

Structural, dielectric and optical studies of magnetoelectric $\text{Bi}_2\text{Fe}_4\text{O}_9$

**Under the Guidance of
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CERTIFICATE

This is to certify that the work in the report entitled “*Structural, dielectric, and optical studies of magnetoelectric $\text{Bi}_2\text{Fe}_4\text{O}_9$* ” by *Miss Sangeeta Kumari Ghatuary*, in partial fulfillment of Master of Science degree in PHYSICS at the National Institute of Technology, Rourkela, is an authentic work carried out by her under my supervision and guidance. The work is satisfactory to the best of my knowledge.

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Date:

Ms. Sangeeta Kumari Ghatuary

ABSTRACT

Multiferroic means the co-existence of two or more ferroic order property, such as ferroelectricity, ferromagnetism and/or ferroelasticity. Most of the multiferroic materials have very low transition temperature but $\text{Bi}_2\text{Fe}_4\text{O}_9$ have transition temperature which is near to the room temperature. $\text{Bi}_2\text{Fe}_4\text{O}_9$ is a type II multiferroic, so it has very strong magnetoelectric coupling. $\text{Bi}_2\text{Fe}_4\text{O}_9$ has a pentagonal symmetric structure. $\text{Bi}_2\text{Fe}_4\text{O}_9$ was sintered at 850°C for 12 hours. Then characterizations were done to study different structural, dielectric and optical properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$.

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1. INTRODUCTION

1.1 Magnetism and its classification

The origin of magnetism lies on orbital and spin motion of electrons. To introduce different types of magnetism is to describe how materials respond in external applied magnetic field. There are following major groups of magnetism:-

(a) Diamagnetism

Diamagnetism is a very small and weak effect in many materials caused by the reaction of the orbiting electrons to an applied magnetic field in accordance with Lenz's law. Hence magnetization and susceptibility both are negative. Diamagnetic substance reduces the density of lines of forces when placed in a magnetic field.

Examples of diamagnetic substances are antimony, bismuth, and mercury, gold and copper.

(b) Paramagnetism:

Paramagnetism is due to the orientations of permanent magnetic dipoles due to the presence of all external magnetic fields. It is associated with the outermost electrons, which are less tightly bound to the atoms. In paramagnetic materials, susceptibility is small and positive. Susceptibility varies inversely with the temperature according to Curie law

$$\chi = C/T$$

Where C is called as Curie constant.

Examples: manganese, platinum, tungsten.

(c) Ferromagnetism:

Ferromagnetic materials exhibit magnetic properties even in the absence magnetic field. Magnetization is increased when an external magnetic field is applied. In ferromagnetic materials spontaneous magnetization occurs only below Curie temperature and above Curie temperature such materials behaves like a paramagnetic materials. Ferromagnetic substances obey Curie Weiss law.

$$\chi = \frac{C}{T - T_c}$$

Here, T_c is known as critical temperature or transition temperature above which ferromagnetic substance changes to paramagnetic substance. These materials find application in transformer cores, permanent magnets and electromagnets, for which large magnetic field are required.

Examples of ferromagnetic substances are iron, cobalt and nickel.

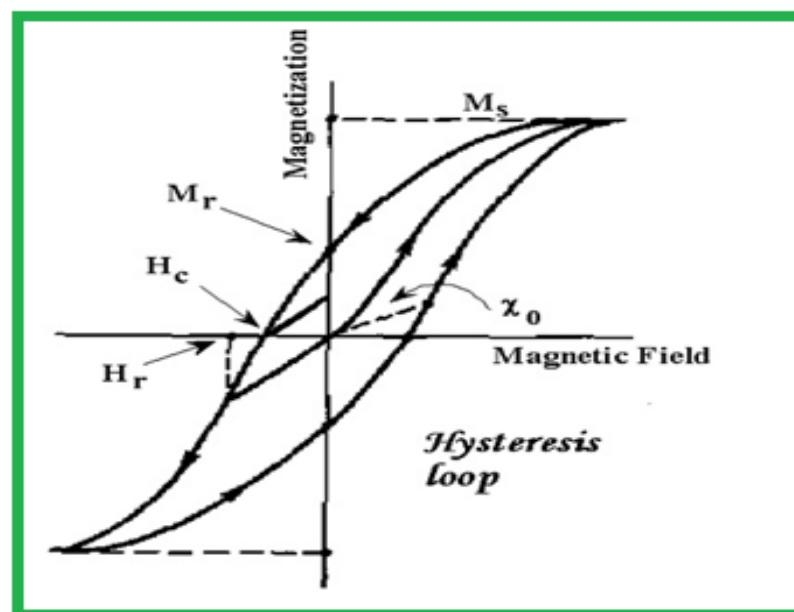


Fig. 1.1: Hysteresis curve between magnetization \mathbf{M} and magnetic field \mathbf{H}

(d) Antiferromagnetism:

In antiferromagnetic materials, the constituent atoms or ions have magnetic dipole moments that are ordered antiparallel to each other. So the net magnetization is always zero.

