Synthesis and Characterization of Ferrihydrite Nanoparticles

A project report submitted

In Partial Fulfillment of the Requirements

For the degree of

MASTER OF SCIENCE

in

PHYSICS

BY

Preeti Saini

(Roll No: 301204007)

Under the guidance of

Dr. S. D. Tiwari

SCHOOL OF PHYSICS AND MATERIALS SCIENCE

THAPAR UNIVERSITY

PATIALA-147004

INDIA

July 2014

Dedicated to my Loving Parents

Certificate

This is to certify that the project report entitled "Synthesis and Characterization of Ferrihydrite Nanoparticles" submitted by Ms. Preeti Saini is in partial fulfillment for degree of Master of Science in Physics in this University. This work has been done under my supervision. She has not submitted this material for credit towards any other degree at this or any other University.

(Dr. S. D. Tiwari)

Assistant Professor

School of Physics and Materials Science

Thapar University, Patiala

Countersigned by

Dr. Kulvir Singh

Head

School of Physics and Materials Science

Thapar University, Patiala

Dr. S.K.Moohapatra

Dean of Academic Affairs

Thapar University, Patiala

Declaration

I hereby declare that the project report entitled "Synthesis and Characterization of Ferrihydrite Nanoparticles" is the work carried out by me under the supervision of Dr. S. D. Tiwari. I have not submitted this work anywhere else for the award of any degree.

Preeti Saini

Acknowledgement

First of all I express my sincere gratitude to my project supervisor Dr. S. D. Tiwari for his guidance and encouragement throughout the course of this work.

I would like to thank Dr. Kulvir Singh, Head SPMS, for his constant support. I thank Dr. B. N. Chudasama for his help in characterization of samples by TGA.

I express words of thanks from the bottom of my heart to the Ph. D. scholars Ms. Chandni Rana and Ms. Anu Gupta for their cordial support and valuable information which helped me in completing this task through various stages.

Lastly, I thank almighty, my parents, brother, sisters and friends for their constant encouragement without which this assignment was not possible.

Preeti Saini

Abstract

Undoped and nickel doped ferrihydrite nanoparticles are prepared by chemical routes. The samples are characterized by x-ray diffractometer, thermogravimetric analyzer and vibrating sample magnetometer. The average crystallite size is found to be about 2 nm. The prepared nanoparticles of undoped and nickel doped ferrihydrite are found to be antiferromagnetic at room temperature.

Contents

CHAPTER 1

INTRODUCTION

1.1 Magnetic Materials

On the basis of behavior of materials in external applied magnetic field all the known materials can be classified into diamagnetic, paramagnetic, ferromagnetic, antiferromagnetic and ferrimagnetic materials [1-3].

Diamagnetic materials are repelled by an external magnetic field. In these materials all the electrons are paired and so net atomic magnetic moment is zero. The magnetization of these materials is always opposite to the applied field. In other words the magnetic susceptibility of these materials is always negative. Also this susceptibility is independent of temperature.

In paramagnetic materials the atoms have unpaired electrons. In presence of external magnetic field the moments try to align themselves along the applied field direction. The magnetization of these materials varies with temperature as $M = C/T$, where C is a constant. This is known as Curie law. Paramagnetic materials remain magnetized as long as the applied field is present. The magnetization of the system becomes zero on the removal of the field.

In ferromagnetic materials the atomic/ionic magnetic moments feel very strong interaction. This interaction is known as exchange interaction. This interaction is capable of aligning the moments in parallel orientation. However the exchange interaction in ferromagnetic materials is short range in nature. Ferromagnetic materials are divided into small region called as magnetic domain. In a magnetic domain all the moments are aligned in same direction. However these domains are randomly oriented giving rise to zero magnetization in absence of any external applied field. Above a critical temperature T_C, known as the Curie temperature, a ferromagnetic material becomes paramagnetic. At this temperature the thermal energy becomes larger than the exchange interaction energy of magnetic moments. Due to this reason any ferromagnetic material becomes paramagnetic above this critical temperature.

In antiferromagnetic materials the neighboring magnetic moments are aligned in opposite direction. Because of this, antiferromagnetic materials give rise to zero magnetization in absence of any external applied field and at lower temperature. Antiferromagnetic materials have small but positive magnetic susceptibility. Antiferromagnetic ordering remains only below a critical temperature called Néel temperature. Above Néel temperature the antiferromagnetic ordering breaks and the material becomes paramagnetic.

