High energy and power density capacitors from solution-processed ternary ferroelectric polymer nanocomposites, *Adv. Mater.* 26 (2014) 6244–6249, <https://doi.org/10.1002/adma.201402106>.
- [5] Q. Fan, M. Liu, C. Ma, L. Wang, S. Ren, L. Lu, X. Lou, C. Jia, Significantly enhanced energy storage density with superior thermal stability by optimizing Ba(Zr_{0.15}Ti_{0.85})O₃/Ba(Zr_{0.35}Ti_{0.65})O₃ Multilayer Structure, *Nano Energy* 29 (2018) 0–20, <https://doi.org/10.1016/j.nanoen.2018.07.007>.
- [6] Z. Yao, Z. Song, H. Hao, Z. Yu, M. Cao, S. Zhang, M.T. Lananan, H. Liu, Homogeneous/Inhomogeneous-structured dielectrics and their energy-storage performances, *Adv. Mater.* 29 (2017) 1601727, <https://doi.org/10.1002/adma.201601727>.
- [7] L. Wang, F. Gao, J. Xu, K. Zhang, J. Kong, M. Reece, H. Yan, Enhanced dielectric tunability and energy storage properties of plate-like Ba_{0.6}Sr_{0.4}TiO₃/poly(vinylidene fluoride) composites through texture arrangement, *Compos. Sci. Technol.* 158 (2018) 112–120, <https://doi.org/10.1016/j.compscitech.2018.02.015>.
- [8] E. Venkatragavaraj, B. Satish, P.R. Vinod, M.S. Vijaya, Piezoelectric properties of ferroelectric PZT-polymer composites, *J. Phys. D Appl. Phys.* 34 (2001) 487–492, <https://doi.org/10.1088/0022-3727/34/4/308>.
- [9] W. Yang, S. Yu, R. Sun, R. Du, Nano- and microsize effect of CCTO fillers on the dielectric behavior of CCTO/PVDF composites, *Acta Mater.* 59 (2011) 5593–5602, <https://doi.org/10.1016/j.actamat.2011.05.034>.
- [10] Z.M. Dang, L. Wang, Y. Yin, Q. Zhang, Q.Q. Lei, Giant dielectric permittivities in functionalized carbon-nanotube/electroactive-polymer nanocomposites, *Adv. Mater.* 19 (2007) 852–857, <https://doi.org/10.1002/adma.200600703>.
- [11] C. Huang, Q. Zhang, Fully functionalized high-dielectric-constant nanophase polymers with high electromechanical response, *Adv. Mater.* 17 (2005) 1153–1158, <https://doi.org/10.1002/adma.200401161>.
- [12] H. Parangusan, D. Ponnammam, M. Al Ali Almaadeed, Flexible tri-layer piezoelectric nanogenerator based on PVDF-HFP/Ni-doped ZnO nanocomposites, *RSC Adv.* 7 (2017) 50156–50165, <https://doi.org/10.1039/c7ra10223b>.
- [13] S. Chen, J. Hu, L. Gao, Y. Zhou, S. Peng, J. He, Z. Dang, Enhanced breakdown strength and energy density in PVDF nanocomposites with functionalized MgO nanoparticles, *RSC Adv.* 6 (2016) 33599–33605, <https://doi.org/10.1039/C6RA01869F>.
- [14] S. Liu, S. Xiao, S. Xiu, B. Shen, J. Zhai, Z. An, Poly(vinylidene fluoride) nanocomposite capacitors with a significantly enhanced dielectric constant and energy density by filling with surface-fluorinated Ba_{0.6}Sr_{0.4}TiO₃ nanofibers, *RSC Adv.* 5 (2015) 40692–40699, <https://doi.org/10.1039/C5RA05095B>.