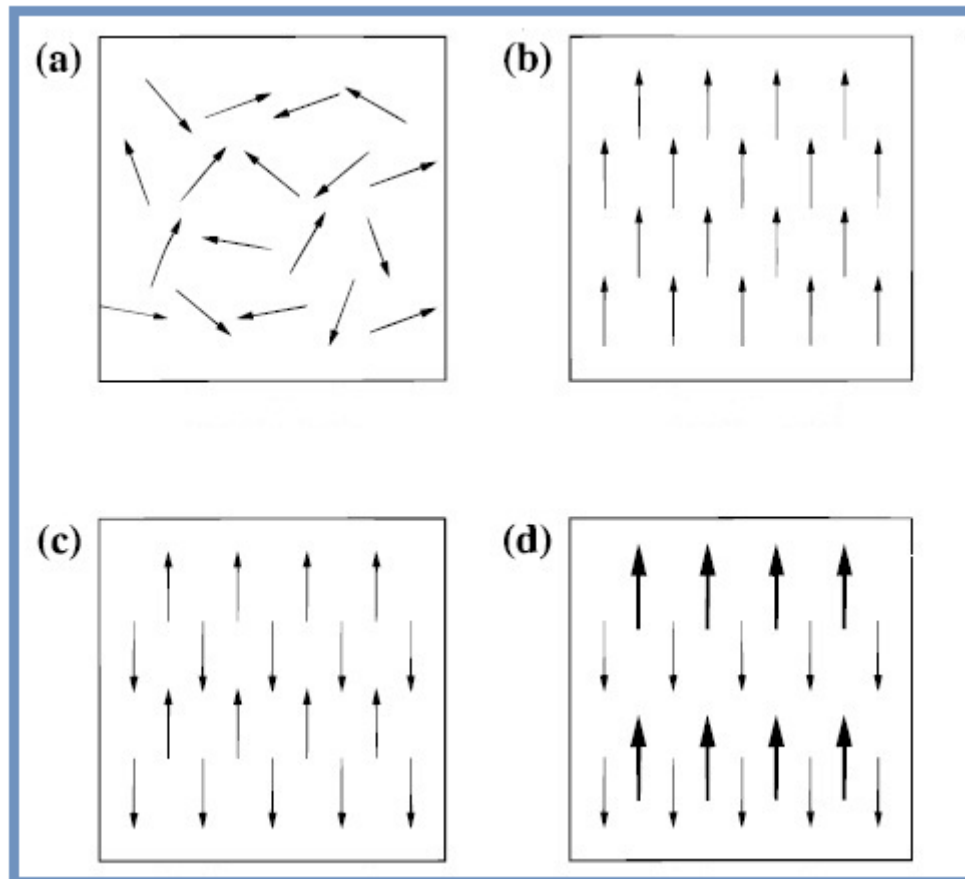


Fig. 1.2: The spin arrangement of (a) paramagnetic (b) ferromagnetic

(c) antiferromagnetic and (d) ferrimagnetic material

(e) Ferrimagnetism:

Ferrimagnetism are just like antiferromagnetism, in which the dipoles are aligned antiparallel to each other, some of the dipoles have larger moments than the other. So the net magnetization can not be zero. Ferrimagnets tend to concentrate magnetic flux like ferromagnets.

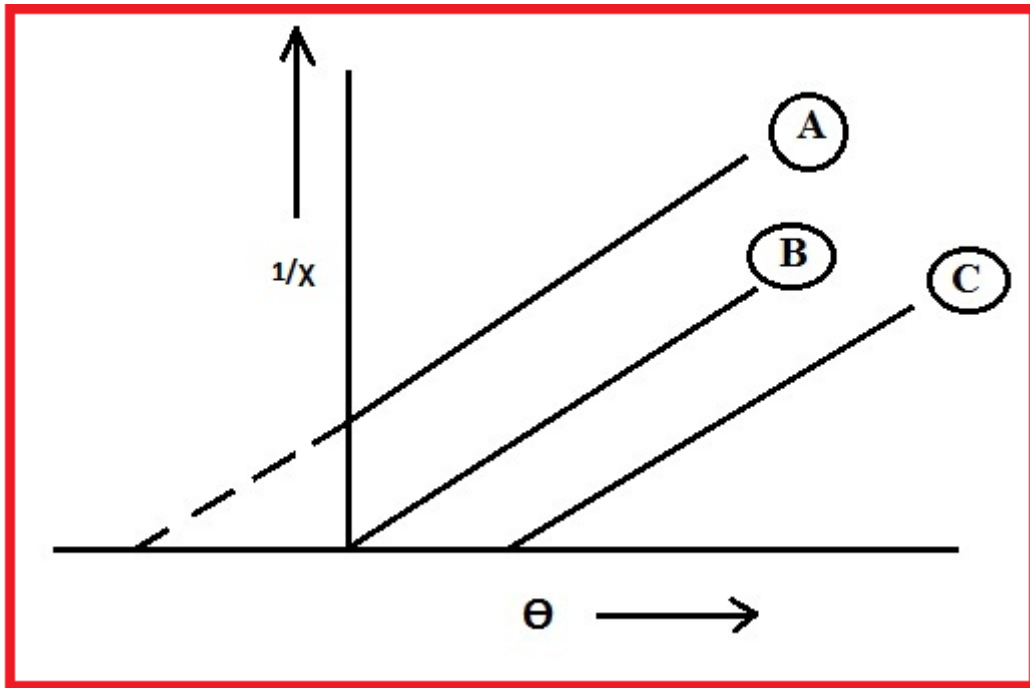


Fig. 1.3: The susceptibility versus temperature for (A) antiferromagnet (B) paramagnet and (C) ferromagnetic substance

1.2 FERROELECTRIC

Ferroelectric materials have spontaneous polarization whose direction can be switched by an applied electric field. Ferroelectric material undergoes phase transition from high temperature to a low temperature phase. In low temperature field that has spontaneous polarization whose direction can be switched by an applied field. Ferroelectric materials have domains and show a hysteresis response to polarization and electric field. Many properties of ferroelectric materials are analogous to ferromagnets, with electric polarization \vec{P} corresponds to magnetization \vec{M} , the electric field \vec{E} corresponds to magnetic field \vec{H} and the electric field displacement \vec{D} corresponds to magnetic flux density \vec{B} . They found

applications as capacitors because of their concentration of electric flux density and used in electrochemical transducer and actuators. Examples of ferroelectric materials are Rochelle salt and perovskite oxides.

