INTERNATIONAL JOURNAL OF ADVANCE RESEARCH, IDEAS AND INNOVATIONS IN TECHNOLOGY

ISSN: 2454-132X
Impact factor: 6.078
(Volume 6, Issue 4)
Available online at: https://www.ijariit.com

Structural and dielectric properties of 'Ni' doped ($Bi_{(2-x)}Ni_xTi_3O_{12}$) polymer thin film

Jyotiprakash Panda
jyotiprakashpanda1997@gmail.com
Centurion University of Technology and Management, Bhubaneswar, Odisha

ABSTRACT

A detailed investigation of the poly-crystalline structure and electrical properties of $Bi_{(2-x)}Ni_xTi_3O_{12}$ ceramics prepared using high temperature solid state reaction technique . A polymer film was prepared by using the ceramic and PMMA polymer for better result, The phase formation of the compounds is studied via X-ray diffraction analysis which revealed that the compositions are of orthorhombic symmetry. The micro structural study was developed through the scanning electron microscopy, which showed a decrement in the grain size with Ni doping. 'Ni' was doped for fairly good conductor of heat and electricity also it enhanced the electrical properties of the composites , The dielectric study of the compounds showed a stabilized dielectric constant and dielectric loss at higher temperature. Dielectric constant found to increase with increase in temperature. Frequency dependent dielectric constant and loss at different temperatures give idea about polar dielectrics. Temperature dependence of DC and AC conductivity at various frequencies showed Negative Temperature Coefficient of Resistance (NTCR) behavior Dependence of AC conductivity on frequency at different temperatures obeyed Josher's universal power law. The temperature dependence of DC and AC conductivity was fitted to arhenius equation and activation energies at different temperatures ranges were calculated to know the conductivity species involved in the conduction process.

Keywords: *Dielectric, Lcrmeter, X-Rd, Sem*

1. INTRODUCTION

1.1 Electroceramics

A single phase crystal ceramic which was Aurivillus types belongs to B.L.S.F structure with general formula $Bi_{(2-x)}Ni_xTi_3O_{12}$. The 'Ni' doped Bismuth titranate (BT) ceramic was prepared by using solid state reaction technique. but the ceramics based polymer thin film was carried out by sol-gel process for characterization. Now a days Some research state's that lead-free ferroelectric materials were widely used for many application like high sensitive sensors and memory devices due to their good di-electric property. The B.L.S.F types ferroelectric materials operates in low voltage. Recently various types of materials like BBT, BST, BNT have been take attention for their electrical conductivity properties. And these types of materials were lead-free and eco-friendly.

1.2 Crystallography

So we make the crystallographic consideration of the Ni doped BT ceramics . it was study to know about structure of atoms , ions or molecules present in an materials. On a 3-D lattice it was arranged in an particular manner . In a aurivillius based compound the BLSF structure are found. This is a type of ferroelectric structure where the materials are well packed by a bismuth oxide layer that is (Bi_2O_2). It have not holds good for piezo electric and pyro electric compound. It holds good only for ferroelectric materials. The O-R group heve the perpendicular to the axis of materials.

In Bismuth titranate ceramics there are only two main element was used. Bismuth oxide and titanium oxide. But it have some limitations .it does not showing any electrical and optical property. We know Ni was a transition element which was electrical conductor and temperature dependent. Show nickel oxide was used as doping element to enhance the dielectric property of the BT ceramics. Polymer shows relaxor behavior which required for censing device. Polymer synthesis was now a very good synthesis process which show very good result. polymer thin film was used for characterization .the x-rd was study by x-ray diffract meter. Morphology was studied by electron emitting process by using scanning electron microscope. by using LCR meter we find ph, conductivity, loss, and dielectric constant. This types of ceramics show spontaneous polarization. Its help for doing mobile sensor and many more electronics component which are eco friendly and useful. It is also temperature dependent material which show very good dielectric property in room temperature.[10] So it is all about electro-ceramics which were used in many memory storing device.

1.3 Crystalline Structures of material ceramics

So we make the crystallographic consideration of the Ni doped BT ceramics . it was study to know about structure of atoms, ions or molecules present in an materials. On a 3-D lattice it was arranged in an particular manner .so here we go the types of crystal structure need to study here:[11]

1.3.1 Perovskite type material: Perovskite material in the composition of ABX_3 . Where A is a cation , B is a cation . and X is anion that bonds to a cubic like structure .

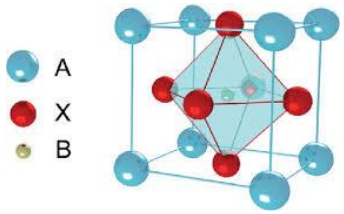
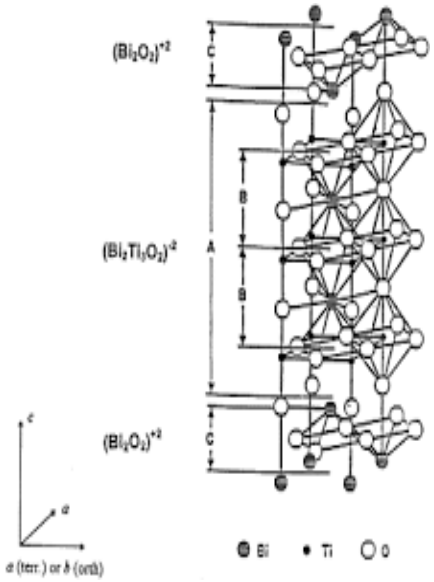


Fig. 1: Calcium titanium oxide ($CaTiO_3$)

1.3.2 BLSF (Bismuth Layer Structure Ferroelectric): In a aurivillius based compound the BLSF structure are found. This is a type of ferroelectric structure where the materials are well packed by a bismuth oxide layer that is (Bi_2O_2). It have not holds good for piezo electric and pyro electric compound .it holds gud only for ferroelectric materials. The O-R group heve the perpendicular to the axis of materials.[12] Shown in fig



The BLSF structure was given that the O-R group is perpendicular to the Bi_2O_3 structure.

1.4 Introduction to the Ni doped BT ceramics

We know from several study that a ceramics made by mixing different types of material in stoichiometric amount. Which later form a good material ceramics which go many more characterization to confirm the performance of the ceramic.[13] Here in my research work i am taking Bi_2O_3 (bismuth oxide) , NiO (nickel oxide) , TiO_2 (titanium oxide) with stoichiometric amount mixed together to form $Bi_2Ni_2Ti_3O1_2$ ceramics which was called the mother element. So for the introduction of the material ceramic is starting with bismuth oxide which was 99.9% pure form and yellow in colour .and nickel oxide also 99.9% and black in colour. The titanium oxide is pure and white in colour .so these three elements mix together to form the mother element which later go for experiment.[14] We find a Ni doped ceramics which was a very good conductor of electricity and give good results as usual. For a better properties we take a ferro electric transition element.