- [15] P. Kim, N.M. Doss, J.P. Tillotson, P.J. Hotchkiss, M. Pan, S.R. Marder, J. Li, J. P. Calame, J.W. Perry, High energy density nanocomposites based on surface-modified BaTiO₃ and a ferroelectric polymer, *ACS Nano* 3 (2009) 2581–2592, <https://doi.org/10.1021/nn9006412>.
- [16] J. Yao, C. Xiong, L. Dong, C. Chen, Y. Lei, L. Chen, R. Li, Q. Zhu, X. Liu, Enhancement of dielectric constant and piezoelectric coefficient of ceramic-polymer composites by interface chelation, *J. Mater. Chem.* 19 (2009) 2817, <https://doi.org/10.1039/b819910h>.
- [17] C. Yang, H.S. Song, D.B. Liu, Effect of coupling agents on the dielectric properties of CaCu₃Ti₄O₁₂/PVDF composites, *Compos. B Eng.* 50 (2013) 180–186, <https://doi.org/10.1016/j.compositesb.2013.02.006>.
- [18] M.A. Subramanian, D. Li, N. Duan, B.A. Reisner, A.W. Sleight, High dielectric constant in ACu₃Ti₄O₁₂ and ACu₃Ti₃FeO₁₂ phases, *J. Solid State Chem.* 151 (2000) 323–325, <https://doi.org/10.1006/JSSC.2000.8703>.
- [19] S. Kaur, A. Kumar, A.L. Sharma, D.P. Singh, Dielectric and energy storage behavior of CaCu₃Ti₄O₁₂ nanoparticles for capacitor application, *Ceram. Int.* 45 (2019) 7743–7747, <https://doi.org/10.1016/j.ceramint.2019.01.077>.
- [20] S. Jesurani, K. Samikannu, K. Thirunavukarasu, Phase formation and high dielectric constant of calcium copper titanate using sol-gel route, *J. Mater. Sci. Mater. Electron.* 23 (2012) 668–674, <https://doi.org/10.1007/s10854-011-0468-9>.
- [21] P. Thomas, K.T. Varughese, K. Dwarakanath, K.B.R. Varma, Dielectric properties of Poly(vinylidene fluoride)/CaCu₃Ti₄O₁₂ composites, *Compos. Sci. Technol.* 70 (2010) 539–545, <https://doi.org/10.1016/j.compscitech.2009.12.014>.
- [22] M. Arbatti, A. Shan, Z. Cheng, Ceramic-polymer composites with high dielectric constant, *Adv. Mater.* 19 (2007) 1369–1372, <https://doi.org/10.1002/adma.200601996>.
- [23] P. Gupta, A. Kumar, M. Tomar, V. Gupta, D.P. Singh, Enhanced dielectric properties and suppressed leakage current density of PVDF composites flexible film through small loading of submicron Ba_{0.7}Sr_{0.3}TiO₃ crystallites, *J. Mater. Sci. Mater. Electron.* 28 (2017) 11806–11812, <https://doi.org/10.1007/s10854-017-6987-2>.
- [24] H. Tang, Z. Zhou, H.A. Sodano, Relationship between BaTiO₃ nanowire aspect ratio and the dielectric permittivity of nanocomposites, *ACS Appl. Mater. Interfaces* 6 (2014) 5450–5455, <https://doi.org/10.1021/am405038r>.