In ferrimagnetic materials the neighboring magnetic moments of atoms/ions are aligned in opposite directions. But the magnitudes of neighboring moments do not equal to each other as in the case of antiferromagnetic materials. Because of this imbalance in magnitudes of magnetic moments, ferrimagnetic materials posses a non zero magnetization. Above a critical temperature the ferrimagnetic ordering breaks and the material becomes paramagnetic.

1.2 Superparamagnetism

Superparamagnetism is shown by small ferromagnetic or ferrimagnetic particles. In superparamagnetic state the anisotropy energy of the particles becomes smaller than the thermal energy. In this situation the magnetization vector of the system can not remain fixed in direction. This behavior is similar to paramagnetism and known as the superparamagnetism. The phenomenon of superparamagnetism is also shown by small particles of antiferromagnetic materials. For these materials the anisotropy energy signifies the energy required to change the direction of all spins by 180^0 [4].

1.3 Literature Review

A brief review of works relevant to this project is summarized below.

Seehra et al. (2000) studied magnetic properties of two-line ferrihydrite nanoparticles. It was found that the value of particle magnetic moment increases with increase in temperature [5].

Punnoose et al. (2004) reported change in the magnetic properties of ferrihydrite nanoparticles on doping with Ni, Mo and Ir. They observed that Ni substitutes the Fe throughout the nanoparticle, whereas doping with Mo and Ir occurs primarily at the surface [6].

Seehra et al. (2004) synthesized silicon doped ferrihydrite and proposed that silicon chemisorbed on the surface of ferrihydrite. Their study predicts that with the increase of silica doping d-spacing increases as a result of which crystallinity decreases [7].

Pannalal et al. (2005) reported that ferrihydrite shows a weak ferromagnetic behavior at room temperature [8].

Jentzsch et al. (2006) studied the reactivity of ferrihydrite doped with aluminum. As the amount of aluminum substitution increases, it was observed that there is an increase in the activation entropy and a decrease in the activation enthalpy. The decrease in activation free energy increases the reactivity of ferrihydrite nanoparticles [9].

Berquo et al. (2007) synthesize silicon doped ferrihydrite at different temperatures and showed that with increase in temperature, particles size increases. Neel temperature for ferrihydrite was found to be about 422 K. Magnetic properties of natural ferrihydrite collected from marine shallow-water hydrothermal system were also studied. Seven line XRD pattern and open hysteresis loop was observed [10].

Michel et al. (2007) gave single phase model for ferrihydrite contradicting the existing model given in literature. It was found that this structure contains 20% tetrahedrally and 80% octahedrally coordinated iron [11].

Paktunc et al. (2013) studied the structure of undoped and Ge doped ferrihydrite. It was concluded that there is not any tetrahedral positions for Fe atoms. So the structure given by Michel et al. was contradicted. But still there is not any final structure for Ferrihydrite. Still it is a matter of debate [12].

CHAPTER 2

EXPERIMENTAL DETAILS

2.1 Synthesis

In this work nanoparticles of ferrihydrite are synthesized by chemical route following the procedure described elsewhere [6]. Aqueous sodium hydroxide solution is added drop wise into aqueous solution containing Fe^{3+} and Ni^{2+} ions in appropriate amount with constant stirring until pH of the system reaches to 10. The resulting precipitate is filtered and washed several times. The precipitate is dried at 70 ^{0}C for overnight. The dried flakes are grinded to get a fine powder sample.

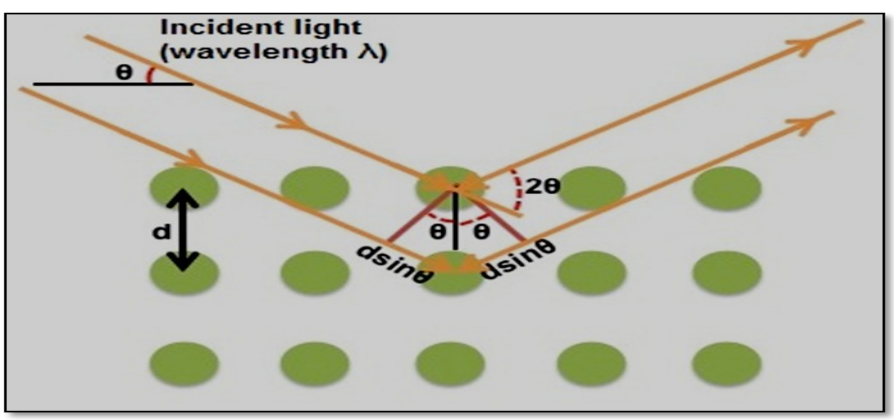
2.2 Characterization Techniques

2.2.1 X-Ray Diffraction

X-ray diffraction technique is used to analyze the structure of a material. X-ray diffraction is based on Bragg's law [1]. According to this law a beam of x-rays incident at an angle θ produces constructive interference if

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

where d and λ are interplanner spacing and wavelength of incident x-rays respectively. Also n = 1, 2, ….. A schematic arrangement of different component in an x-ray diffractometer is shown in following figure.



