# Synthesis and Characterization of Bismuth Ferrite and its Composites

*A Thesis Submitted*

In Partial Fulfillment of the Requirements
for the degree of

**Master of Technology**

in

**Materials Science and Engineering**

by

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# CERTIFICATE

This is to certify that the thesis entitled, **"Synthesis and Characterization of Bismuth Ferrite and its Composites"**, submitted by Mr. Vishwambhar Nath Shukla in the partial fulfillment of the requirement for the degree of Master of Technology in Materials Science and Engineering of this university. This work has been done under the joint supervision of Dr. R. K. Kotnala and Dr. S. D. Tiwari. The matter embodied in this thesis has not been submitted to any other degree of this or any other university.

The thesis work has been carried out from 12.01.2009 to 01.07.2009.

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# DECLARATION

I hereby declare that the entitled work **"Synthesis and Characterization of Bismuth Ferrite and its Composites"** is the original work carried out by me under the supervision of Dr. R. K. Kotnala and Dr. S. D. Tiwari. I am responsible for all the contents of this thesis. The matter embodied in this thesis has not been submitted anywhere else for the award of Degree.

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# CERTIFICATE

It is Certified that **Mr. Vishwambhar Nath Shukla**, student of M. Tech. Materials Science and Engineering from Thapar University, Patiala, Punjab, has completed the dissertation entitled ***"Synthesis and Characterization of Bismuth Ferrite and its composites"*** under my supervision at National Physical Laboratory (NPL) in Magnetic Standards Division. The above said project has been carried out during the period from 12th January, 2009 to 1st July, 2009.

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# ABSTRACT

$BiFeO_3$ - $BaTiO_3$ composites are prepared by using sol-gel synthesized $BiFeO_3$ and $BaTiO_3$. The samples are characterized by X-ray diffractometer and vibrating sample magnetometer. Results and analysis indicate for suppression of the cycloidal spin arrangements in the composite compared to that in bulk $BiFeO_3$.

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# CHAPTER-1

# INTRODUCTION

## 1.1 Multiferroic Materials

Materials exhibiting spontaneous magnetization, electric polarization or strain are called as ferroic materials [1]. In these materials the changes in the physical properties take place because of phase transitions around some critical temperature. Above this transition temperature the material is in a non ferroic state. In this non ferroic state the physical properties of the materials are not very interesting. However if the material is cooled below the critical temperature then the non ferroic material undergoes a spontaneous phase transition. In this state the physical properties of the material become very interesting. Occurrence of the phase transition below the critical temperature is due to small changes in the crystalline structure of the non ferroic material. Because of theses changes in dimensions and shape of the unit cell the point symmetry of the material is lowered. This is called as the breaking of the symmetry. This breaking of the symmetry is responsible for the formation of ferroic phase on cooling the non ferroic material below the critical temperature.

The term multiferroic materials have been in use to refer those materials which possess two or more properties of ferroic materials simultaneously in a single phase [2]. The three basic ferroic materials are ferromagnetic, ferroelectric and ferroelastic. These days the definition of multiferroic materials is extended to also include the non primary ferroic materials, such as antiferromagnetic or ferrimagnetic. The study of multiferroic materials is very important due to the involved physics [3] as well as their technological applications [4].

## 1.2 Bismuth Ferrite and its Composites

$BiFeO_3$ is a well studied multiferroic material ([3] and references there in). Bulk $BiFeO_3$ is known to have a rhombohedrally distorted perovskite structure in the R3c space group [5]. In this compound the ferroelectric transition temperature is about 1103 K [6] and the antiferromagnetic to paramagnetic transition temperature is about 643 K [7, 8].

$BaTiO_3$ is known to have five phases in solid form [9]. These are hexagonal, cubic, tetragonal, orthorhombic, and rhombohedral. All of these phases except cubic are ferroelectric.

Addition of $BaTiO_3$ in $BiFeO_3$ may affect the functional properties of the $BiFeO_3$. But synthesis of such materials must be pure and cost effective. Bearing these particulars in mind the sol-gel technique for the synthesis seems to be a suitable method. The magnetic properties of such materials could be very important in predicting the dielectric behaviors of the

materials. These reasons motivated to study the magnetic properties of $BiFeO_3$ - $BaTiO_3$ composites prepared by using sol-gel synthesized $BiFeO_3$ and $BaTiO_3$.

# CHAPTER-2

# EXPERIMENTAL TECHNIQUES

## 2.1 X-ray Diffratometer

X-rays are electromagnetic radiations. Its wavelength is smaller than that of visible light. X-ray tube is used to generate these rays. In this tube a high voltage is applied across the electrodes. Because of this high voltage the electrons in the tube get accelerated and hit a metal target (anode). X-rays are produced due to this. X-rays tubes containing copper targets are commonly used for structural characterization of materials.