- [25] W. Li, Q. Meng, Y. Zheng, Z. Zhang, W. Xia, Z. Xu, Electric energy storage properties of poly(vinylidene fluoride), *Appl. Phys. Lett.* 96 (2010) 192905, <https://doi.org/10.1063/1.3428656>.
- [26] P. Martins, A.C. Lopes, S. Lanceros-Mendez, Electroactive phases of poly(vinylidene fluoride): determination, processing and applications, *Prog. Polym. Sci.* 39 (2014) 683–706, <https://doi.org/10.1016/j.progpolymsci.2013.07.006>.
- [27] X. Cai, T. Lei, D. Sun, L. Lin, A critical analysis of the α , β and γ phases in poly(vinylidene fluoride) using FTIR, *RSC Adv.* 7 (2017) 15382–15389, <https://doi.org/10.1039/C7RA01267E>.
- [28] J. Li, Q. Meng, W. Li, Z. Zhang, Influence of crystalline properties on the dielectric and energy storage properties of poly(vinylidene fluoride), *J. Appl. Polym. Sci.* 122 (2011) 1659–1668, <https://doi.org/10.1002/app.34020>.
- [29] N. Betz, A. Le Moël, E. Balanzat, J.M. Ramillon, J. Lamotte, J.P. Gallas, G. Jaskierowicz, A FTIR study of PVDF irradiated by means of swift heavy ions, *J. Polym. Sci., Part B: Polym. Phys.* 32 (1994) 1493–1502, <https://doi.org/10.1002/polb.1994.090320821>.
- [30] Z. Z. T.C.M. Chung*, Study of VDF/TrFE/CTFE terpolymers for high pulsed capacitor with high energy density and low energy loss, 2007, <https://doi.org/10.1021/MA0627119>.
- [31] S. Kaur, A. Kumar, A.L. Sharma, D.P. Singh, Influence of annealing on dielectric and polarization behavior of PVDF thick films, *J. Mater. Sci. Mater. Electron.* 28 (2017) 8391–8396, <https://doi.org/10.1007/s10854-017-6556-8>.
- [32] P. Thakur, A. Kool, A. Hoque, B. Bagchi, S. Roy, Improving the thermal stability, electroactive β phase crystallization and dielectric constant of NiO nanoparticle/C-NiO nanocomposite embedded flexible poly(vinylidene fluoride) thin films, *RSC Adv.* 6 (2016) 26288–26299, <https://doi.org/10.1039/c6ra03322a>.
- [33] P. Thakur, A. Kool, N.A. Hoque, B. Bagchi, F. Khatun, P. Biswas, D. Brahma, S. Roy, S. Banerjee, S. Das, Superior performances of *in situ* synthesized ZnO/PVDF thin film based self-poled piezoelectric nanogenerator and self-charged photo-power bank with high durability, *Nano Energy* 44 (2018) 456–467, <https://doi.org/10.1016/j.nanoen.2017.11.065>.
- [34] P. Thakur, A. Kool, B. Bagchi, S. Das, P. Nandy, Enhancement of β phase crystallization and dielectric behavior of kaolinite/halloysite modified poly(vinylidene fluoride) thin films, *Appl. Clay Sci.* 99 (2014) 149–159, <https://doi.org/10.1016/j.clay.2014.06.025>.
- [35] P. Thakur, A. Kool, B. Bagchi, S. Das, P. Nandy, Effect of *in situ* synthesized Fe₂O₃ and Co₃O₄ nanoparticles on electroactive β phase crystallization and dielectric