2.1: A beam of x-rays falling on a set of parallel atomic planes at an angle θ [13].

2.2.2 Thermogravimetric Analyzer

Thermogravimetric analyzer is used to check thermal stability of a material. In this the sample is heated at a constant heating rate in appropriate atmosphere. The mass of the sample is recorded as a function of temperature. Changes in the mass of sample at different temperatures are analyzed for possible reasons. A schematic diagram of a thermo gravimetric analyzer is shown in following figure.

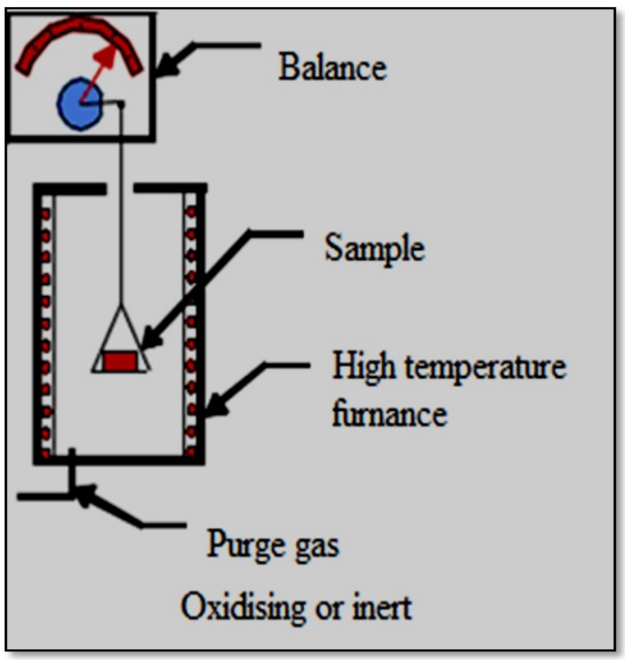


Figure 2.2: Schematic diagram of thermogravimetric analyzer [14].

2.2.3 Vibrating Sample Magnetometer

A vibrating sample magnetometer is used to measure magnetization of a sample. This instrument is based on Faraday's law of induction. According to this law a changing magnetic flux induces an emf.

The sample is magnetized by applying an external magnetic field. This magnetized sample is allowed to vibrate inside a coil. The induced emf across the coil is measured. This emf is directly proportional to the magnetization of the sample. After a proper calibration the magnetization of sample can be measured as a function of applied magnetic field, temperature and time.

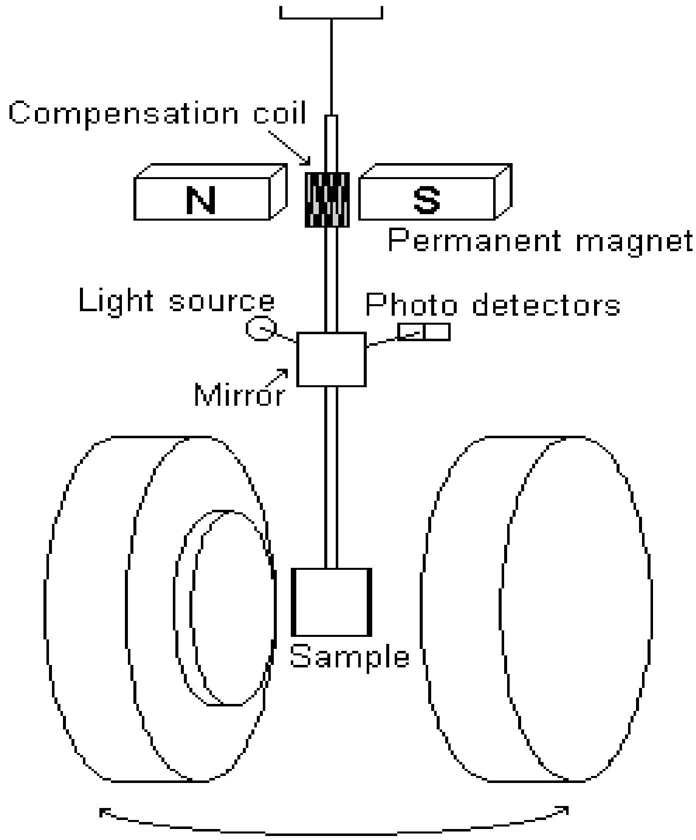


Figure 2.3: Schematic diagram of vibrating sample magnetometer [15].

