ELECTRIC TRANSPORT PROPERTIES STUDY OF SPINEL $ZnCr_2O_4$

Thesis on partial fulfillment of degree of science in physics

SUBMITTED BY

SABYASACHI JENA

ROLL-412PH2098

Under the guidance of

Prof. S. Panigrahi

DEPARTMENT OF PHYSICS AND ASTRONOMY

NATIONAL INSTITUTE OF TECHNOLOGY. ROURKELA

ROURKELA-769008, ODISHA, INDIA

2013-2014

National institute of technology

Rourkela

Certificate

This is to certify that the thesis entitled "ELECTRIC TRANSPORT PROPERTIES STUDY OF SPINEL $ZnCr_2O_4$" submitted by Sabyasachi Jena for the partial fulfillment of degree of Master of Science in physics, National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in this project has not been submitted to any other University/ Institute for the award of any degree.

Prof. S. Panigrahi

Place: Rourkela

Date: 16.04.2014

Dept. of Physics and Astronomy

National Institute of Technology. Rourkela

Rourkela-769008

ACKNOWLEDGEMENT

I would like to thank Prof Simanchala Panigrahi for his valuable guidance and constant supervision as well as providing necessary information regarding the project. I am especially grateful to PhD scholars Mr. Rakesh Muduli, Mr. Ranjit Panda, Mr. Joyti Prakash Dhal, Mr. Ranjit pattanayak, Mrs. Priyambada nayak for their valuable suggestions and clarifying all my doubts. I would like to acknowledge my deep sense of gratitude to Prof. Dhrubananda Behera for allowing me to use the facilities in his laboratory. I would also like to thank Radha raman Nayak of xrd laboratory for his valuable help.

I also express my thankfulness to PhD scholar Rakesh Muduli for helping me in completing my project and analyzing the data.

Last but not the least I would like to express my gratefulness to my parents for their endless support without which I could not have completed my project work.

Rourkela

Date-16.04.2014

SABYASACHI JENA

CONTENTS

List of figures

ABSTRACT

We have carried out the electric transport property study of spinel ZnCr2O4 insulating oxide by the help of complex impedance and modulus technique. The sample was synthesized by conventional method and crystallinity of phase was analyzed by xrd pattern. Surface morphology and porosity was observed from the scanning electron microscope image. Direct band gap (Eg=3.4eV) and indirect band gap (Eg=1.49eV) was found from UV spectroscopic analysis. Co contribution of grain and grain boundary effect is found at room temperature and continued some point below 200^{o}C. Electrode surface polarization was found responsible for conduction mechanism in the sample at high temperature at and above 200^{o}C. Grain effect is supposed to be dominant below the room temperature (RT). The conductivity behavior is found to obey Jonscher's universal power law. Frequency exponent study revealed three different conduction mechanism, (a) quantum mechanical tunneling, 200^{o}C < T < 260^{o}C, (b) small polaron conduction mechanism at 260^{o}C < T < 355^{o}C and (c) Correlated barrier hopping at 355^{o}C < T < 400^{o}C. The activation energies were found to be 0.74eV, 1.40eV and 1.07eV for the above stated temperature range respectively for corresponding conduction process.

CHAPTER-1

Introduction

There has always been a querscity for researchers to know and develop the theories which would explain the mode of transportation of energy in a solid. The flow of energy in the form of heat or thermal energy, charge or electric energy or spin wave or magnetic energy takes place in different modes which has been developed its experimental and theoretical base from last two centuries. With the evolution of wave theory and scattering phenomena, several experimental design was set up to demystify the microscopic world. Elastic and non-elastic scattering process and their application to study the material core helped a lot to come with a success. The born of quantum theory was a boon to the human society which able to explain so many properties shown by the solids. The wave particle duality concept further enhances the research field. The assumption of electron wave, neutron or proton wave helped to analyze so many unsolved questions. The Bragg's diffraction condition and experiment with X- ray revealed the arrangement of atoms and their regularity.

The heat energy transfer in a material takes place without the material itself in motion. The thermal conductivity and the temperature gradient determine how much heat will flow through the solid. The specific heat of the material determines the rate of increase in its temperature. Dulong-Petit has stated that the specific heat of solid is constant which is equal to 3R, where R- universal gas constant. This result agrees at sufficient high temperature but drastically fails at low temperature below the room temperature. Later, Einstein and Debye were able to explain by considering the quantized lattice vibrations known as phonons. For non-metals having low thermal conductivity value, the thermal energy is transported inside the materials through the activation of all possible lattice vibrational modes at that particular temperature. For metals, both the thermal conductivity and electrical conductivity is very high. The electron fluid is supposed to be responsible to carry the thermal energy forward, as it was explained b Fermi model.