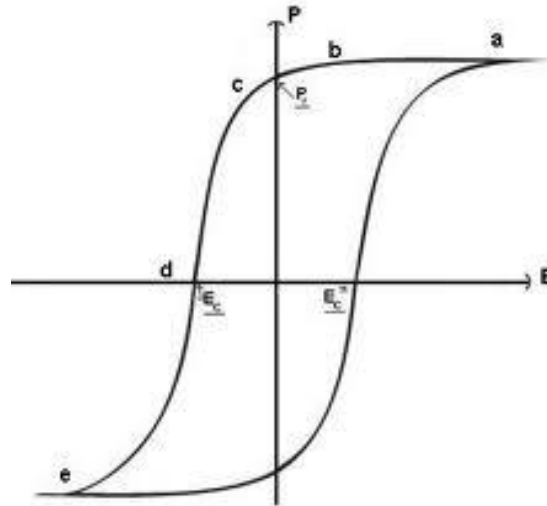


Fig. 1.4: Hysteresis curve between electric polarization \mathbf{P} and electric field \mathbf{E} .

1.3 FERROELASTICITY

Ferroelasticity is a phenomenon in which a material exhibit spontaneous strain. In ferroelastic, materials have spontaneous deformation that can be reoriented by an applied stress. In ferroics, ferroelasticity is equivalent to ferromagnetism and ferroelectricity.

Example of ferroelastic material is nickel titanium alloy.

1.4 SPIN FRUSTRATION

Spin frustration is an important phenomenon in magnetism. It happens in anti-ferromagnetism. In anti-ferromagnetism each spins are opposite to each other with equal magnitude. If three magnetic ions are placed at the corner of the triangle then each spin

should be opposite to their neighbour spin. Once the first two spin align antiparallel to each other then the third spin was frustrated, because of two possible orientations, either up or down. The third cannot simultaneously minimize the interactions.

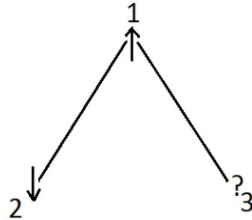


Fig. 1.5: Spin frustration in antiferromagnetic materials. In position (3) spin has frustrated.

1.5 MULTIFERROIC

Electricity and magnetism combined into one common discipline in the 19th century. Multiferroics means the co-existence of either two or more than two ferroelectricity, ferromagnetism and ferroelasticity in a material. They have a spontaneous magnetization that can be re-oriented by an applied magnetic field, a spontaneous polarization that can be re-oriented by an applied electric field and a spontaneous deformation that can be re-oriented by an applied stress. Boracites were first known multiferroic. Multiferroics are found application in conventional actuators, transducers and storage devices. In a system there are two types of ordering:-

- (a) Ferromagnetism- the spontaneous ordering of spin and orbital magnetic moments.
- (b) Ferroelectricity- the spontaneous ordering of electric dipole moments.

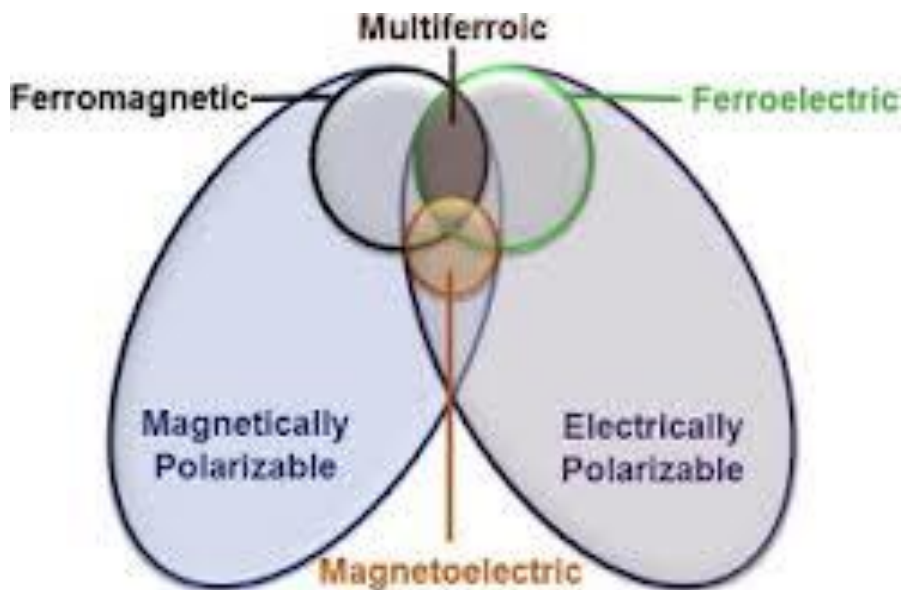


Fig. 1.6: Magnetolectric coupling in multiferroic material. [Current Opinion in Solid State and Materials Science 16, 199 (2012)]

When the above two co-exist in a single material in the absence of external electric field and magnetic field then this materials are said to be multiferroics.

MAGNETOELECTRIC COUPLING

Magnetolectric coupling was first developed by Landau and Dzyaloshinskii. Magnetolectric coupling is a phenomenon in which the magnetization is induced by the electric field. There the symmetric consideration is essential to classify all the possible magnetolectric tensor via magnetic point group.