X-ray diffractometer works on the principle of Bragg's law [10]. A crystal consists of parallel atomic planes. If a beam of X-ray falls on such a plane then according to Bragg's law the diffracted beam will have a maximum intensity if

$$2d \sin\theta = n\lambda$$

where $d$ is spacing between atomic planes, $\lambda$ is wavelength of X-ray used, θ is angle of diffraction and $n$ = 1, 2, …..

The X-ray diffractometer gives a plot of intensity of diffracted beam as a function of the angle 2θ. Using this plot the values of $d$ can be calculated and thus the material can be characterized.

Figure 2.1: X-ray Diffractometer at NPL, New Delhi.

In this study a X-ray diffractometer from RIGAKU, Japan (Model: D/Max-3C) having X-ray generator with copper target, 3 kW power X-ray detector, scintillation counter, goniometer and 16bit microprocessor for structural characterization of all the prepared samples is used.

## 2.2 Vibrating Sample Magnetometer

A vibrating sample magnetometer (VSM) is used to measure magnetization of a given material [11]. It operates on the principle of Faraday's law of induction, which tells that a changing magnetic field produces an electric field. A sample is magnetized by applying an external magnetic field. Now this magnetized sample is allowed to vibrate inside a pick up coil. The alternating magnetic field because of the vibration of the magnetized sample will cause an electric field across the pick-up coil according to Faraday's law of induction. This voltage or current is proportional to the magnetization of the sample. A lock-in amplifier is used to amplify the induction current. The various components are hooked up to a computer interface. Using controlling and monitoring software, the magnetization of the sample can be measured.

Figure 2.2: Vibrating Sample Magnetometer at NPL, New Delhi.

A Lake Shore's new 7400 series Vibrating Sample Magnetometer is used in the present work. This magnetometer consists of water cooled electromagnet for producing magnetic field. The temperature can be varied continuously from 10 to 1273 K and the magnetic field can be varied up to 1.2 T.

# CHAPTER-3

# EXPERIMENTS, RESULTS AND DISCUSSIONS

# 3.1 Bismuth Ferrite

Polycrystalline sample of bismuth ferrite ($BiFeO_3$) is prepared using a sol-gel method. Structural characterization of this sample is done with the help of X-Ray diffraction. Its magnetization is measured using VSM.

## 3.1.1 Synthesis

The bismuth ferrite can be synthesized by different methods such as solid state route [12], co-precipitation [13], sol-gel [14] etc. Among these methods, the sol-gel synthesis seems to be easy and reliable method to prepare bismuth ferrite.

$BiFeO_3$ is prepared by using citrate gel auto combustion method [15, 16], using analytical grade $Fe(NO_3)_3.9H_2O$ and $Bi(NO_3)_3.5H_2O$ as starting materials. Metal nitrates are taken in the required stoichiometric ratio, dissolved in a minimum amount of ethylene glycol and are mixed together. The mixed metal nitrate solution is then added to the citric acid solution in 1:1 molar ratio. The pH of the clear solution thus obtained is 1.0. Analytical grade liquor ammonia (30%) is then added drop by drop under constant stirring in order to make the pH of the solution to 6.0. The resulting solution is continuously heated on the magnetic stirrer at 70 $^0$C in order to allow gel formation. The gel so formed is kept on stirrer at 70 $^0$C for 36 hours in order to remove the adsorbed water. During this process the gel swells into a fluffy mass, which eventually breaks into brittle flakes. This precursor is then sintered at 830 $^0$C for 2 hours. The rate of increase of temperature for this sintering is 5 $^0$C per minute. The sintered product is allowed to cool at rate of 5 $^0$C per minute. Finally the resulting material is grinded to get fine powder sample.

## 3.1.2 Structural Characterization

Room temperature X-ray diffraction pattern of the prepared powder sample is shown in Figure 3.1. For this material the *d* values are calculated using the Bragg's law. These calculated *d* values are compared with the reported *d* values for $BiFeO_3$ in literature. It is found that the calculated and reported values are almost same. This indicates that the prepared powder sample is single phase $BiFeO_3$.