The charge transport in insulating solids which have low electrical conductivity puts several questions before researchers. Most of the metals are found to be good conductors. The band theory has successfully explained regarding the conducting, semiconducting and insulating behaviour of solids. The concept of valence band, conduction band and their position as well as

their overlapping is the determining factor of behaving whether as conductor, semiconductor or insulator. The free flow of electron and it's density in the conduction band contributes to large value of conductivity. The electrical resistance arises due to the scattering of these electrons with the lattice vibration centers. The electron-phonon interaction is the major contributing factor towards electrical resistivity apart from the role of presence of impurities and lattice defects.

The spin interaction among the neighboring atoms occupying several lattice sites is the major cause of source of magnetism. The interaction energy which depends upon the interaction potential due to spin rotation governs the possible magnetic moment value within the solid.

About $ZnCr_2O_4$

Spinel ZnCr2O4 is crystallized with the space group of Fd3m having reported lattice parameter a=58.280 A˚. The spinel oxide is represented by the form of AB_2O_4. The structural unit cell is of cubic form. Here the Zn^{2+} which is a non magnetic ion has a strong tendency towards the tetrahedral site whereas the magnetic Cr^{2+} occupies the octahedral site. The spinel $ZnCr_2O_4$ makes a first order phase transition from paramagnetic to antiferromagnetic at 12.5K.The paramagnetic phase has a cubic structure whereas the antiferromagnetic structure has a tetragonal structure. It can be used as a catalyst in various reactions for example it is very effective as an air depollution catalyst. It has crystal group of Fd3m having lattice parameter of a=58.280 A˚.

CHAPTER-2

STRUCTURE OF $ZnCr_2O_4$

The spinel structure is named after the mineral spinel ($MgAl_2O_4$). The general composition of spinel structure is AB_2O_4. It is essentially cubic structure, with the O - ions forming a fcc lattice. The cations (usually metals) occupy 1/8 of the tetrahedral sites and 1/2 of the octahedral sites and there are 32 O-ions in the unit cell. Generally the A site is a divalent atom having radius between 80pm and 110pm. Example Mn, Zn Mg, Fe and Cu and B has the radius between 75pm and 90pm and is generally a trivalent atom. Example Ti, Fe, Al, and Co. The spinel consists of closely-packed array of 32 oxide ions arranged in a cubic manner which creates 64 tetrahedral holes and 32 octahedral holes in a single unit cell. A unit cell consists of eight formula units $(AB_2O_4)8$).

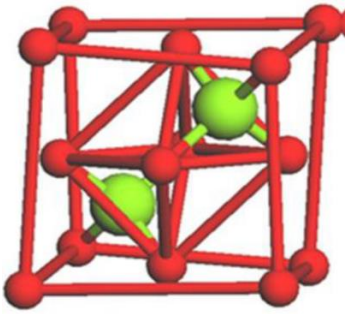


FIGURE 1.1- Presence of two kinds of occupied tetrahedral sites in spinel sub-cell a.

The spinel structure is commonly described by two types of sub-cells

Consider structure A and structure B in Figures 1.1 and 1.2 respectively. Structure 1.1: clearly shows the occupation of the 2 tetrahedral sites within one-eighth of the unit cell, and structure 1.2 shows that the octahedral site is occupied by a cation.

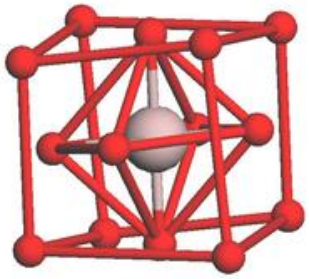


FIGURE 1.2: Presence of octahedral site in spinel sub-cell b.

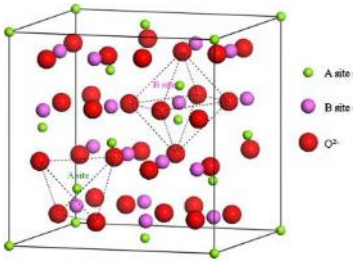


Figure 2: Diagrammatic sketch of the spinel crystal

Dielectric:-

A dielectric is an electrical insulator which can be polarized with the application of electric field. With the presence of an external field the electric charges are polarized which causes electric polarization. In a dielectric material when the field is applied polarization takes place due to shift of positive and negative charge centers from their equilibrium position. As a result it develops an internal electric field which reduces the external field. The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy inside the material. The dielectric properties of a substance such as dielectric constant, dielectric loss, relaxation time, modulus, impedance etc. have provided an insight to the structure of the molecules of the system. Dielectric or electrical insulating materials are the materials in which electrostatic field can persist for a long time.