TYPES OF MULTIFERROICS

Depending on the microscopic origin of multiferroicity, these classes of compounds are divided in two major categories:

I. Type I multiferroic

II. Type II multiferroic

(i) Type- I Multiferroics

In these types of materials electricity and magnetism have different source and they appear independent of one another. So there is a coupling between them. In these materials coupling between ferroelectricity and magnetism is weak. In these materials ferroelectricity occurs at higher temperature than magnetism. Ferroelectric and magnetic transition occurs at above room temperature. Polarization is very high of the order of $10\text{-}100 \mu\text{c}/\text{cm}^2$. There are four different subclasses of type-I multiferroics:

(a) MultiferroicPervoskites

There are many magnetic materials among pervoskites and also many ferroelectrics. Pervoskites like BaTiO_3 is ferroelectric. Magnetism needs partially filled d shells of a transition metal, but all ferroelectric pervoskites contain transition metal ions with empty d shell. Ferroelectricity in these systems caused by the off-centre shifts of transition metal ion, which forms strong covalent bonds with one oxygen using their empty d states. The presence of d electrons of magnetic transition metals suppresses this process, preventing ferroelectricity in magnetic pervoskites. This is called as “ d^0 vsd n ” problem. Solution to this problem is by making mixed pervoskites with d^0 and d^n ions.

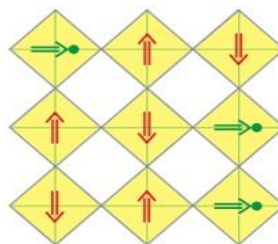


Fig. 1.7: Polarization coexisting with magnetic order in Type I Multiferroics

(b) Ferroelectricity due to lone pair :

In BiFeO_3 , BiMnO_3 and PbVO_3 , Bi^{3+} and Pb^{2+} plays important role in the origin of ferroelectricity. Electrons which don't take part in chemical bonding they are called lone pairs. In these ions, there are two outer 6s electrons. They have high polarizability as the condition required for ferroelectricity.

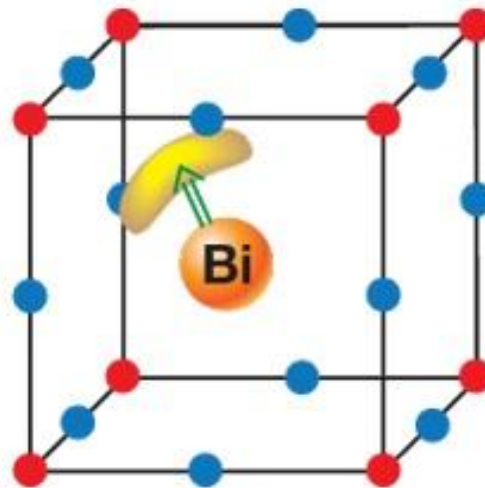


Fig.1.8: Ordering of lone pairs Bi^{3+} and Pb^{2+} ions

(c) Ferroelectricity due to charge ordering:

In charge ordered systems, the co-existence of inequivalent sites with different charges, and inequivalent bonds leads to ferroelectricity. Ferroelectricity and type-I multiferroicity can be charge ordering. After charge ordering, both sites and bonds turn out to be inequivalent, this leads to ferroelectricity.

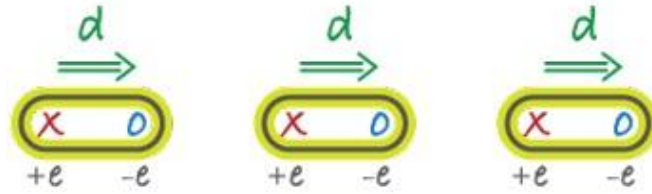


Fig. 1.9: In charge ordered systems, the coexistence of inequivalent sites with different charges, and inequivalent bonds, leads to ferroelectricity.

(d) Geometric ferroelectricity:

The geometric mechanism of polarization in YMnO_3 describes the tilting of rigid MnO_5 block with a magnetic Mn remaining at the center. This tilting occurs to provide closer packing and the oxygen ions move closer to the small Y ions. Because of the tilting, the Y-O bonds form dipoles and the system becomes ferroelectric.

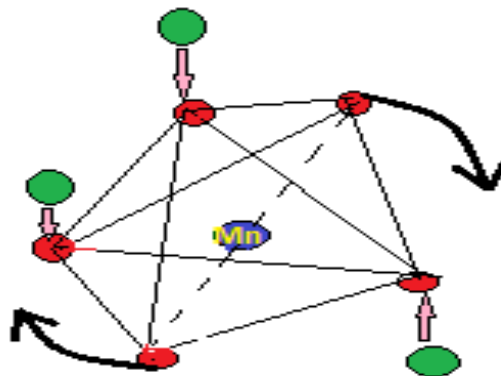


Fig.1.10: Generation of polarization due to tilting of MnO_5 polyhedra in YMnO_3 .

(ii) Type –II Multiferroics

In these types of materials magnetism causes ferroelectricity implying a strong coupling between them. In these multiferroics, magnetoelectric coupling is very strong. Polarization is usually very small compared to type-I multiferroic, it is of the order $10^{-2} \mu\text{C}/\text{cm}^2$. There are two subclasses of type-II multiferroics.

(a) Spiral type- II - multiferroics:

Most of the type II multiferroic belongs to this subgroup. Ferroelectricity appears with a spiralling magnetic phase, mostly of cycloid type. Magnetic frustration is a source of spiral magnetic ordering in insulators. Therefore these multiferroics are usually found in frustrated systems.

(b) Collinear magnetic structures:

The second group of magnetically driven ferroelectrics are those in which ferroelectricity appears in collinear magnetic structures. So, that all magnetic moments are aligned along a particular axis without involvement of the spin orbit interaction. Polarization in these materials can appear as a consequence of exchange interactions because the magnetic coupling varies with the atomic positions. At high temperature the distance between the ions along the chains are the same, the chain has inversion symmetry. Magnetic ordering breaks the inversion symmetry, the spins forms an antiferromagnetic structure. Due to exchange interaction the distortion of ferromagnetic and antiferromagnetic bonds are different.