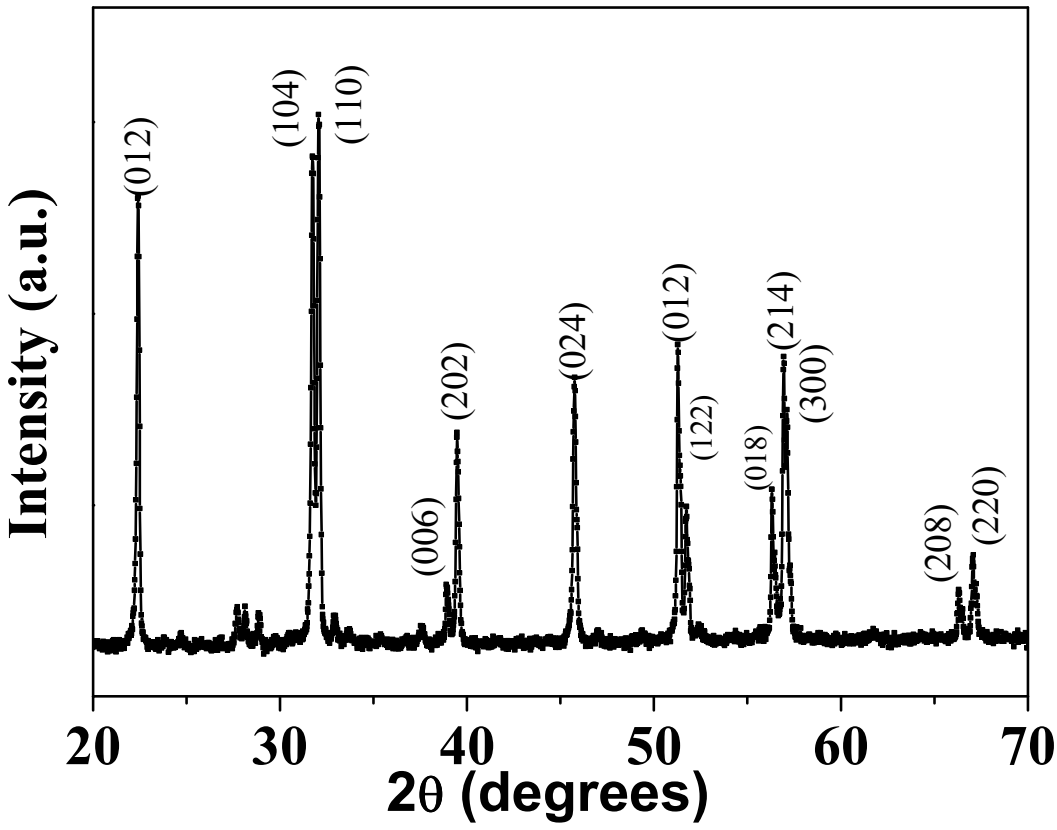


Figure 3.1: Room temperature X-ray diffraction pattern of $BiFeO_3$.

## 3.1.3 Magnetization

The magnetization of $BiFeO_3$ powder sample as a function of applied magnetic field is shown in Figure 3.2. $BiFeO_3$ prepared by solid state reaction method is known to be antiferromagnetic at room temperature [17]. But Figure 3.2 shows that there is small coercivity with no signature of saturation of the magnetization in the sol-gel prepared $BiFeO_3$. This observation shows that the antiferromagnetic ordering has broken a little in sol-gel prepared $BiFeO_3$ sample and thus producing small ferromagnetic behavior with small coercivity value.