CHAPTER 3
RESULTS AND DISCUSSION

3.1 Structural characterization

Room temperature x-ray diffraction patterns for undoped and nickel doped ferrihydrite nanoparticles are shown in Figures 3.1 and 3.2 respectively. It is noticed that both the samples are poorly crystalline. The observed broad peaks in the patterns indicate that the samples are nanocrystalline. The average crystallite size is calculated using the modified Scherer formula. [16]

$$d = \frac{0.9\lambda}{\cos\theta_B (B_M - B_S)},$$

where λ is the wavelength of the r-rays, θ_B is the Bragg's angle, B_M is the full width at half maximum of the sample and B_S is the FWHM of a standard sample. The average crystallite size for undoped and nickel doped ferrihydrite samples are found to be about 2 nm.

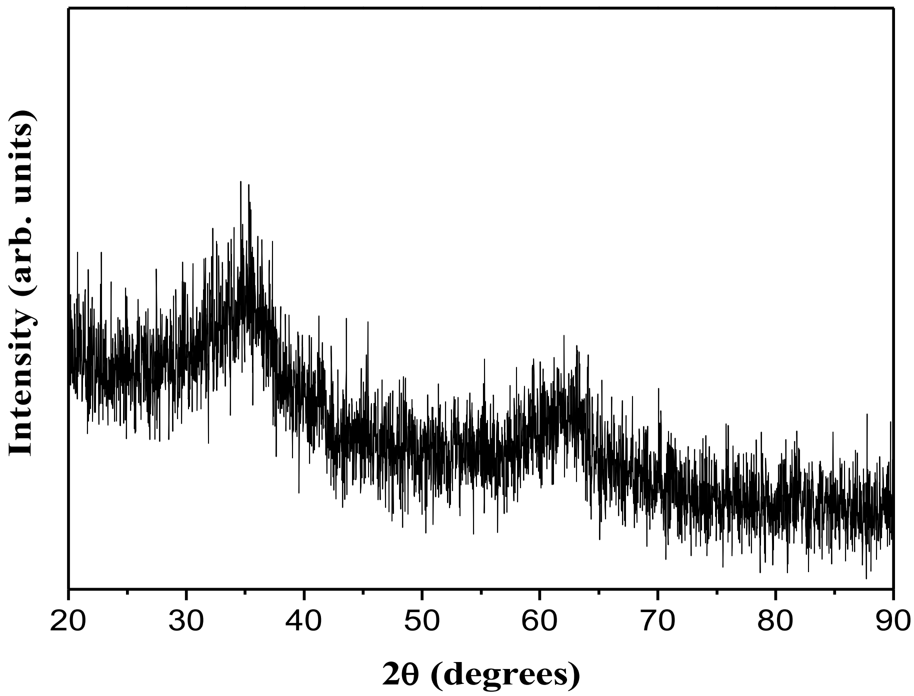


Figure 3.1 X-ray diffraction pattern for ferrihydrite nanoparticles.