1.6 WHY THERE ARE FEW MULTIFERROICS?

Due to scarcity of coexistence of ferroelectric and ferromagnetic materials few multiferroic materials exists. Multiferroic materials were developed since 1960 but after that for a long period of time they weren't developed due to insufficient laboratory conditions. Also for under developed technology multiferroic materials aren't developed since last few decades. There are some major factors which prevents the co-existence of ferroelectricity and ferromagnetism. They are as follows:

(a) Symmetry: There are 31 point groups allows polarization and there are 31 point group allows magnetization. But there are only 13 point group which allows both the polarization and magnetization. This represents a considerable reduction of multiferroic materials. Therefore from symmetric point of view less number of multiferroic materials exist.

(b) Electrical properties: Ferroelectric materials are insulator and ferromagnetic materials are conductor. So we assume that the lack of the simultaneous occurrence of both ferromagnetic and ferroelectric property. There are also very few antiferromagnetic ferroelectrics, even though antiferromagnets are usually insulating materials.

(c) Chemistry of “ d^0 -ness”: Magnetism occurs due to partially filled d-orbit, the tendency for it to make a distortion that removes the centre of symmetry is eliminated. But ferroelectricity occurs due to empty d-orbit. This could be the result of a number of effects, including size, more dominant distortion and electronic properties.

1.8 APPLICATIONS

Multiferroics have tremendous application in areas as diverse as data storage, sensing, actuation and spintronics where electric field control of magnetic spin would consume significantly less power than magnetic field control, which requires electric current to generate magnetic fields.

2. MOTIVATION BEHIND PRESENT WORK

Most of the multiferroic materials were observed at very low temperature. $\text{Bi}_2\text{Fe}_4\text{O}_9$ is a material where magnetoelectric coupling was realized at 265 K which is near to the room temperature with good degree of tenability. As $\text{Bi}_2\text{Fe}_4\text{O}_9$ is type II multiferroic, so magnetoelectric coupling is very strong. $\text{Bi}_2\text{Fe}_4\text{O}_9$ has pentagonal symmetric structure. So that it is very interesting to study in the field of pentagonal symmetric structure

3. PREVIOUS REPORT

In Fe^{3+} lattice in the $\text{Bi}_2\text{Fe}_4\text{O}_9$ compound is found to be magnetic pentagonal lattice. This lattice is subject to antiferromagnetic interaction which leads to geometric frustration. The pentagon is 5 edges polygon. It is impossible to tile a plane with regular pentagons; there must be gap to fill. If the tiling of a plane with non-regular pentagons, then it is known as Cairo pentagonal tiling. In $\text{Bi}_2\text{Fe}_4\text{O}_9$ there are two different sites of four iron atoms: Fe_1 occupies a tetrahedral position and Fe_2 occupies octahedral position. The structure, columns of edge sharing Fe_2 octahedra form chains along the c-axis and these chains are linked together by corner sharing Fe_1 tetrahedra and Bi atoms. In this structure there are five magnetic superexchange interactions J_1 and J_5 . The structure can be viewed as layer perpendicular to the c-axis the magnetic coupling of these layers along c- direction involves only Fe_2 atoms in the octahedron columns and is achieved through two interactions, J_1 between the atoms with in the unit cell and J_2 between the atoms of adjacent cells. Each Fe_1 interacts with its nearest Fe_1 via J_4 and with two nearest neighbour Fe_2 pair via J_3 and J_5 . The projection of this layer along c-axis forms a pentagonal lattice with three slightly different bonds per pentagon. This geometry is equivalent to a distorted Cairo lattice.

The compound $\text{Bi}_2\text{Fe}_4\text{O}_9$ displays a very original non-collinear magnetic structure, made of four Fe_1 moments and four Fe_2 ions forming interpenetrating patterns of four-fold spin rotations. This materialisation of a pentagonal Cairo lattice opens new prospective in the field of magnetic frustration.

4. CRYSTAL & MAGNETIC STRUCTURE OF $\text{Bi}_2\text{Fe}_4\text{O}_9$

Crystal Structure

A crystal structure is a regular arrangement of atoms in one of the fourteen space lattices. The crystal structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ found to be orthorhombic. It belongs to space group Pbam. At low temperature below 240-265 K the material undergoes phase transition to an antiferromagnetic state. The larger unit cell structure is monoclinic. The unit cell parameters are $a=7.967 \text{ \AA}$, $b=8.443 \text{ \AA}$ and $c=5.996 \text{ \AA}$.

Magnetic Structure

In $\text{Bi}_2\text{Fe}_4\text{O}_9$, there are two types of Fe atoms are present

(i) Octahedral Fe

(ii) Tetrahedral Fe

Each octahedral Fe atom is surrounded by six oxygen atoms and each tetrahedral Fe atom is surrounded by four oxygen atoms. Spins of tetrahedral Fe atom are parallel to the octahedral Fe atom. But octahedral Fe atoms are parallel to nearest octahedral Fe atom. This causes spin frustration in $\text{Bi}_2\text{Fe}_4\text{O}_9$.