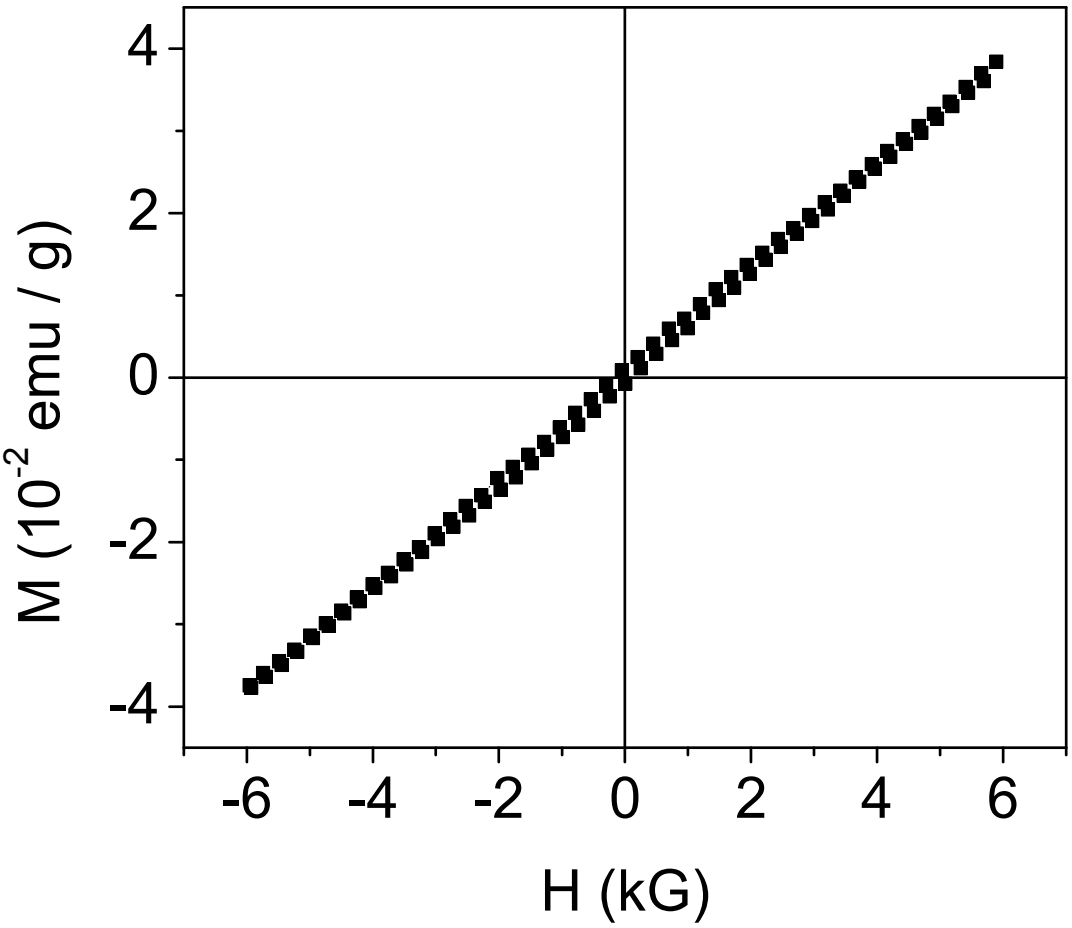


Figure 3.2: Magnetization as a function of magnetic field for $BiFeO_3$ at room temperature.

## 3.2 Barium Titanate

### 3.2.1 Synthesis

In 20 ml of ethylene glycol required amounts of barium nitrate and titanium isopropoxides and citric acid are added and mixed properly. Now this solution is put on a magnetic stirrer hot plate and heated at 40 $^0$C with continuous stirring for 1 hour. This forms a pale yellowish colored solution. This solution is again heated at 70 $^0$C with continuous stirring for 40 hours on a magnetic stirrer hot plate. This results in formation of a viscous gel having dark brown color.

The formed gel is taken to a high temperature furnace and heated at 70 $^0$C for 3 hours. The heating is continuously monitored and evolution of fumes is observed. In this way the gel is

converted into a solid. This solid is allowed to cool and finally grinded. The powder is now sintered at 1150 $^0$C for 5 hours. The rate of increase of temperature for this sintering is 5 $^0$C per minute. The sintered product is allowed to cool at rate of 5 $^0$C per minute. The powder is again grinded.

### 3.2.2 Structural Characterization

X-ray diffraction pattern of $BaTiO_3$ samples prepared by sintering at 1150 $^0$C is shown in Figure 3.3. This figure shows that the prepared sample is single phase $BaTiO_3$.