Polarization:-

A dielectric sample when placed in an external field E acquires a net dipole moment indicating that the dielectric material is polarized due to the presence of the external applied field. The polarization of the sample is generally represented presented as.

$$P=<m>/v$$

Where <m> is the resulting dipole moment of volume v

Types of polarization:-

1. Deformation polarization-

Broadly classified into two independent ways

i. **Electron polarization –**

The electron polarization is the displacement of nuclei and electron in the atom in the presence of an externally applied electric field. Due to the lighter mass of electron they have a quick response to the field changes; they may even follow the field at optical frequencies.

ii. **Atomic polarization-**

The atomic polarization is due to the displacement of atoms or atomic groups in the molecule due to the presence of external electric field.

2. Orientation polarization-

When an external field is applied it tends to align the dipoles along itself. The rotational motion of the dipoles and the thermal motion of dipoles counteract each other. So the orientation polarization is a strong frequency and temperature dependent parameter

3. Ionic polarization–

When an ionic lattice is placed inside an external applied field the cations are forcefully displaced towards the direction of an applied field while the anions move away from the field direction. Thus it gives a resultant dipole moment to the entire system.

4. Space charge polarization

When the thermal energy of the systems become very large the charge carriers accumulate on the surface of the material. These charge carriers also respond the externally applied field as a result the electron can hop from one site to nearer vacant site .This creates a special type of polarization called space charge polarization

CHAPTER 3

Experimental methods

Synthesis of the material:

There are several synthesis methods are available such as;

- Solid state reaction method
- Auto –Combustion method
- Sol-gel method
- Co-precipitation method

Solid state reaction method:-

It is a very popular method of synthesis of bulk materials. At room temperature the solids will never react with each other. So the solid precursors are heated up to a high temperature where proper reactions take place at higher rate indicating that the thermodynamic and kinetic factors play an important role in this method. The advantage of this method is that no unwanted waste is formed. The final product obtained in this method is structurally pure in solid form. The properties of the finally sintered sample depends on the sintering temperature

Auto-combustion method:-

Combustion synthesis (CS) is an effective and inexpensive method for the preparation of various metals which has industrial applications. Auto combustion method has become very popular wide across many countries because nanomaterial can be easily prepared by this method

Sol-gel method:-

A sol is a stable suspension of colloidal solid particles or polymers in a liquid. A gel is porous, three-dimensional continuous solid network surrounding a continuous liquid phase. In certain condition of temperature, pH and concentration the sol undergoes a phase transition and it passes into a gel state. This process is called gelation and the final product is a gel. It is a very popular method for material synthesis.

Co-precipitation method:-

In this method, the initial precursors are properly mixed with each other by ball milling process or hand grinding and the reaction rate is highly dependent on the particle size of the reactants, the degree of homogenization etc. It is highly dependent on the grain size and temperature also.

Equimolar calculation for starting materials

Molecular weight of ZnO = 81.408 g mol^{-1}

Molecular weight of Cr_2O_3 = 151.99 g mol^{-1}

Molecular weight of $ZnCr_2O_4$ = 233.3988 g mol^{-1}

The governing reaction is

$$ZnO + Cr_2O_3 = ZnCr_2O_4$$

For the preparation of 4gm of sample

Amount of ZnO

= {(molecular weight of ZnO)/ (molecular weight of $ZnCr_2O_4$)}*4

= (81.408/233.3988)*4

= 1.39518 gm.

Amount of Cr_2O_3

= {(molecular weight of Cr_2O_3)/ (molecular weight of $ZnCr_2O_4$)}*4

= (151.99/233.3988)*4

= 2.60482 gm.

Amount of $ZnCr_2O_4$

= Amount of ZnO+ Amount of Cr_2O_3

= 1.39518+2.60482

= 4.0000 gm.

Synthesis of $ZnCr_2O_4$

The solid state route is one of the best methods to prepare the sample. The precursors taken are ZnO and Cr_2O_3.