1.5 Uses of polymer

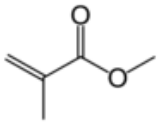
Polymer consists of many monomers combining together to form. So many macro molecules mixed together to form a polymer. So for chemical method there are 2 method;

1. co-precipitation method
2. sol-gel method

In my work i used sol-gel method for better synthesis and characterization[15]. In sol-gel method we used polymer to get polymer thin film. Polymers are basically 3 types given below :

1. poly-ethylene
2. poly- propylene
3. poly –vinyl

PMMA(Poly Methyl Metha Cryalate) polymer were widely used in polymer synthesis process which have molecular formula-C5O2H8 and melting point-160 degree.[16] Now a days the uses of polymer were widely used for characterization process because its gives better result .



Structure formula of pmma polymer. It is also known as acrylic glass.

1.6 Literature review

In 1600 century the materials ceramics were widely used for some industrial work . many more materials were invented and characterized by many scientists. Introduction to many materials are used for dielectric properties of the material ceramics which undergo later gives some usefulness of matter. [17] In 1700 century the bulk ceramics are used for characterization where there are some mistakes for some years. By passing the years to years the methods are developing.[18] There are many paper regarding material science but a few which i read to know about a current work . i have the topic where the ceramics is BT show i read some current work about BBT, BZT to know how the ceramic sample made and than characterized by several methods like X-rd ,SEM , FTIR , UV, RAMAN, Dielectric study by LCR meter etc.[19]

In 1756 the 1 st ceramics was developed by foreign scientists. but in that time there was no development for using the ceramics after so many years and so many discovery various types of ceramics were used in various platform. so it was found very good in material physics world.[20] Some past of year we discovered the crystalline structure of the material like perovskite and BLSF . now we study about double pervoskite structure. The BT ceramics always show BLSF. In 1949 there are discovery of many more materials which converted into good dielectric material. Dielectric material was invented for showing its special properties of conduction electricity.[21] first the power form of the ceramic was going into characterization to give its internal property of the material. now many chemical methods are used for preparing any other form of ceramics which may give good properties. so now also in chemistry there was many research about ceramic fluid. In detailed investigation we found many article about the electro ceramics synthesis and characterization. So polymer was first invented by multiplexing monomers in the year1967. Then polymer was used in many polythene company foe its relaxor behaviour. most widely used polymer are poly-vinyl. PMMA polymer was a sugar like structure used in many synthesis process.[22]

1.7 Thesis objectives

1.7.1 Why Ni was used as doping element?

In Bismuth titranate ceramics there are only two main element was used. Bismuth oxide and titanium oxide. But it have some limitations .it does not showing any electrical and optical property. We know Ni was a transition element which was electrical conductor and temperature dependent. Show nickel oxide was used as doping element to enhance the dielectric property of the BT ceramics[23]

1.7.2 Why polymer synthesis was done?

Polymer shows relaxor behaviour which required for censing device. Polymer synthesis was now a very good synthesis process which show very good result. polymer thin film was used foe characterization. Here we do some process:

1. The xrd was study by x-ray diffract meter.
2. SEM was studied by electron emitting process by useing microscope.
3. By using LCR meter we find ph, cond, loss, and dielectric constant
4. The compound show relaxing and good dielectric properties.[24]

2. SAMPLE PREPARATION

2.1 Introduction

We know the ceramics are found in the form of power so its required preparation of a mother element . so we have to required to know the molar mass of every ceramics. By equilibrium the chemical equation then we take the mother element for 15 gm . so by the problem of stoichiometric amount . it need to be calculate carefully because if there was any significant error then the ceramics was giving some different result or not showing any properties.[25] In my research work for preparing $Bi_2Ni_2Ti_3O_{12}$ ceramics i used 3 material power named as :

1. Bi_2O_3 (Bismuth oxide) taken 8.3 gm
2. TiO_2 (Titanium oxide) taken 4.5 gm
3. NiO (Nickel oxide) taken 2.2 gm

So these 3 power form of ceramics mix together to form 15 gm Ni doped BT ceramics which was going for synthesis and characterization. for preparing the ceramics we should taken the element properly. It is the 1 st process where a ceramics or a sample was preparation for experiment. [26] By taking the sample we need to synthesize them by many process :

2.1.1 General Method of Preparing Ceramics Samples:

- **Mechanical Methods**

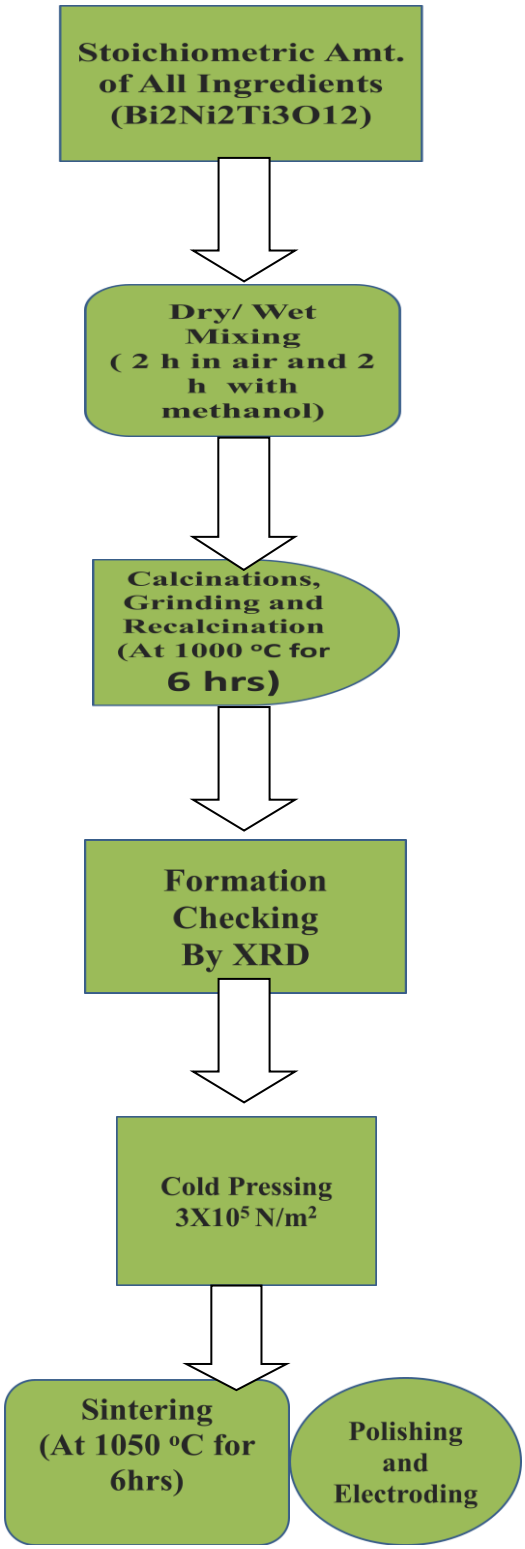
1) Mixed Oxide Process (MOP) or solid-state reaction process
2) High Energy Ball Milling