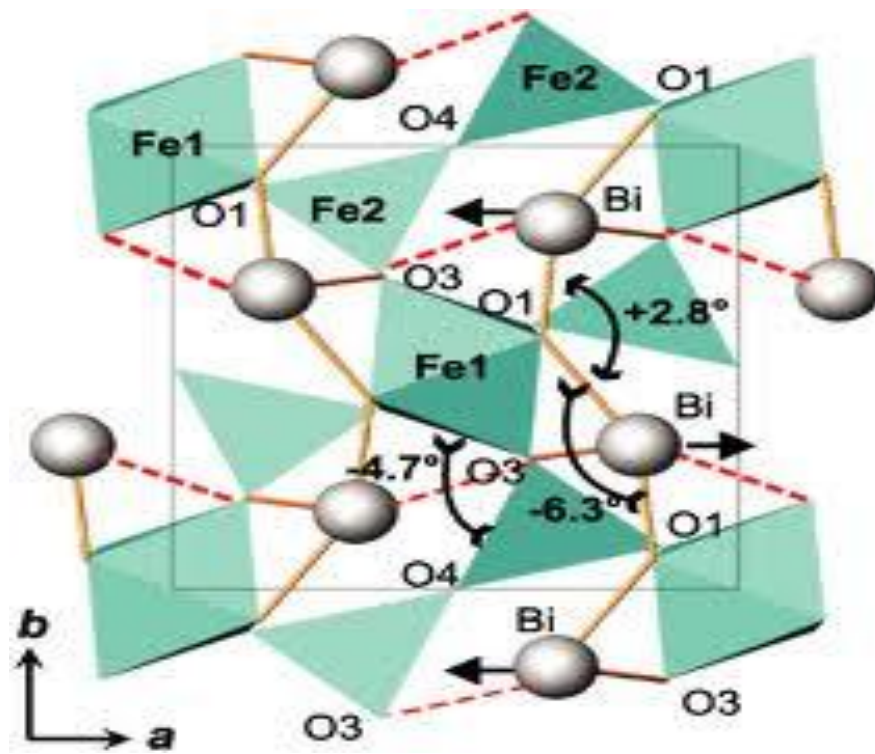


Fig. 4.1: Orthorhombic structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$

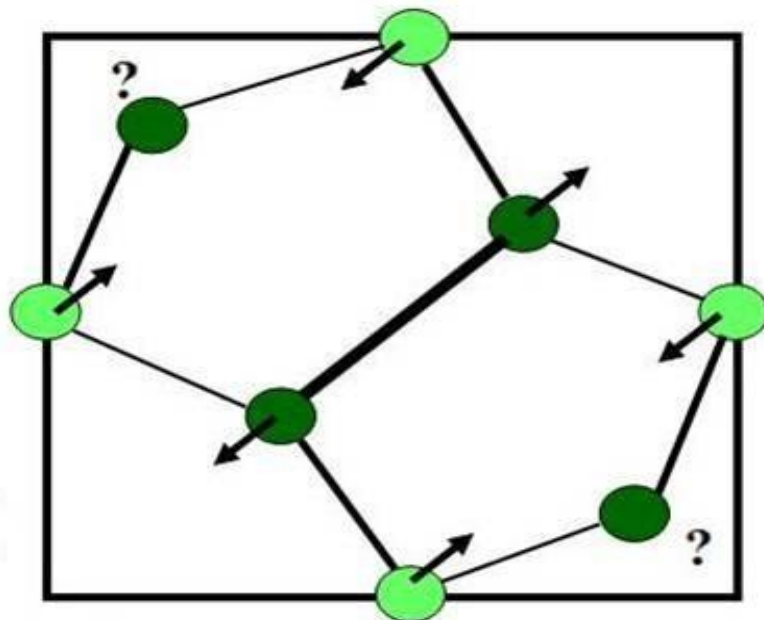


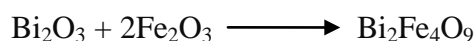
Fig.4.2: Magnetic structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$

5. SAMPLE PREPARATION

Solid state reaction route

It is the most widely used method for preparation of polycrystalline solid from a mixture of solid starting materials. Solids do not react together at room temperature over normal time scales and it is necessary to heat them to much higher temperature often in order for the reactions. The factor in which the feasibility and rate of a solid state reaction include, reaction condition, structural properties of reactants, surface area of the solids, their reactivity and thermodynamic free energy change associated with the reaction. A solid state reaction allows the reactants to chemically react without the presence of the solvents. With normal reaction technique, scientists need to remove the residual solvent from the resulting product after the reaction has finished. But in this process there is no residual solvent. $\text{Bi}_2\text{Fe}_4\text{O}_9$ is synthesized by a traditional solid state reaction route at a temperature over 850°C for 12 hours. However, because of some of disadvantages of this method such as high temperature impurity readily present with other compounds, large dimension and condition cannot be easily controlled, so new methods of the preparation have been investigated. $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample can be prepared by using Fe_2O_3 and Bi_2O_3 as starting materials. The starting materials are taken in a calculated ratio for crystalizing the compound.

To prepare the sample of 2gm of $\text{Bi}_2\text{Fe}_4\text{O}_9$, we take Bi_2O_3 and Fe_2O_3 . The chemical equation will be given by



Atomic weight of Bi = 208.9804

Atomic weight of Fe = 55.85

Atomic weight of O = 15.999

Molecular weight of Fe_2O_3 is 159.697gm

Molecular weight of 2 Fe_2O_3 is 319.394gm

Molecular weight of Bi_2O_3 is 465.9578gm

Molecular weight of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is 785.3518gm

2gm of $\text{Bi}_2\text{Fe}_4\text{O}_9$ needs 1.1866gm of Bi_2O_3 .

2gm of $\text{Bi}_2\text{Fe}_4\text{O}_9$ needs 0.8134gm of Fe_2O_3 .

Grinding:

Then the samples were taken to grind for 3 hours for proper mixing of sample, usually in an agate mortar and pestle.