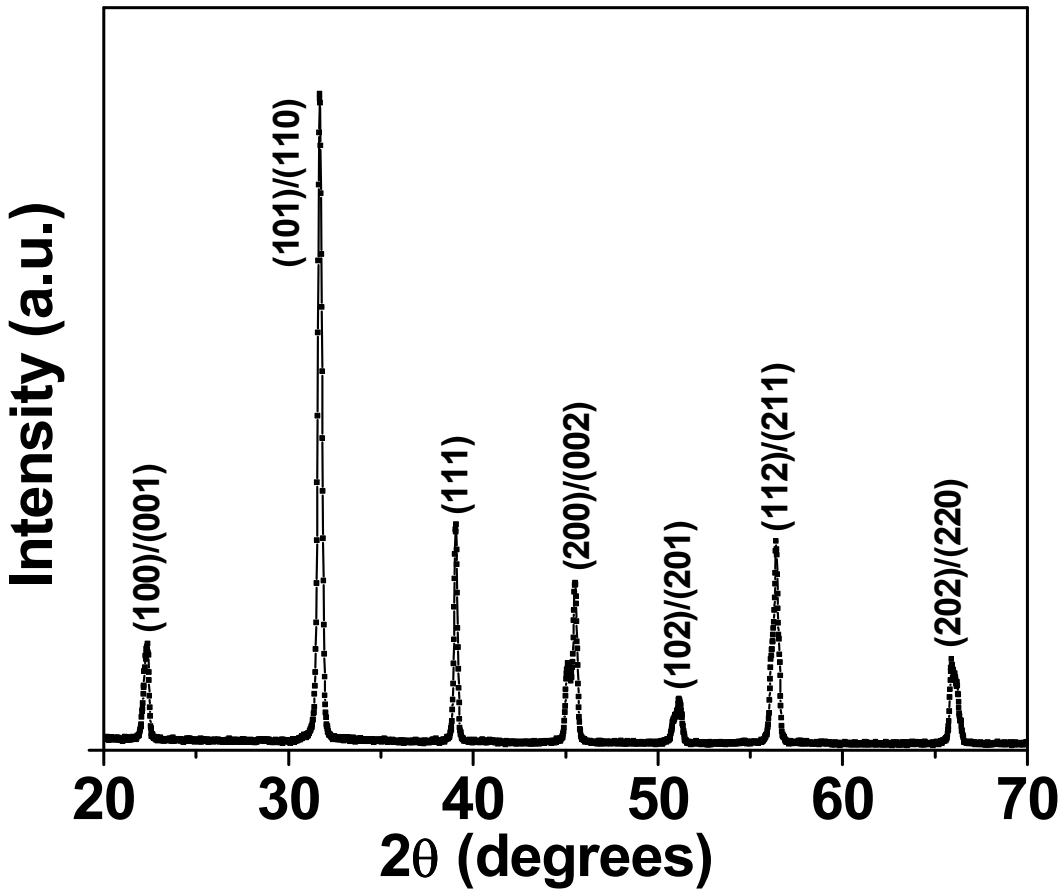


Figure 3.3: Room temperature X-ray diffraction pattern of $BaTiO_3$.

## 3.3 *x* $BiFeO_3$ – *(1-x)* $BaTiO_3$ Composites

In previous sections the synthesis of $BiFeO_3$ and $BaTiO_3$ in detail has been discussed. Now these materials are further used for the synthesis of composites of $BiFeO_3$ and $BaTiO_3$.

### 3.3.1 Synthesis

*x* $BiFeO_3$ – *(1-x)* $BaTiO_3$ composites with $x = 0.9$ and 0.8 are prepared. For this the earlier prepared powder samples of $BiFeO_3$ and $BaTiO_3$ are taken in appropriate amounts and mixed together properly. Pellets of these mixtures are made in the form of circular disc with diameter 14 mm and 2 mm thickness using hydraulic pressure. Sintering of these pellets is done at 900 $^0$C for two hours. The rate of increase of temperature for this sintering is 5 $^0$C per minute. The sintered products are allowed to cool at rate of 5 $^0$C per minute. Finally the pallets are grinded to get powder samples of *x* $BiFeO_3$ – *(1-x)* $BaTiO_3$ composites.

### 3.3.2 Structural Characterization

X-ray diffraction patterns of two different composites are shown in Figures 3.4 and 3.5. These figures confirm the formation of the composites.