- **Chemical Methods**

1) 1Co-precipitation method
2) 2Sol-gel process

In my project I used mixed oxide method for formation of ceramics and used sol-gel process for polymer thin film which were later characterized:

2.2 Solid state reaction technique



So these are the process of solid state reaction technique described below. So 1st we taken stoichiometric amount of all ingredients to make a ceramics then by grinding dry for 2 hours and by methanol 2 hours .then the forming ceramics go to calcinations in the furnace for 6 hours. then the calcined ceramic was going for x-rd to check the formation if not then regulate the process again.[27]

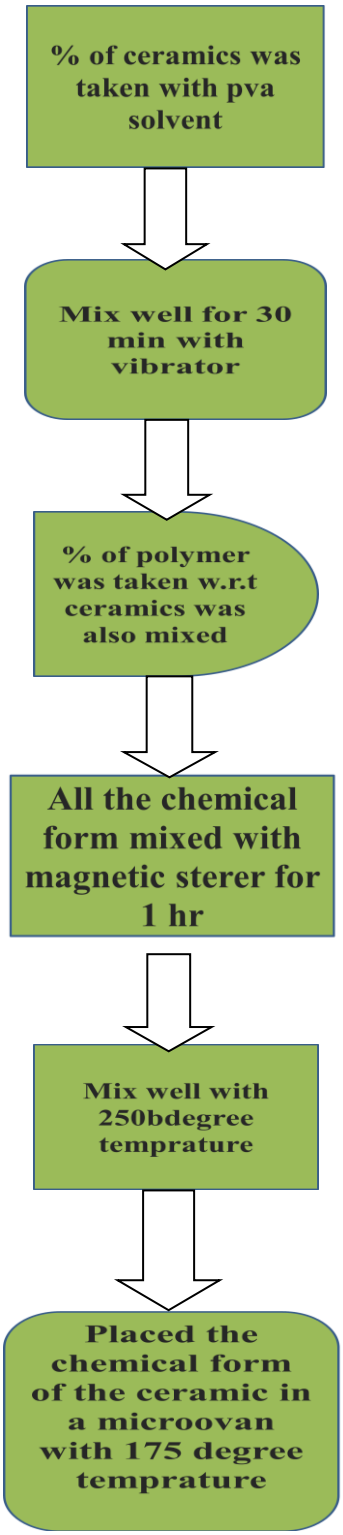
2.2.1 Calcinations: So it is the process to give heat to solid in a high temperature and removing the volatile substance. It is a purification process. Here the temperature is high then the solid are in pure powder form. It is necessary for every ceramic preparation. When used this process always do precautions because it is danger. if the formation was not done then recalcined it immediately .[28]

2.2.2 Sintering: It is the process to giving heat to a solid without any disturbance. The process was done for checking the surface morphology of the ceramics we used. This is a very useful process to give the study of structure.[29]

2.2.3 Electroding: The sintered pellet was coated with electrical materials such as silver , gold graphite , platinum etc. In order to stydy the electrical conduction process we need to do it properly.

2.2.4 Preparation of the compound: The crystalline sample of $Bi_2Ni_2Ti_3O_{12}$ was prepared using solid state reaction technique using high purity ingredients Bi_2O_3 (99.9%) , TiO_2 (99.9%) , NiO (99.9%) were weighted as per the composition . these compounds are taken by solving the problem for 15 gm . the bismuth oxide (Bi_2O_3) taken 8.3 gm and Nickel oxide (NiO) taken 2.2 gm , titanium oxide (TiO_2) was taken 4.5 gm . the 3 compound mix together to form 15 gm of Ni doped BT ceramics which was go for synthesis and characterization.[30] By dry and wet mixing the ceramic was formed and by calcinations the homogeneous form of the ceramics was taken out then the ceramics undergo polymeric react ion technique which was done by sol-gel method .and the thin film was prepared by using polymer synthesis methods.

2.2.5 Preparation of polymer based NBT thin films



The bulk ceramic was taken with some % like 3 ,4 ,5 and it mixed with an appropriate PVA solvent solution then it dispersed with a electronic vibrator for 1 hr also PMMA polymer was taken w. r .t the ceramic % and mixed with magnetic steer with some temperature and added the dispersed ceramic PVA solution and the process was taken for 1 hr . them a chemical solution of polymer based NBT ceramics was prepared for thin film the solution was placed in a micro-ovan for 2 hr with 175 degree temperature. After that the polymer thin film was slowly removed . the thin film was taken for characterization like X-rd , SEM , Dielectric study by LCR meter , etc. [31]

2.3 Experimental techniques

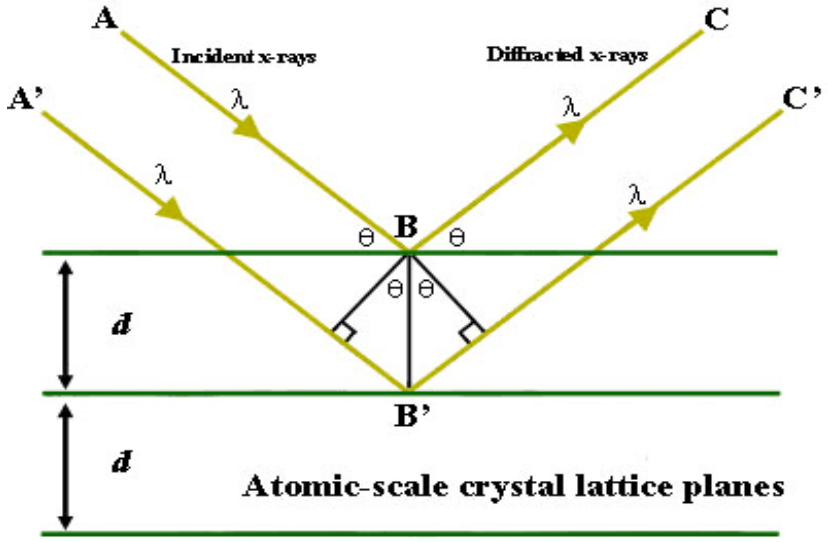
2.3.1 X –ray diffraction: x-ray diffraction is a elastic scattering . in a crystallography experimental sc it determine the molecular structure of the lattice which was undergo to give some properties. In this technique photons are emitted by using x-ray . when the ray was emitted to the ceramic surface then it emits photon and some temperature. By using Bragg's law the lattice placing and parameter was found:

Bragg's law states that when X-ray are scattered from the crystal lattice there would be some peaks which were measured with the intensity w.r .t the scattered angle (2 theta);[32]

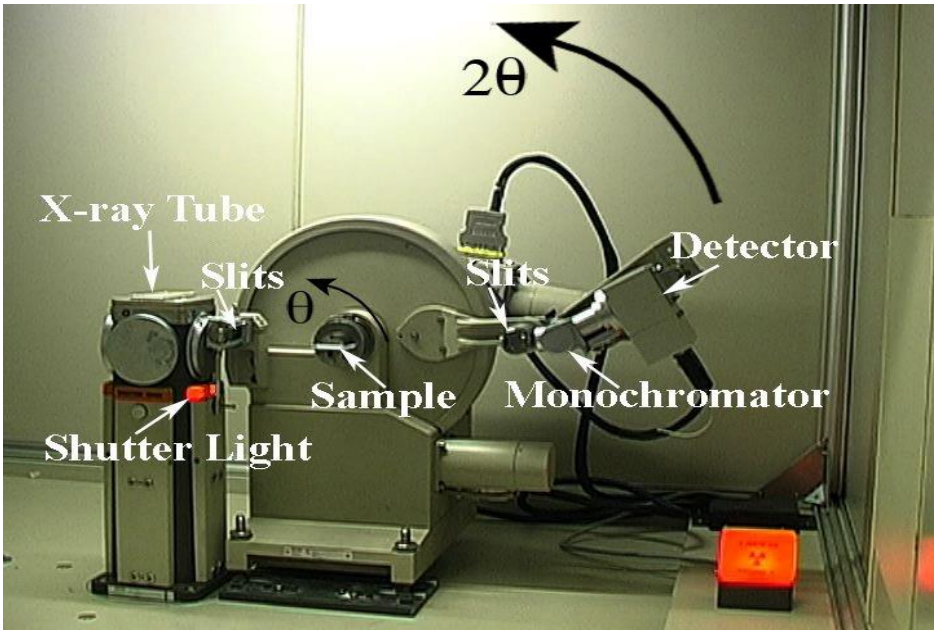
2dsin theta=n lambda

Where d is spacing, n is integer , and lambda is wavelength.

So when the incident rays are coming from X – ray it emerges some angle when it puts it in lattice crystal. We do X-rd for checking the formation of the compound with room temperature the material which show good properties and formation was widely used in many industry and sensing devices. It was a quite good process for check the ceramics peak. [33]The graph was plotted between angle (2 theta) and intensity of the ceramics. and the whole process was taken with a diagram given below :



So the x-rd techniques was performed inX-ray Diffract meter which was shown below:



2.3.2 Scanning Electron Microscopy (SEM): Scanning electron microscope is the types of microscope which produces image of the sample by scanning with a focused beam of electron to the surface. The electrons interact with the atoms produces different types of signal that contain information about the internal morphology of the composites.[34] The electronic beam was scanned with some pattern and combined with the intensity of signal to produce a image . in some SEM mode there are exhibits a secondary signal that can also be detected . the results or the image formation was depends on signal intensity , and the prepare sample. So the instruments and the process was given below:

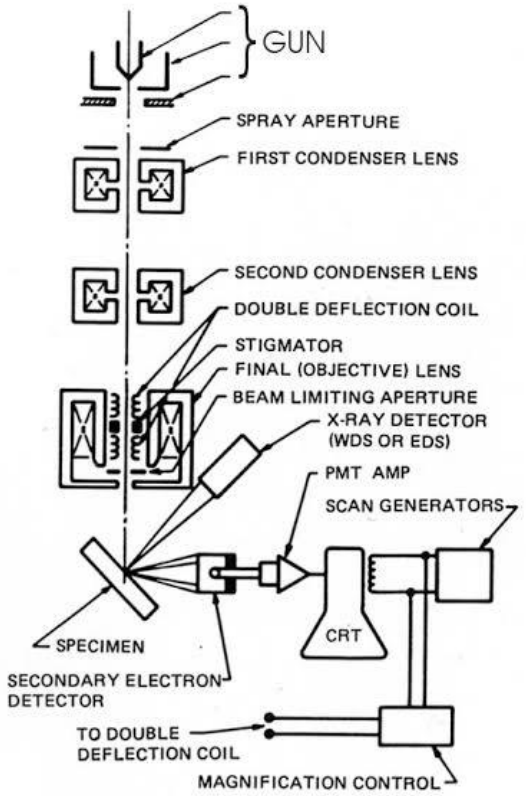


Figure 1.11. Schematic drawing of the electron and x-ray optics of a combined SEM–EPMA.

It was the SEM process or schematic diagram given . so the scanning electron mix together to form a image in which the ceramic surface was studied. It can be the resolution better than 1 nanometre. in a SEM an electron beam is emitted from a gun fitted with cathode which was a filament of tungsten. The electronic beam has an range of 0.3 to 35 Kev. [35]

2.3.3 Dielectric by LCR meter: LCR meter is used to measure inductance(L), resistance(R), capacitance(C), of a material. So by measuring its dielectric properties we know how the ceramics work in electrical instrument. Here we find dielectric constant, loss , impedance , and conductivity of the material. So dielectric constant was defined as the ratio between capacitance of material and capacitance of air in a medium .[36]

$$\text{Dielectric constant} = E_m/E_0$$

by measuring the permittivity of the material with various frequency we should find out the dielectric constant of a medium. Also we find the impedance with varying Z.