Pressing:

After grinding the samples were taken for palletization by using dye in a hydraulic press. The powdered samples were pressed at 5 atm pressure.

Sintering:

Then the samples were kept inside the furnace for sintering 850°C for 12 hours. The ramping rate of temperature is $5^\circ\text{C}/\text{min}$. After sintering the pellets were again grind for half an hour. Then again the pellets were prepared and kept inside the furnace at 850°C for 12 hours. Then for further study the samples are characterized by SEM, XRD, dielectric measurement and UV visible spectroscopy.

6. EXPERIMENTAL TECHNIQUE USED FOR THE SAMPLE CHARACTERISATION

6.1 X-RAY DIFFRACTION

X-ray diffraction is one of the x-ray scattering techniques, which are non-destructive analytical techniques revealing information about crystallographic structure, chemical composition and physical properties of materials. X-ray diffraction is a technique which tells the information about the crystal structure. It gives information about the arrangement of atoms in a sample. XRD is based on constructive interference of monochromatic x-rays and crystalline sample. The monochromatic x-rays are generated by cathode ray tube, filtered to produce monochromatic radiation, collimated to concentrate them, and directed towards the sample. X-rays are incident beam of x-ray striking the sample surface, and then the incident beam gets diffracted. It follows Bragg's law of diffraction.

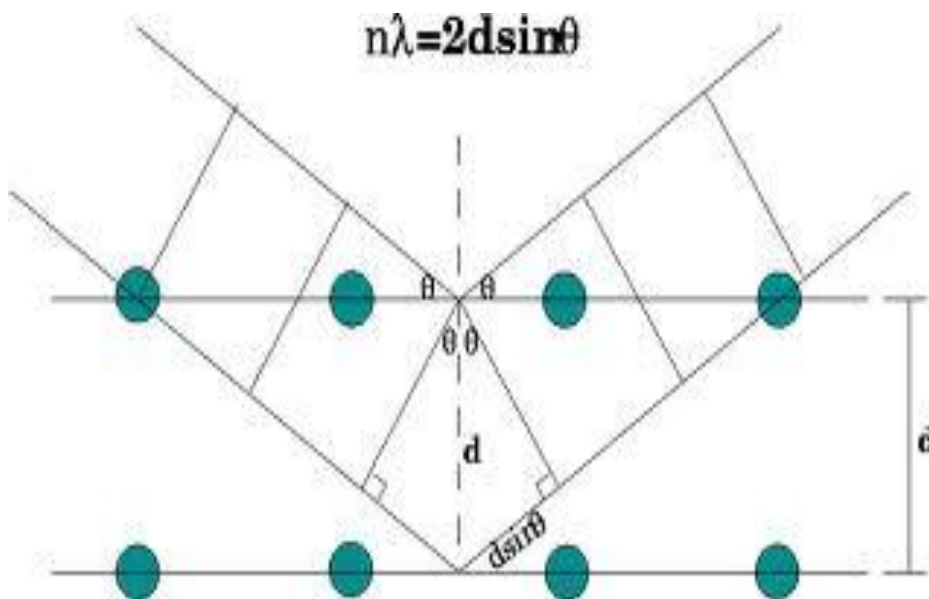


Fig.6.1: Diffraction through a plane

Bragg's law is given as

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

where $n = 1, 2, 3, 4, \dots$

This law relates the wavelength of electromagnetic radiation (λ) to the diffraction angle (Θ) and the lattice spacing (d) in a crystalline sample.

These diffracted x-rays are then detected, processed and counted. By scanning the sample through a range of angles (2Θ), all possible diffraction direction of lattice can be obtained.

6.2 SCANNING ELECTRON MICROSCOPY

Scanning electron microscopy is a type of electron microscope that produces an image of sample by scanning it with a focused beam of electrons. The electron beam when interacts with the surface of the sample, the electrons present in the sample produces various signal such as secondary electrons, back scattered electrons, transmitted electrons etc. These signals can be detected by the detector and that contain the information about the sample surface. The electron beam, which typically has an energy ranging from a few 100 eV to 50 KeV, is focused by one or two condenser lenses into a beam with a very fine focal spot sized 1 nm to 5 nm. The beam passes through pairs of scanning coils in the objective lens, which deflect the beam in a raster fashion over area of sample surface. Generally in all SEM, secondary electrons are used for the image formation. In standard detection mode, secondary electron imaging, SEM can produce very high resolution image of the sample surface.