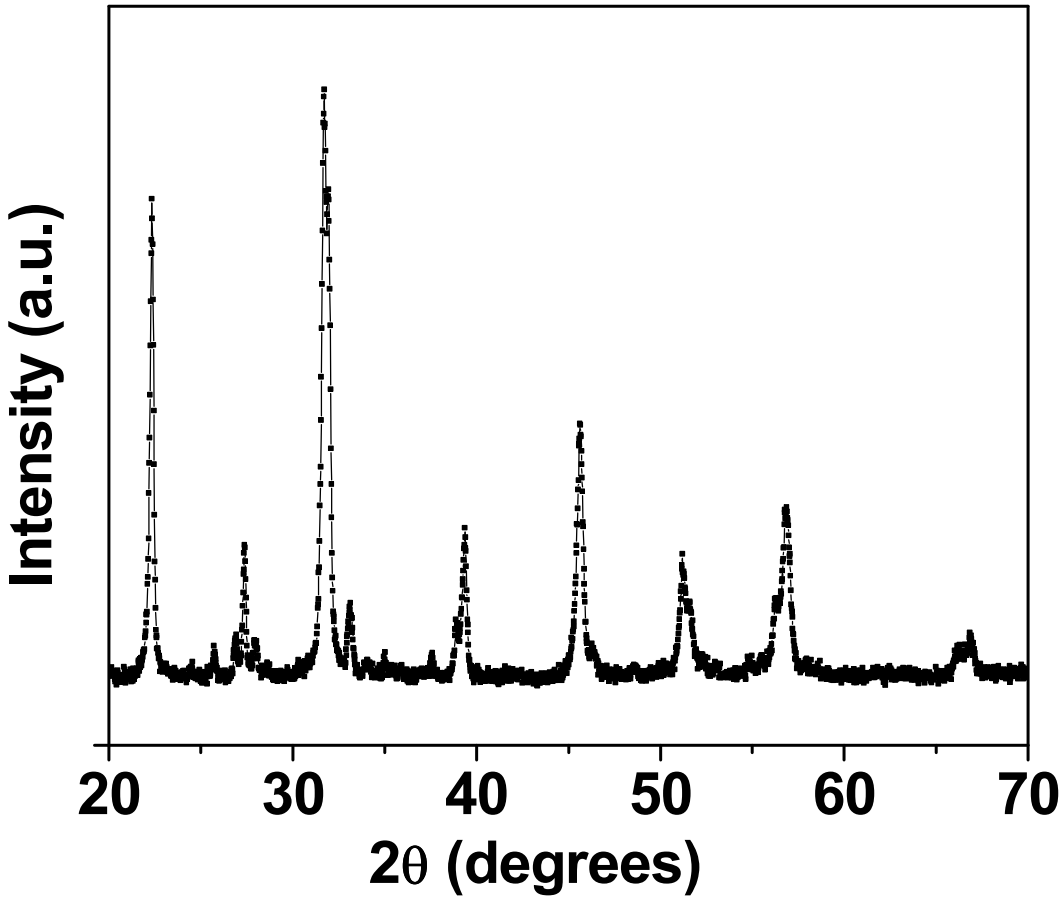


Figure 3.4: Room temperature X-ray diffraction pattern of 0.9 $BiFeO_3$ – 0.1 $BaTiO_3$.

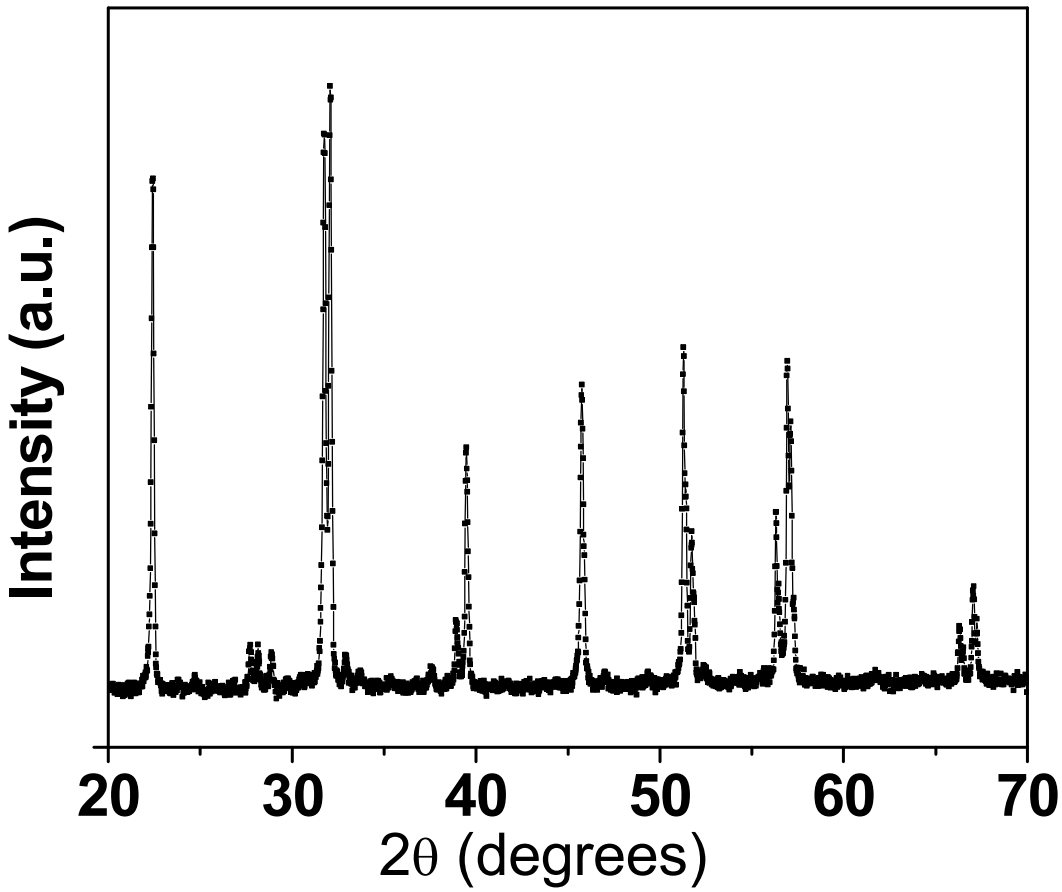


Figure 3.5: Room temperature X-ray diffraction pattern of 0.8 $BiFeO_3$ – 0.2 $BaTiO_3$.