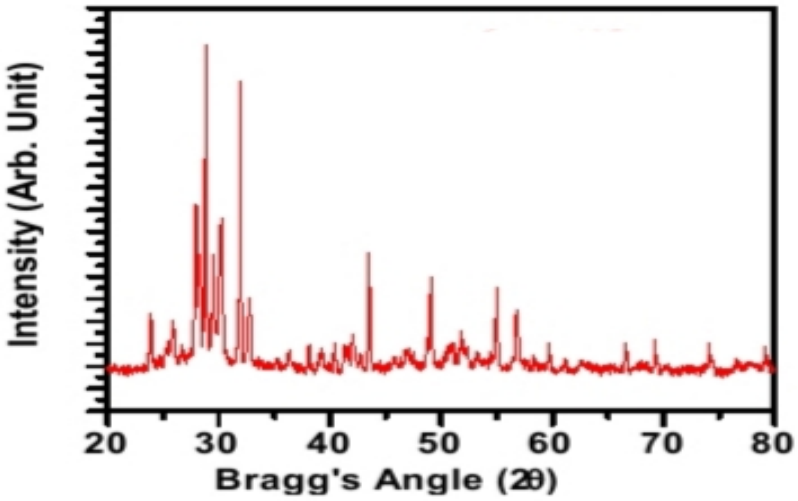
Dielectric of the ceramics was measured by various graphs which show changing of frequency with the respectable data. So a typical LCR meter was given below by the diagram: [37]

The process was studies by coating electronic device materials. The PH value , Cp , Cv , loss was found in computer with varying frequency. so the process was used as very good and its used in many electrical conductivity checking process. The dielectric property was measured by using the LCR meter which was later showing by the graph analysis. [38]

3 RESULT AND DISCUSSION

3.1 X-ray diffraction

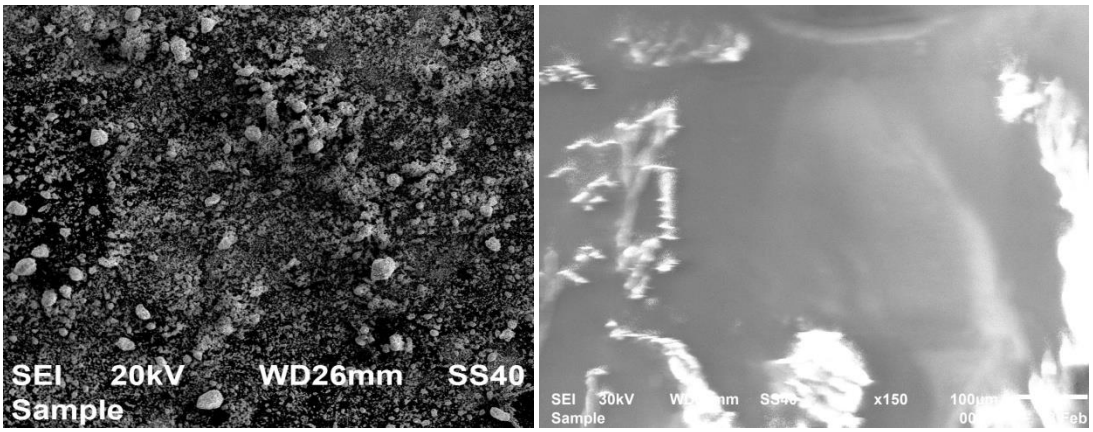
3.1.1 Result: The X-ray diffraction patterns of $Bi_2Ni_2Ti_3O_{12}$ ceramic is presented in Fig. 1. It is also observed fron X-rd (200)/(020) peaks are shifting towards higher angles and (200)/(200) peaks gets smaller with Ni content. [39] The lattice parameters were calculated by POWD SOFTWARE. The lattice parameter increases with Ni content, The decrement in the lattice parameters is due to The compositional confirmation was carried out by using Energy dispersive X-ray analyser (EDX). So the Ni doped Bt ceramics which was calcined in 1000 degree temperature given below . the graph show the X-RD of a polymer thin fil which was sintered at 1000 degree. The peaks was found at a room temperature nearly 30 degree . the ceramic was work as a very good temperature dependent and showing good results. The X-rd graph was doing very smooth in origin . the Ni doped BT ceramics obtained a crystalline lattice of tetragonal shape.[40] The graphical representation is:



3.1.2 Discussion: The X-ray diffraction patterns of $Bi_2Ni_2Ti_3O_{12}$ ceramic is present in fig -1 . it was confirm at a room temperature of 30 degree . *XRD pattern show the tetragonal crystal system and lattice parameter of the selected unit cell was refined using the least-square sub-routine of standard computer program package 'POWD'.* The lattice show it was a pervoskite types material.[41]the X rd shows decrement with increasing in intencity, so for finding the crystal structure of the material we have to study the x-rd analysis.

3.2 SEM

3.2.1 Result



3.2.2 Discussion: This figure shows the Surface morphology of the $Bi_2Ni_2Ti_3O_{12}$ ceramics. From figure it is observed that all the samples are composed of packing well and show good SEM. The size of the ceramics was very good. So the polymer thin film and also bulk ceramics show significant image. By use of scanning electron microscope we get the image of 1-2 Nm. The surface of the material was well packed by the ceramics. The grain size slightly increases in. polymer thin film.[42]we use the silver coating polymer thin film for a better SEM. The SEM indicates the micro molecules are significantly low. the scanning of electron in the surface was small and well distributed through the polymer thin film.

3.3 Dielectric study

3.3.1 GRAPHS: The graphs shows the Relative permittivity, dielectric loss, Impedance, Dielectric constant of the Ni doped BT ceramics. By measuring the capacitance, inductance, resistance of a ceramics using LCR meter it found to be good dielectric materials. Ni gives a new electrical properties to the BT ceramics shown in the several graphs. Impedance was studied for the electrical behaviour of the material which was shown good. We plot the graph with varying the frequency with all the parameter.[43]

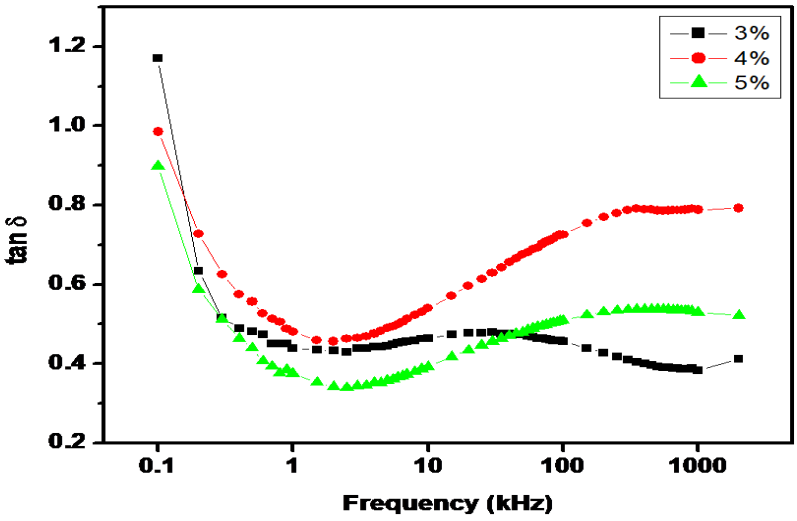


Fig. 2:

Dielectric constant

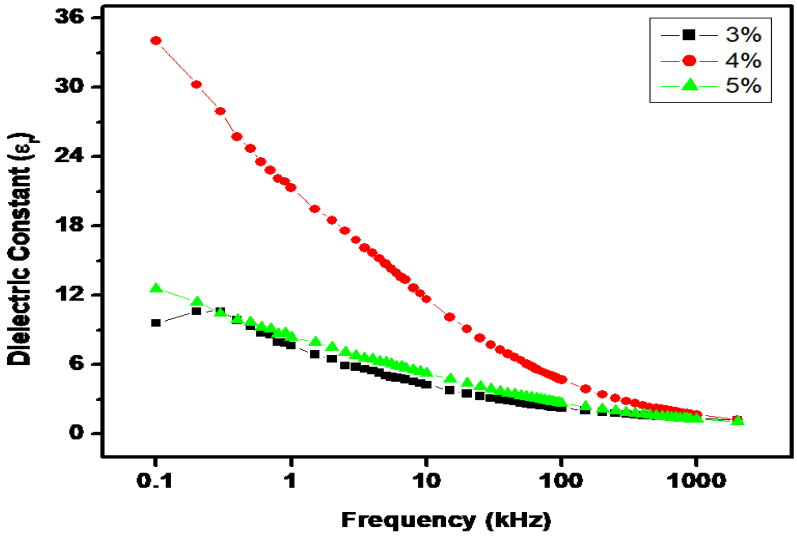


Fig. 3:

Conductivity

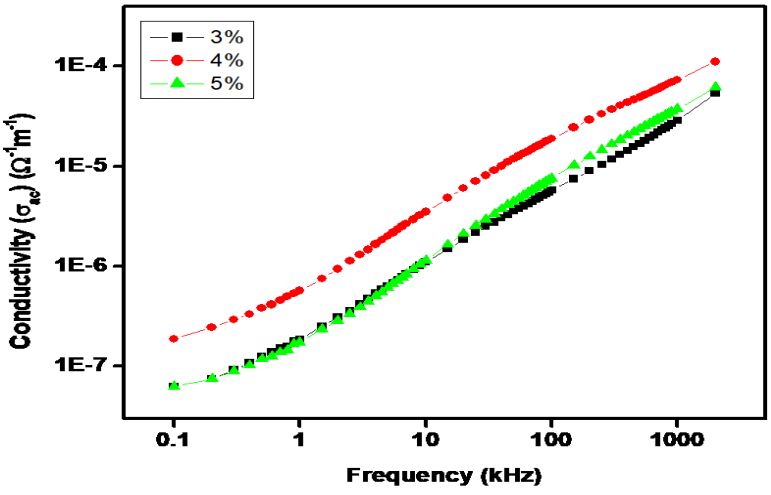


Fig. 4:

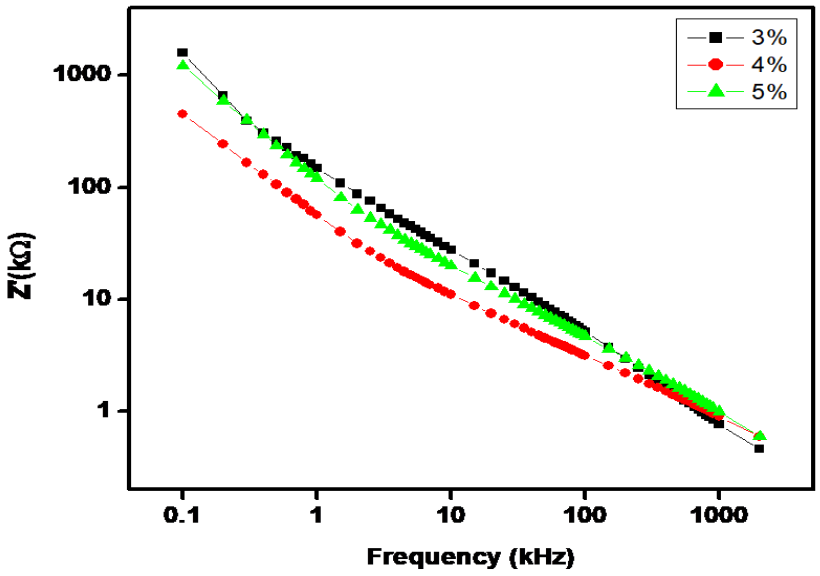


Fig. 5:

Impedance

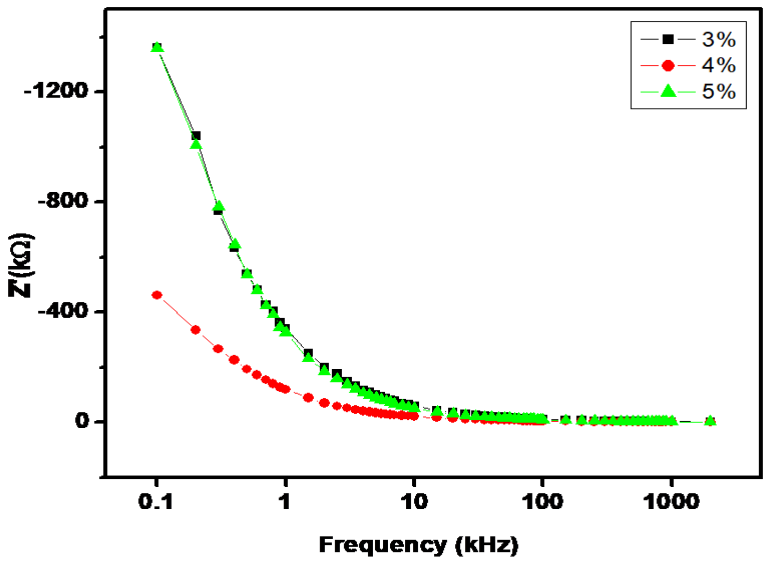


Fig. 6:

Modulus

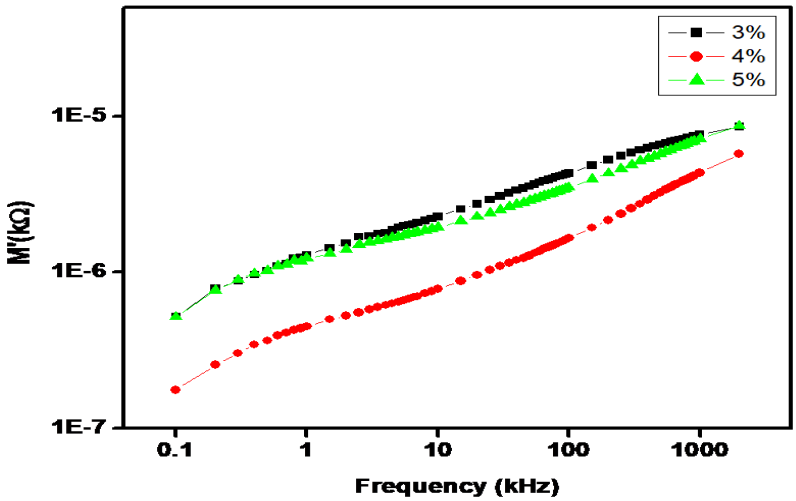


Fig. 7:

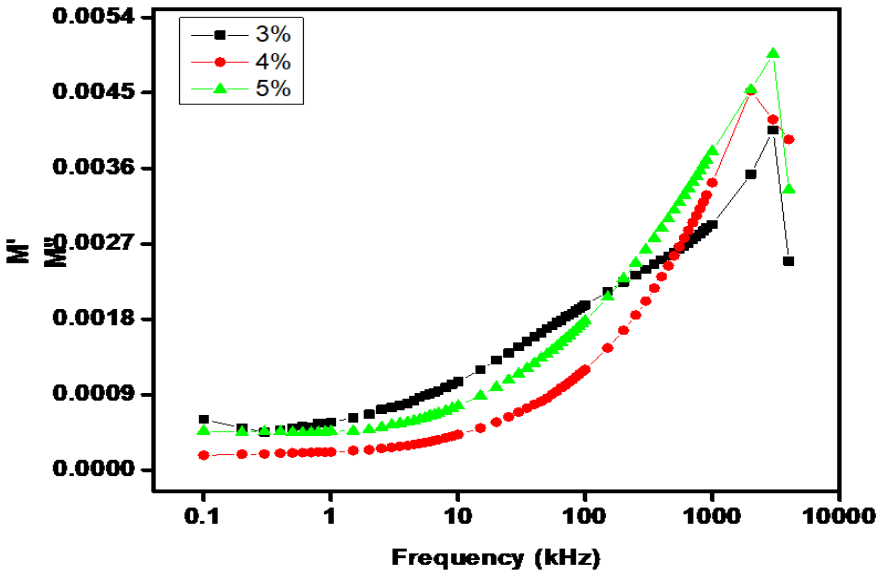


Fig. 8:

Complex impedance

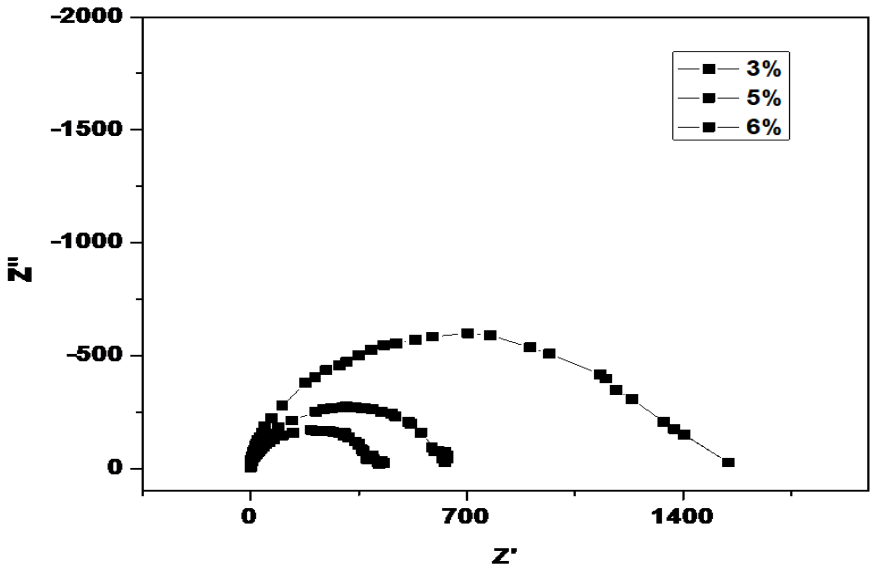


Fig. 9:

3.4 Discussion

So the dielectric of the ceramic was studied by the study of dielectric constant, dielectric loss, permittivity , impedance etc shown in the above figure.

- Figure-2 shows relative permittivity of the ceramics. Which gives when the frequency or temperature of a ceramics rise then its permeability decreases . in the above graphs the permeability decreases on the frequency of 1khz .
- Figure-3 shows the dielectric constant of the ceramics with respect to frequency, it decreases with increase of frequency. Thus Ni doped BT ceramic shows good dielectric behaviour.
- Figure-4 indicates the electrical conductivity with respect to frequency, when the frequency rises the electrical conductivity of the material ceramics increases .so the ceramics was used for many electrical conduction material.[44]
- Figure-5 represents impedance of the ceramics. the graphs drawn in between frequency and Z. Thus impedance of the ceramics decreases with increase in frequency. so it indicates the Ac conductivity of the material. Where Fiure-6 indicates dc conductivity of the ceramics was slowly decrease and constant at a point where the frequency was rises.
- Figure-7,8 represents susceptibility of the materials which shows increasing with increasing in frequency. when the M of the ceramics increase then the certain rise in frequency the susceptibility or the mobility of the ceramics decreases.
- Figure-9 shows impedance loss or dielectric loss which is minimum in Ni doped BT ceramics so it was a good dielectric composites compare to others. [45]

3.5 Result

- It is observed that relative permittivity decrease with rise in frequency, which is a general feature of polar dielectric materials. Which show relaxer behavior.

- Frequency range drops significantly with a rise in frequency. In the high frequency spectrum, the value of Z' is bigger and obtains with an increase in frequency. It may be due to the charge distribution.
- The ac conductivity (σ_{ac}) of the material was increase with rise in frequency.
- The Modulus' value is 0.1 (nearly) at low frequency and increase with rise in frequency, due to the long-range mobility of charge carriers. [46]
- The dielectric materials posses' good dielectric and conductivity with rise in frequency.