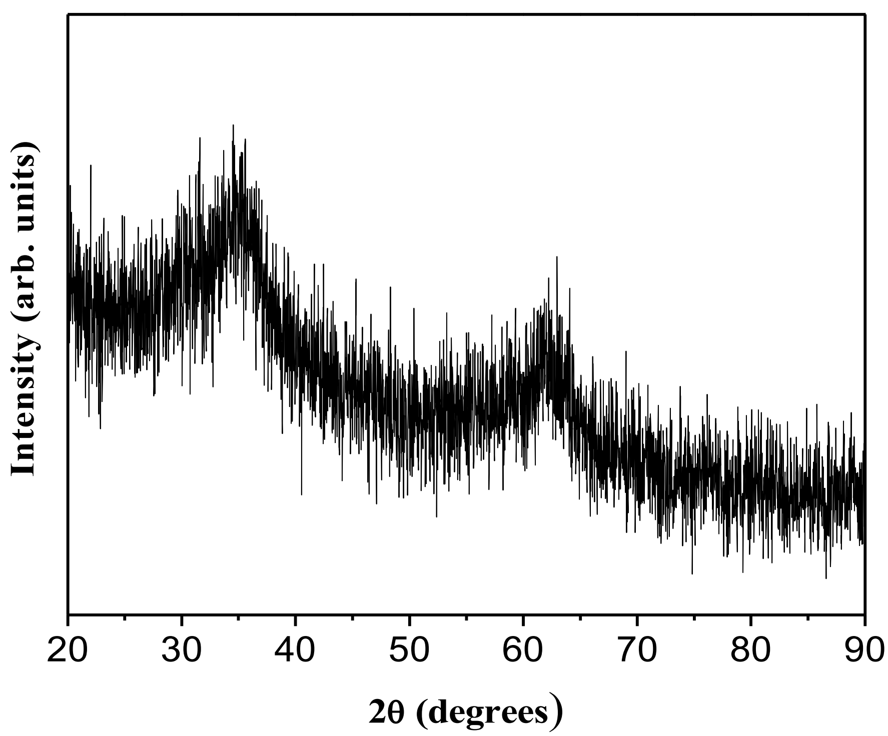


Figure 3.2 X-ray diffraction pattern for nickel doped ferrihydrite nanoparticles.

3.2 Thermogravimetric Analysis

Many compounds are not stable and decompose to other compounds on heating. Thermal stability of a compound can be checked by thermogravimetric analysis. In this analysis mass of sample is recorded as a function of temperature. During this process the sample is heated at a constant heating rate in air. Result of this analysis is shown in Figure 3.3.

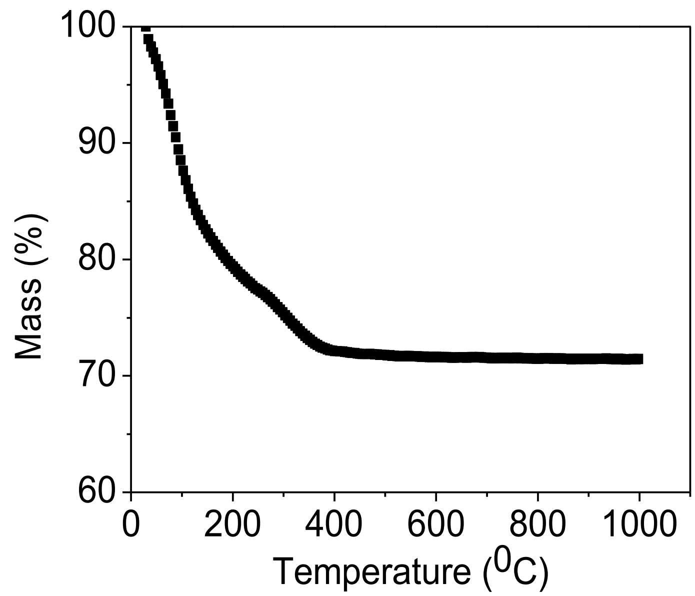


Figure 3.3: Thermogravimetric analysis of undoped ferrihydrite nanoparticles.

This figure shows that the mass of sample becomes almost constant at about 380 ^{0}C. Above this temperature the material is converted into hematite.

3.3 Magnetization measurement

Magnetization of undoped and nickel doped ferrihydrite nanoparticles are measured using a vibrating sample magnetometer. These measurements, at room temperature, are shown in Figure

3.4. This figure shows that there is no hysteresis. Both samples are found to be antiferromagnetic at room temperature. It is also clear that the magnetization of nickel doped ferrihydrite nanoparticles is slightly larger than that of undoped sample.