### 3.3.3 Magnetization

The magnetization as a function of magnetic field for the prepared composists are shown in Figures 3.6 and 3.7. These figures show hysteresis loops in the measurements but still there is no sign of saturation in the magnetization curves. It means that there is some kind of ferromagnetic ordering in the prepared composite systems.

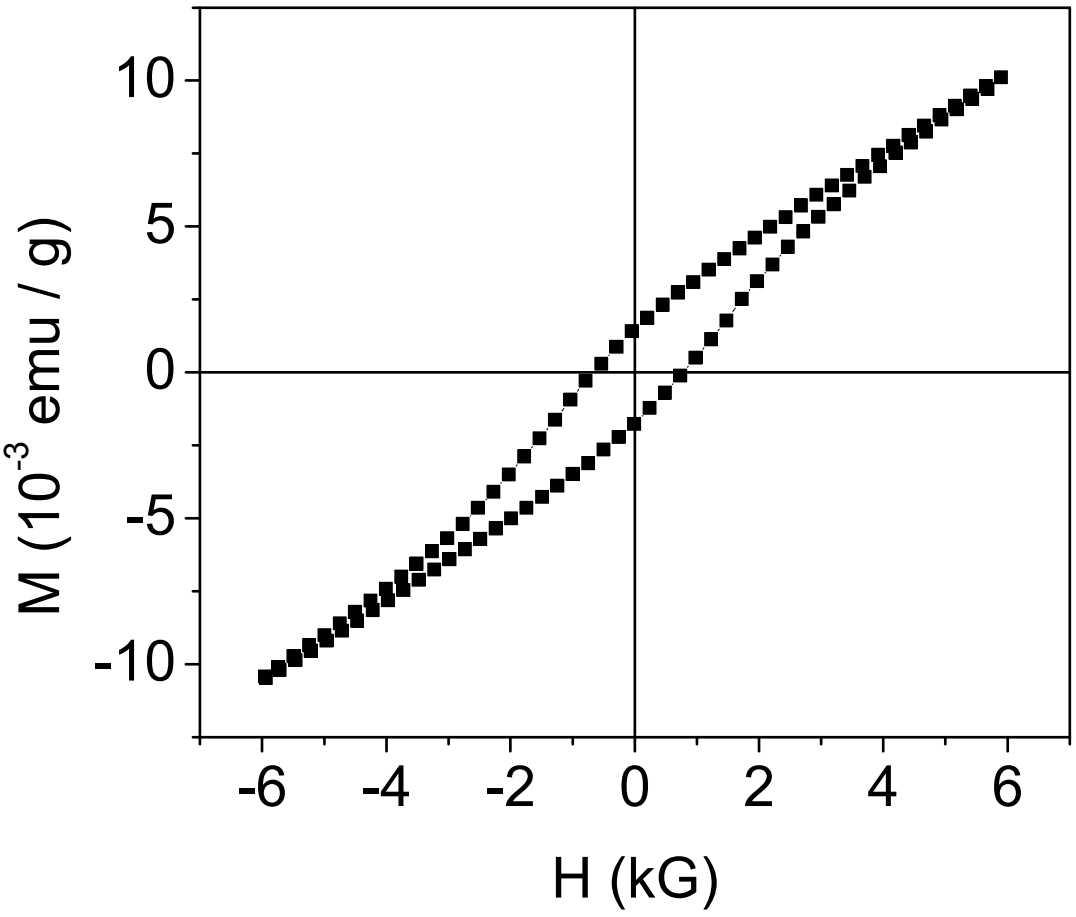


Figure 3.6: Magnetization as a function of magnetic field at room temperature for 0.9 $BiFeO_3$ – 0.1 $BaTiO_3$.