- properties of poly (vinylidene fluoride) thin films, *Phys. Chem. Chem. Phys.* 17 (2015) 1368–1378, <https://doi.org/10.1039/c4cp04006f>.
- [36] V. Sencadas, S. Lanceros-Méndez, V. Sencadas, S. Lanceros-Méndez, R. Sabater Serra, A. Andrio Balado, J. Gómez Ribelles, Relaxation dynamics of poly (vinylidene fluoride) studied by dynamical mechanical measurements and dielectric spectroscopy, *Eur. Phys. J. E* 35 (2012) 4–5, <https://doi.org/10.1140/epje/i2012-12041-x>.
- [37] B. Hahn, J. Wendorff, D.Y. Yoon, Dielectric relaxation of the crystal-amorphous interphase in poly(vinylidene fluoride) and its blends with poly(methyl methacrylate), *Macromolecules* 18 (1985) 718–721, <https://doi.org/10.1021/ma00146a024>.
- [38] J.W. Sy, J. Mijovic, Reorientational dynamics of poly(vinylidene fluoride)/Poly (methyl methacrylate) blends by broad-band dielectric relaxation spectroscopy, *Macromolecules* 33 (2002) 933–946, <https://doi.org/10.1021/ma9907035>.
- [39] C.V. Chanmal, J.P. Jog, Dielectric relaxations in PVDF/BaTiO₃ nanocomposites, *Express Polym. Lett.* 2 (2008) 294–301, <https://doi.org/10.3144/expresspolymlett.2008.35>.
- [40] B. Behera, P. Nayak, R.N.P. Choudhary, Structural and impedance properties of KBa₂V₅O₁₅ ceramics, *Mater. Res. Bull.* 43 (2008) 401–410, <https://doi.org/10.1016/j.materresbull.2007.02.042>.
- [41] M. De, S. Hajra, R. Tiwari, S. Sahoo, R.N.P. Choudhary, H.S. Tewari, Structural, dielectric and electrical characteristics of BiFeO₃-NaNbO₃ solid solutions, *Ceram. Int.* 44 (2018) 11792–11797, <https://doi.org/10.1016/j.ceramint.2018.03.263>.
- [42] J.C. Maxwell, A treatise on electricity & magnetism - volume 2 : james clerk Maxwell : free download, borrow, and Streaming : internet archive, New York. <https://archive.org/details/ATreatiseOnElectricityMagnetism-Volume2/page/n5>, 1954. (Accessed 13 May 2019).
- [43] H. Frolich, Theory of Dielectrics Dielectric Constant and Dielectric Loss, Clarendon Press, Oxford, 1949. <https://www.worldcat.org/title/theory-of-dielectrics-dielectric-constant-and-dielectric-loss/oclc/2287477>. (Accessed 13 May 2019).
- [44] H.S. Nalwa, in: Hari Singh Nalwa (Ed.), Ferroelectric Polymers : Chemistry, Physics, and Applications, 1995. Version detailsTrove, <https://trove.nla.gov.au/work/21097975?selectedversion=NBD11604830>. (Accessed 13 May 2019).
- [45] C.P. Wong, T. Marinis, Jianmin Qu, Rao Yang, A precise numerical prediction of effective dielectric constant for polymer-ceramic composite based on effective-medium theory, *IEEE Trans. Compon. Packag. Technol.* 23 (2000) 680–683, <https://doi.org/10.1109/6144.888853>.
- [46] S. Liu, Shaohui, J. Zhai, W. Jinwen, X. Shuangxi, Z. Wenqin, Enhanced energy storage density in poly (vinylidene fluoride) nanocomposites by a small loading of surface-hydroxylated Ba_{0.6}Sr_{0.4}TiO₃ nanofibres, 2014, <https://doi.org/10.1021/am4042096>.
- [47] S. Liu, S. Xue, S. Xiu, B. Shen, J. Zhai, Surface- modified Ba (Zr_{0.3}Ti_{0.7})O₃ nanofibers by polyvinylpyrrolidone filler for poly (vinylidene fluoride) composites with enhanced dielectric constant and energy storage density, *Nat. Publ. Gr.* (2016) 1–11, <https://doi.org/10.1038/srep26198>.
- [48] A. Rajabtabar-Darvishi, R. Bayati, O. Sheikhejad-Bishe, L.D. Wang, W.L. Li, J. Sheng, W.D. Fei, Giant dielectric response and low dielectric loss in Al₂O₃ grafted CaCu₃Ti₄O₁₂ ceramics, *J. Appl. Phys.* 117 (2015), 094103, <https://doi.org/10.1063/1.4914052>.

Nanoparticle Synthesis-Shobhneek Kaur

ORIGINALITY REPORT

14%

SIMILARITY INDEX

7%

INTERNET SOURCES

13%

PUBLICATIONS

2%

STUDENT PAPERS

PRIMARY SOURCES

1

iopscience.iop.org

Internet Source

1%

2

worldwidescience.org

Internet Source

1%

3

Tzu-Chun Tai, Hung-Wei Wu, Yu-Ming Lin, Sin-Pei Wang, Yeong-Her Wang, Shoou-Jinn Chang. "Effects of Average Power-Handling Capability on DC-Sputtering Aluminum Nitride Thin Film on Ceramic Substrate", 2018 IEEE/MTT-S International Microwave Symposium - IMS, 2018

Publication

1%

4

Biplab Dutta, Navonil Bose, Epsita Kar, Sukhen Das, Sampad Mukherjee. "Smart, lightweight, flexible NiO/poly(vinylidene fluoride) nanocomposites film with significantly enhanced dielectric, piezoelectric and EMI shielding properties", Journal of Polymer Research, 2017

Publication

1%

5

www.freepatentsonline.com