The different synthesis techniques that have been done are:

- proper mixing of precursors
- Calcination
- Pellet formation
- Sintering

Proper mixing of precursors:-

For the preparation of $ZnCr_2O_4$, the constituent precursors ZnO and Cr_2O_3 are weighted in an electronic digital balance to an accuracy of 0.0001 mg. The weighted precursors are mixed and grinded properly by using an agate mortar pestle for about 5 hours.

Calcination:-

This is a thermal process in which the well grinded mixed precursors are subjected to a suitable temperature for a well calculated duration for the formation of desired phase. The twin reactions such as thermal decomposition of precursors and reaction of decomposed compounds take place. This process is completely meant to remove the volatile elements, carbon dioxides, carbonates, water contents etc. The present sample is calcined at 1200^0c for 12 hours

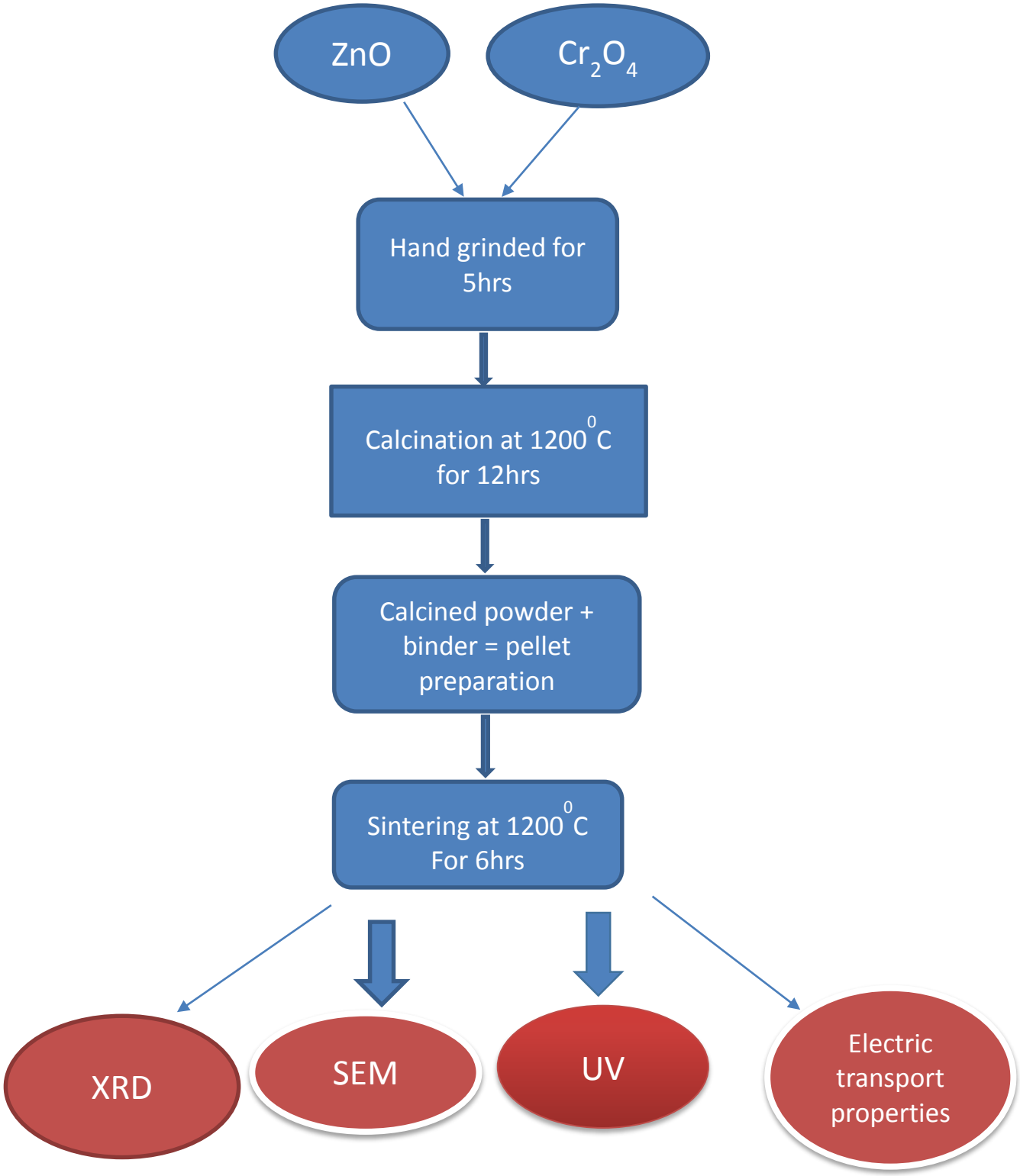
Pellet formation:-

The calcined powders supposed to be characterized by different techniques are required to take a proper shape according to the need. The (PVA) solution is used as a binder which is added to the calcined powders for a firm holding. The pellets are prepared by the help of the pelletizer by applying a pressure of 5 ton. After the formation of the pellets sintering is done.