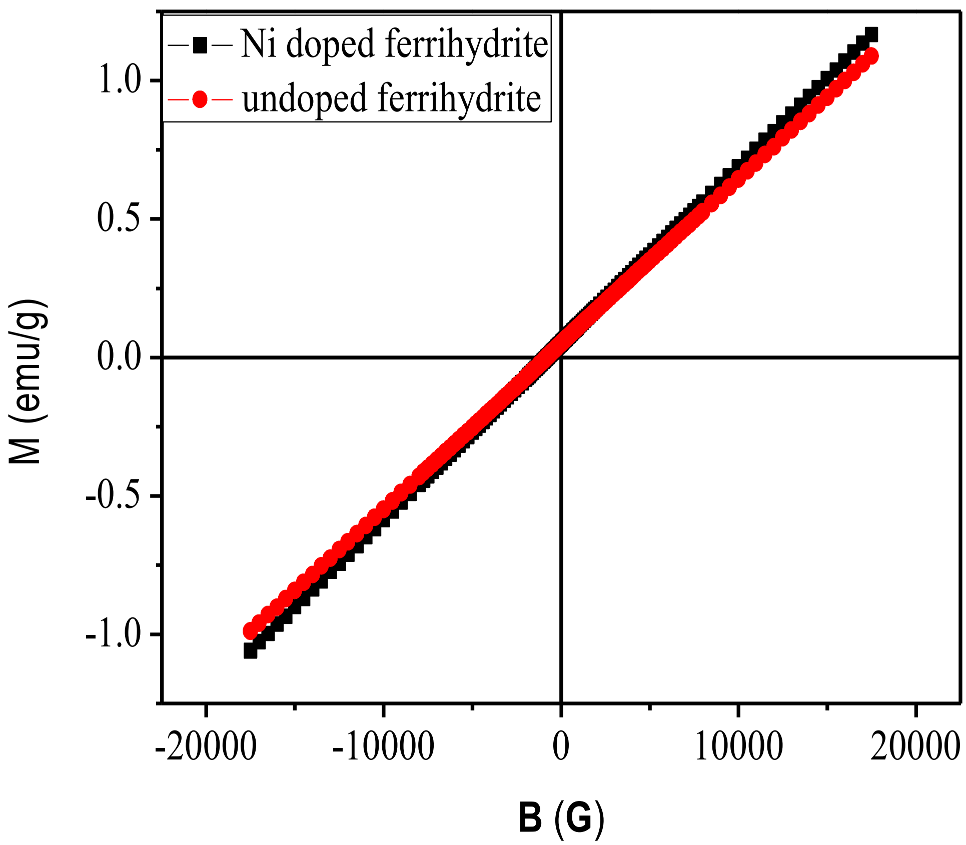


Figure 3.4: Magnetization as a function of applied magnetic field at room temperature for undoped and nickel doped ferrihydrite nanoparticles.

CHAPTER 4

CONCLUSION

In this work undoped and nickel doped ferrihydrite nanoparticles are synthesized by chemical routes. Samples are characterized by x-ray diffraction, thermogravimetric analyzer and vibrating sample magnetometer. Both samples are found to be poorly crystalline. Average crystallite size for both the samples is found to be about 2 nm. Ferrihydrite is found to decompose into hematite on heating. Magnetization of ferrihydrite nanoparticles increases due to doping with nickel. Both samples are found to be antiferromagnetic at room temperature.

References

[1]. C. Kittel , *Introduction to solid state physics* (John Wiley and Sons, Inc.,7th ed.,1996).
[2]. A.J. Dekker, Solid state physics (Macmillan India Limited, 1996).
[3]. A. Sharma, *Condensed matter physics* (Modern Publishers,1st ed., 2005).
[4]. I. S. Jacobs and C. P. Bean, in Magnetism, edited by G. T. Rado and H. Suhl (Academic, New York, 1963), Vol. III, p. 271.
[5]. M. S. Seehra, V. S. Babu, and A. Manivannan and J. W. Lynn, Physical Review B **61**, 3513 (2000).
[6]. A. Punnoose and T. Phanthavady , Physical review B **69**, 054425 (2004).
[7]. M. S. Seehra, P. Roy, A. Raman, A. Manivannan, Solid State Communications **130**, 597 (2004).
[8]. S. J. Pannalal, S. A. Crowe, M. T. Cioppa, David T.A. Symons, A.Sturm, D. A. Fowle, Earth and Planetary Science Letters **236**, 856 (2005).
[9]. T. L. Jentzsch and R. L. Penn, J. Phys. Chem. B **110**, 11746 (2006).
[10]. T. S. Berquo, S. K. Banerjee, R.G. Ford, R. L. Penn, T. Pichler, Journal of Geophysical Research **112** , B02102 (2007).
[11]. F. M. Michel, L. Ehm, S.M. Antao and P. L. Lee, Science **316**, 1727 (2007).
[12]. D. Paktunc, A. Manceau and J. Dutrizac, American Mineralogist **98**, 848 (2013).
[13]. cnx.org/content/m46149/latest/?collection=col10699/latest.
[14]. http://www.itc.tu-bs.de/Abteilungen/Makro/Methods/dsc.pdf.
[15]. http://www.student.nada.kth.se/~f93-jwe/expeq.htm.
[16]. B.D. Cullity, Elements of X-ray diffraction, Addison-Wesley Publishing Company Inc., p.99 (1967).