4. CONCLUSION

Single phase layered perovskite BT ceramic was prepared by solid state reaction route and sol-gel methods.. Structural properties of the compositions were investigated by using X-ray diffraction. The surface morphology was well packed in polymer based thin film. The impedance was studied that the Z value decreases with increase in frequency. The dielectric constant was constant in increase of frequency and the loss is minimal. so the Ni doped ceramics was found to be good dielectric and less loss which was used for many electrical based sensors. At room temperature tetragonal crystal system was confirmed. Dielectric constant increases with increase in frequency. The higher value of dielectric constant at low frequency is due the presence of different type of polarization in the composite. Ac Conductivity increases with increase in frequency. [47]

5. REFERENCES

[1] Nava Setter, J.Eur.Cer.Soc., 21, 1279-1293 (2001).
[2] N. SETTER and R. WASER, J.Act.Mater., 48, 151-178 (2000).
[3] MaltiGoel, J.Cer.International., 30, 1147-1154 (2004).
[4] B.Jaffe, W.R Cook, and H.Jaffe, "Piezoelectric ceramics", John Wiley and Sons, New York, USA (1960).
[5] J.C.Burfoot and G.W.Taylor, "Polar dielectrics and their applications" University of California Press, Los Angeles, CA (1979).
[6] J.Valasek, J.Phys.Rev., 15, 537 (1920).
[7] G.Busch and P.Scherrer, Naturwissenschaften., 23, 737 (1935).
[8] B.M.Wul, I.M.Goldman, Dokl.Akad.Nauk SSSR, 46, 154 (1945).
[9] A.J.Moulson and J.M. Herbet, Electroceramics: Materials, Properties, applications" Chapman and hall, New York, USA (1997).
[10] W.G.Cady, Piezoelectricity, Dover Publications, New York (1962).
[11] M.Deri, Ferroelectric ceramics, Gordon and Breach, New York (1969).
[12] M.E.Lines and A.M Glass, Principles and applications of ferroelectric and related materials, Clarendon Press, Oxford (1977).
[13] T.Mitsiu, I.Tatsuzaki and E.Nakamura "An introduction to the physics of ferroelectrics", Gorden and Breach Science Publishers, Ltd., London (1976).
[14] D.Damjanovic, "Ferroelectric, dielectric and piezoelectric properties of ferroelectric thin films and ceramics", J. Rep.Prog.Phy., 61, 1267-1324 (1998).
[15] Jaffe B, Jaffe H, Cook WR, Piezoelectric ceramics, 1st edn. Academic Press, London (1971).
[16] HaertlingGH,Buchanan RC, Piezoelectric and electro-optic ceramics in ceramic materials for electronics, 2nd edn. Marcel Dekkar, Newyork (1991).
[17] Uchino K, mater.Res.Bull, 18, 42 (1993).
[18] Newnhan RE, Functional composites for sensors and actuators, Pennsylvania Academy of Science,PA, USA (1998).
[19] Sahoo B, Jaleel VA, Panda PK, J.MatSci and Engg B., 126, 80 (2006).
[20] Sahoo B, Panda PK, J.Mat Sci., 42, 4270 (2007).
[21] Yugong W, Zhang H, Zhang Y, Jinyi M, Daohua X, J.Mat Sci., 38, 987 (2003).
[22] Ringgaard E, Wuritzer T, J.Eur. Cer.Soc., 25, 2701 (2005).
[23] Takenaka T, Nagata H, J.Eur. Cer.Soc., 25, 2693 (2005).
[24] Yi L, Moon K, Wong CP, J. Science., 308, 1419 (2005).
[25] Shimamura K, Takeda H, Kohno T, Fakuda T, J. Cryt. Growth., 163, 388 (1996).
[26] G.Goodman, J.Ame.Cer.Soc., 36, 368 (1958).
[27] M.H.Francombe and B.Lewis, J.Acta.Cryst., 11, 696 (1958).
[28] Somolenskii G.A, Isupov V.A and Agranovskaya, Soviet.Phy.Solid.State., 3, 651 (1959).
[29] Somolenskii G.A, Isupov V.A and Agranovskaya, J.Soviet.Phy.Solid.State., 3, 149 (1961).
[30] Subbarao E.C, J.Chem.Phy., 34, 695 (1961).
[31] Subbarao E.C, J.Ame.Cer.Soc., 45, 166 (1962).
[32] Ikegami S and Ueda E., Jap.J.Appl.Phy., 13, 1572 (1974).
[33] Tadashi Takenka and koichiro Sakata, Jpn.J.Appl.Phy., 19, 31-39 (1980).
[34] Kaoru Miura and Masahiro Tanaka, Jpn.J.Appl.Phy., 37, 2554-2558, (1998).
[35] In-Sook Yi, and Masaru Miyayama, Jpn.J.Appl.Phy., 36, 1321-1324 (1997).
[36] Scott J.F and Paz de Araujo C.A., Science., 246, 1400 (1989).
[37] Paz de Araujo C.A, Cuchiaro J.D, McMillan L.D, Scott M.C et.al, Nature (London) 374, 627 (1995).
[38] Desu S.B and Vijay D.P., J.Mat.Scie and Engg.B., 99, 75 (1995).
[39] Sang-OukRyu, PhD thesis,Virginia University, (1999).
[40] Newnham R.E, Wolfe R.W and Dorrian J.F, J.Mat.Res.Bull., 6, 1029 (1971).
[41] Jae-Sun Kim, Cheol-Hoon Yang, Soon-Gil Yoon, et.al.,J.Appl.Surf.Sci., 140, 150-155 (1999).
[42] Yuji Noguchi, Ichiro Miwa, Yu Goshima and Masaru Miyayama, Jpn.J.Appl.Phy., 39, 1259-1262 (2000).
[43] Hiroshi Irie and Masaru Miyayama, J.Appl.Letts., 79, 251-253 (2001).
[44] Kazumi Kato, Kazuyuki Suzuki, Desheng Fu et.al.,Jpn.J.Appl.Phy., 41, 2110, 2114 (2002).

[45] Masaru Yokosuka., Jon.J.Appl.Phy., 41, 7123-7126 (2002).
[46] Minglei Zhao, Chunlei Wang, WeilieZhong, et.al.,Jpn.J.Appl.Phy., 41, 1455, 1458 (2002).
[47] Harihar B, Venkataramana and Varma K.B.R., J.Phys&Chem of Solids., 64, 2105-2115 (2003).