Sintering:-

Sintering is a high temperature thermal treatment for densification of ceramic materials. The thermal energy promotes proper and control grain growth as well as to reduce porosity among them. The pellets are subjected to a temperature just below its melting point for calculated hrs. The present sample is sintered at1200^0c for 6 hours.

Flowchart for material synthesis



Characterization techniques

The characterization techniques include

- X-ray diffraction(XRD)
- Scanning electron microscope(SEM)
- UV-Visible spectroscopy
- Conduction mechanism by impedance analysis.

X-Ray diffraction (XRD):

X-rays are electromagnetic waves with extremely small wavelengths (usually order of 10^{-10} m). X-ray diffraction technique is used to analyze the crystal structure because the wavelength of x-ray radiation is very close to the inter planar spacing of most of the materials. The XRD technique is based on the principles of constructive interference.

Bragg's law of diffraction

Bragg's law describes the relation between the angle at which x-ray of particular wavelength diffracts and the wave length.

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

Where d- inter planar spacing

θ- Scattering angle

n- Represents the order of diffraction

λ – Wavelength of x radiation

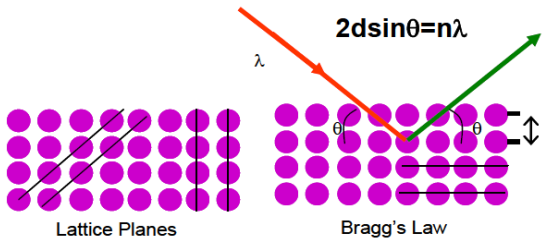


FIGURE 3. SCHEMATIC DIAGRAM OF BRAGGS DIFFRACTION

The phase composition of a material can be determined by the help of XRD

Scanning electron microscopy (SEM):

The scanning electron microscopy techniques requires a focused beam of electron to extract the structural information point by point.

The high spatial resolution of an SEM makes it a powerful technique to characterize a specimen of the order of nanometer to micrometer scale. The primary object of SEM is to study the surface or near surface structure of bulk specimen. The operating voltage of SEM ranges from 30-60 KV. One of the main features of the SEM is that, in principle, any radiation emitted from the specimen or any measurable change in the specimen can be used to provide the signal to modulate the c.r.t and thus provide the contrast