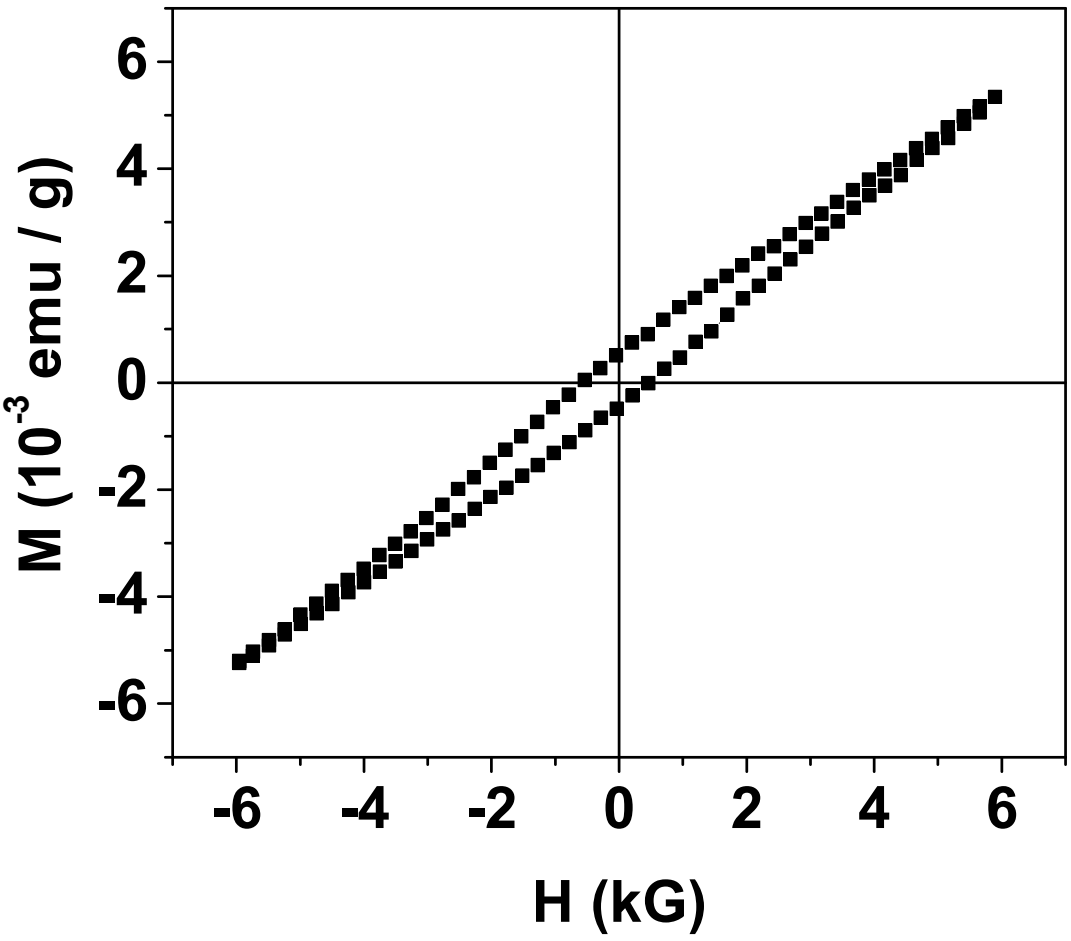


Figure 3.7: Magnetization as a function of magnetic field at room temperature for 0.8 $BiFeO_3$ – 0.2 $BaTiO_3$.

Pure $BiFeO_3$ is antiferromagnetic in nature and shows no hysteresis in magnetization as a function of magnetic field measurements. In this system the antiferromagnetic cyclodical magnetic ordering is known to quench the magnetic moment and a very small magnetic moment is observed. The observation of $M - H$ loop with non zero coercivities, as shown in Figures 3.6 and 3.7, in the $x$ $BiFeO_3$ – $(1-x)$ $BaTiO_3$ composite systems suggests that the cycloidal spin arrangements in pure $BiFeO_3$ may have suppressed in the prepared composite systems [18].

# CHAPTER-4

# CONCLUSIONS

In the present study, *x* $BiFeO_3$ – *(1-x)* $BaTiO_3$ composites are prepared using the sol-gel synthesized $BiFeO_3$ and $BaTiO_3$. Structural characterizations of all the synthesized samples are done with X-ray diffractometer. Pure $BiFeO_3$ is known to be antiferromagnetic and does not show any hysteresis in magnetization as a function of magnetic field measurements. But a hysteresis loop in the magnetization versus magnetic field curves is observed for the synthesized composits. This indicates for some kind of ferromegnetic ordering in the system. Suppression of the cycloidal spin arrangements in the composite compared to that in bulk $BiFeO_3$ may be responsible for this behavior.

The present work is only aimed to study the magnetic behavior of the synthesized *x* $BiFeO_3$ – *(1-x)* $BaTiO_3$ composites. One may further do the detailed study of the dielectric and ferroelectric behaviors of this composite system in future.

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