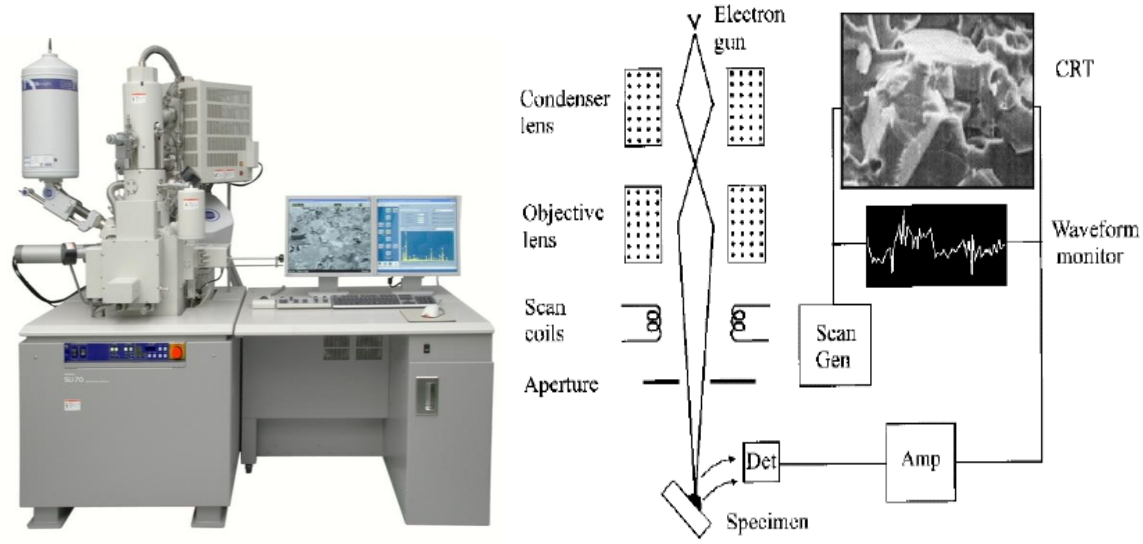


FIGURE 4 SCHEMATIC DIAGRAM OF SEM AND ITS WORKING STRUCTURE

Resolution of SEM image depends on three major parameters

- Nature of specimen
- Instrument performance
- Selection of imaging parameter

All the above three aspects operate concurrently and neither of them should be ignored or over emphasized

UV-Visible spectroscopy:

UV –visible spectroscopy analysis is primarily based upon the absorbance reflectance and transmittance spectroscopy in the UV visible spectral region. That means it uses the radiation in the UV-visible range which also affects the color of the material involved. Under this electromagnetic spectrum the molecules undergo electronic transition. This technique is complementary to fluorescence spectroscopy. The fluorescence spectroscopy involves the transition of electron from excited state to ground state, while absorption measures transitions from the ground state to the excited state. The UV-Visible spectrometer records the transmittance, absorbance and reflectance of the sample from the UV range to which human eye is not so sensitive to detect. In this work the UV visible spectroscopy has been used to measure the band gap of $ZnCr_2O_4$ by using knubelka-munk function.

Dielectric study:

A dielectric is an electrical insulator which can be polarized with the application of electric field. With the presence of an external field the electric charges are polarized which causes electric polarization. In a dielectric material when the field is applied polarization takes place due to shift of positive and negative charge centers from their equilibrium position. As a result it develops an internal electric field which reduces the external field. The study of dielectric properties is concerned with the storage and dissipation of electric and magnetic energy inside the material. The dielectric properties of a substance such as dielectric constant, dielectric loss, relaxation time, modulus, impedance etc. have provided an insight to the structure of the molecules of the system. Dielectric or electrical insulating materials are the materials in which electrostatic field can persist for a long time.

CHAPTER-4

Result and discussion

XRD analysis:

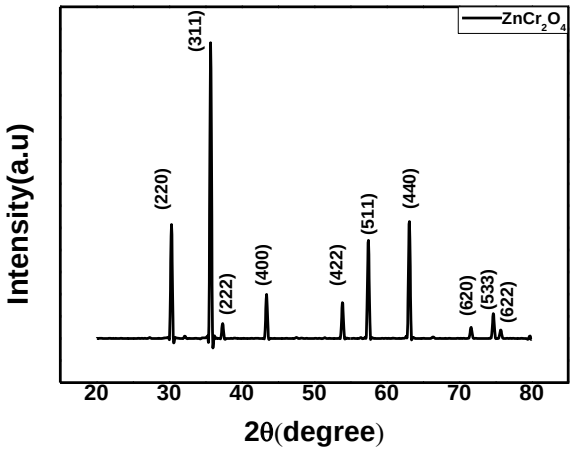


FIGURE 5.XRD pattern of the zinc chromite

Fig 5 shows the XRD pattern of the zinc chromite. These matches to JCPDS file no 22-1107 from which we confirm the formation of $ZnCr_2O_4$ at our set sintering temperature which sustains its spinel structure. With absolute no impurity peaks, the obtained pattern indicates the prepared material is of good quality with higher degree of crystallinity.

SEM analysis:

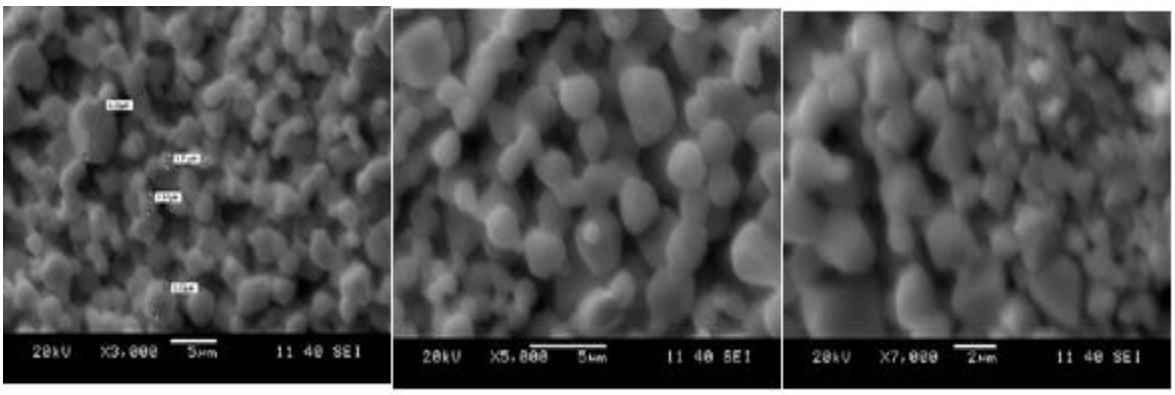


FIGURE 6. SEM images of the zinc chromite.

Figure (6) shows the sem image of our prepared sample ZnCr2O4. The grains are of mostly homogeneous nature found in the order of micrometer. The good crystallinity of grains also

matches with XRD results. the observed small pores indicates incompletion of densification process.

UV spectroscopy:

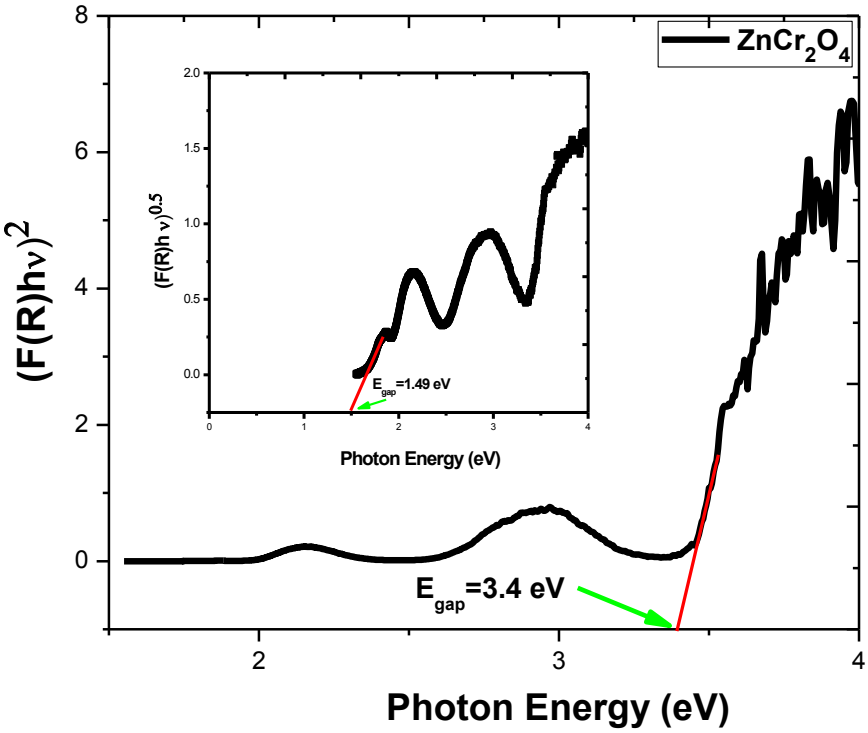


FIGURE 7. UV spectroscopy of $ZnCr_2O_4$

We have calculated both the direct and indirect band gap of Zinc chromite by analyzing UV visible spectroscopy. The direct and indirect band gap of zinc chromite is found to be 3.4eV and 1.49 eV.

DIELECTRIC STUDY:

The variation of the dielectric constant ($\mathcal{E}_r$) with temperature at different frequency for $ZnCr_2O_4$ system is shown in Fig. 1.

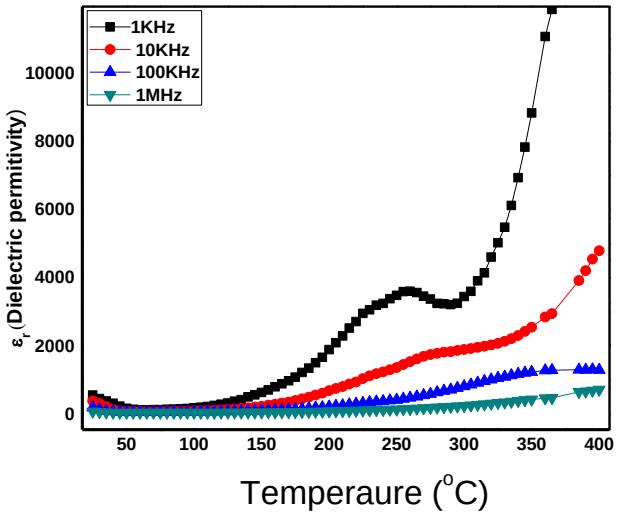


FIGURE 8. TEMPEARTURE DEPENDENCE OF DIELECTRIC CONSTANT

It is seen that the dielectric constant increases as the temperature increases. From room temperature to around 200^OC, ε_r values are constant and above 200^OC, the sample shows interesting change in the dielectric properties. At low frequency (1 KHz) ε_r value is maximum, with the increasing frequency the value of ε_r goes on decreasing and attains minimum value for frequency 1MHz. With the increase in temperature the electrons gain more and more thermal energy so they can easily follow the high frequency region. In solids the dielectric value depend on grain, grain boundary and the surface polarization effect.

The complex modulus study highlights the lowest capacitive region whereas it is able to suppress the high capacitive regions like electrode effect. So it is an effective tool to know the region of peaks and to analyze the effect for which the peak arises The variation of real parts of impedance (Z') with frequency at different temperature shows that Z' value is maximum at lower frequency and decreases as the frequency increases. At temperature 100^OC Z' value is maximum and at 400^OC Z' value is independent of frequency. At room temperature to 200^OC the Z'' value decreases as the frequency increases but from 225^Oc to 400^Oc the Z'' value increases initially and reaches maximum value (Z'') and then decreases as the frequency increases. The Z'' value

decrease with increase temperature and the peak position shift to higher frequency side. This indicates multiple relaxation in the material. This multiple relaxation may be due to the fluctuation in the structure .The Z value decreases with increasing temperature denoting the increase in capacitance value and decrease in resistance of the material means increase in conductivity.

CHAPTER-5

CONCLUSIONS

We have carried out the electric transport property study of spinel ZnCr2O4 insulating oxide by the help of complex impedance and modulus technique. The sample was synthesized by conventional method and crystallinity of phase was analyzed by xrd pattern. Surface morphology and porosity was observed from the scanning electron microscope image. Direct band gap (Eg=3.4eV) and indirect band gap (Eg=1.49eV) was found from UV spectroscopic analysis. Co contribution of grain and grain boundary effect is found at room temperature and continued some point below 200oC. Electrode surface polarization was found responsible for conduction mechanism in the sample at high temperature at and above 200oC. Grain effect is supposed to be dominant below the room temperature (RT). The conductivity behavior is found to obey Jonscher's universal power law.

REFERENCES

1) Cheng Peng and LianGao, (2008) 2388–2390
2) Nirpendra Singh and JooYullRhee, November 2010, pp. 1233-1237
3) S. Boumaza, A. Bougueliac, R. Bouaraba, M. Traric 34 (2009) 4963 – 4967
4) [4] Na Liu, Zhongshan Yuan, Shudong Wang, Chunxi Zhang, Shujuan Wang, Deyi Li 33 (2008) 1643 – 1651.
5) Dana Gingasu, IoanaMindru, LuminitaPatron, DanielaC.Culita, JoseMariaCalderon-Moreno, Lucian Diamandescu, MarcelFeder, OvidiuOprea
6) R. Nayak and S. Panigrahi, Effect of TiO2 on Electrical Properties of ZnCr2O4 Synthesized by Conventional Ceramic Route, M.Sc Thesis, 2011.
7) D.Fu, M.Endo, H.Taniguchi, T.Taniyama, and M.Itoh, Appl. Phys. Lett. 90, (2007) 252907.
8) I. Grinberg and A. M. Rappe, Appl. Phys. Lett. 85, (2004) 1760.
9) M. Valant, A. K. Axelsson, and N. Alford, J. Eur. Ceram. Soc. 27, (2007) 2549.
10) I. Levin, V. Krayzman, J. C. Woicik, J. Karapetrova, T. Proffen, M. G. Tucker, and I. M. Reaney, Phys. Rev. B 79, (2009) 104113 .
11) A. Kania, S. Miga, Mater. Sci. Engg. B 86 (2001).
12) P.Sciau, A.Kania, B.Dkhil, E.Suard, and A. Ratuszna, J.Phys.: Condens. Matter 16 (16), (2004) 2795.
13) http://shodhganga.inflibnet.ac.in
14) R.L.johnson-WIlke, D.S tinberg. Y hanetal, physicsl review B. 84,134114
15) Mohammad Yazdanbaksh, Iman Khosravi, Elaheh K.Goharshadi, journal of Hazardous materials, 184,(2010) 684-689.