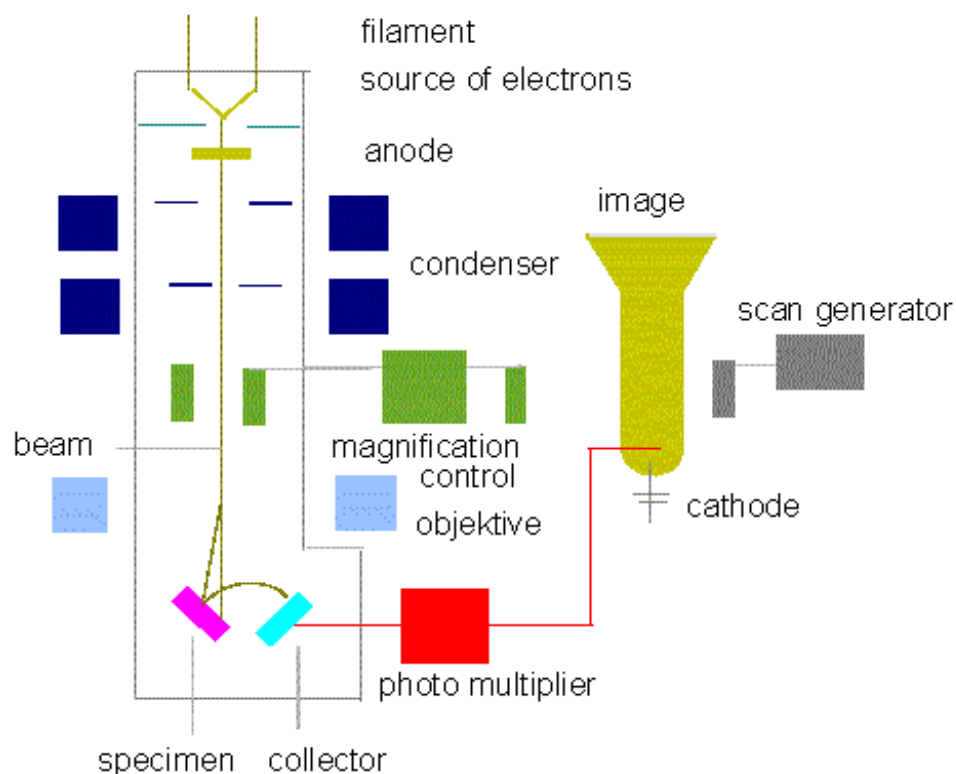


Fig.6.2:Schematic diagram of SEM.

For SEM image of sample, first we take the sample of $\text{Bi}_2\text{Fe}_4\text{O}_9$ in pallet form. Then the surface is coated with platinum over which a beam of electrons falls and finally it is put into a SEM machine for imaging.

6.3 DIELECTRIC SPECTROSCOPY

Dielectric spectroscopy (sometimes called impedance spectroscopy), and also known as Electrochemical Impedance Spectroscopy (EIS), measures the dielectric properties of a medium as a function of frequency. It is based on the interaction of an external field with the electric dipole moment of the sample, often expressed by permittivity. Dielectric constant is defined as to be the measure of the polarisability of a material that is how strongly it resist the movement of polar molecule. Permittivity can be expressed as a complex quantity with a real and an imaginary part.

$$\epsilon = \epsilon' - \epsilon''$$

Tangent loss is given by

$$\tan\delta = \epsilon''/\epsilon'$$

Dielectric constant is a property of an electrical insulating material equal to the ratio of capacitance of capacitor filled with given material to the capacitance of the capacitor in vacuum.

Impedance measurements are a basic means of evaluating electronic components and materials. Every material has a unique set of electrical characteristics that are dependent on its dielectric or insulation properties. The dielectric property analysis was conducted by using an Impedance/Gain Phase Analyser. The Impedance/Gain phase analyser is an integrated solution for efficient measurement and analysis. Different dielectric properties are measured from 40°C to 400°C temperature range.

6.4 UV VISIBLE SPECTROSCOPY

Atoms or molecules of the sample interact with electromagnetic radiation in wide variety of ways. They may absorb or emit EMR. Ultraviolet (200-400 nm) and visible (400-800 nm) radiation are found towards, short wavelength, high frequency, end of electromagnetic spectrum. The information obtained from these techniques can be processed to yield images or spectra which reveal the structural, chemical, geometric or physical details of the materials. Energy absorbed in the UV or visible region causes a change in the electronic excitation of the molecule, and hence results in corresponding change in its ability to absorb light in the UV-visible region of the electromagnetic radiation. This leads to colour transition.

The relationship between energy absorbed in an electronic transition and the frequency (ν), and wavelength (λ) of radiation producing the transition is given as:

$$\Delta E = h \nu = hc / \lambda$$

Where,

h is Planck's constant

c is the velocity of light

ΔE is Energy absorbed in an electronic transition in a molecule from ground state (lower energy) to excited state (higher energy).

The energy absorbed depends on the energy difference between ground state and excited state; smaller the difference, larger the wavelength of absorption. The principal characteristics of an absorption band are the position and intensity. The position of an absorption band corresponds to the wavelength of radiation whose energy is equal to that required for an electronic transition. This characterization is used to determine the band gap of the sample.

7. RESULT & DISCUSSION

7.1 X-RAY DIFFRACTION ANALYSIS

X-ray diffraction (XRD) pattern of $\text{Bi}_2\text{Fe}_4\text{O}_9$ sintered at 850°C for 12 hours are shown in Fig.7.1. XRD peak intensity ratios observed in the XRD pattern suggest that polycrystalline behaviour with good crystallinity was formed by the solid state reaction route.

In XRD the samples are scanned in a continuous mode from 10° - 80° with a scanning rate of 2° per minute. From XRD analysis it is found that crystal structure of Bi₂Fe₄O₉ is orthorhombic and all the peaks are indexed using search test programme JCPDFWIN. The prominent peaks in the plot are indexed to various [h k l] planes of Bi₂Fe₄O₉. There are some low intensity peaks which are not matched with Bi₂Fe₄O₉ peaks, marked *. These peaks are obtained may be due to impurity in Fe₂O₃ and Bi₂Fe₃.

The lattice parameters are obtained from literature survey such as a, b, c are 7.965Å, 8.440 Å and 5.994 Å respectively. Here I calculated these parameters by taking three [h k l] values from the XRD plot.

For orthorhombic structures the relation between [h k l] and a, b, c is given by solving these values of a, b c are found as 7.96 Å, 9.12 Å, and 5.26 Å respectively. To calculate the crystallite size of by Scherrer's formula

$$t = 0.9 \lambda / (\beta \cos \theta)$$

Where, λ is the wavelength of x-ray,

β is the line broadening at half the maximum intensity, after subtracting the instrumental line broadening in radians.

Θ is the Bragg angle.

From the above formula the crystallite size of Bi₂Fe₄O₉ is found to be 51.62nm.

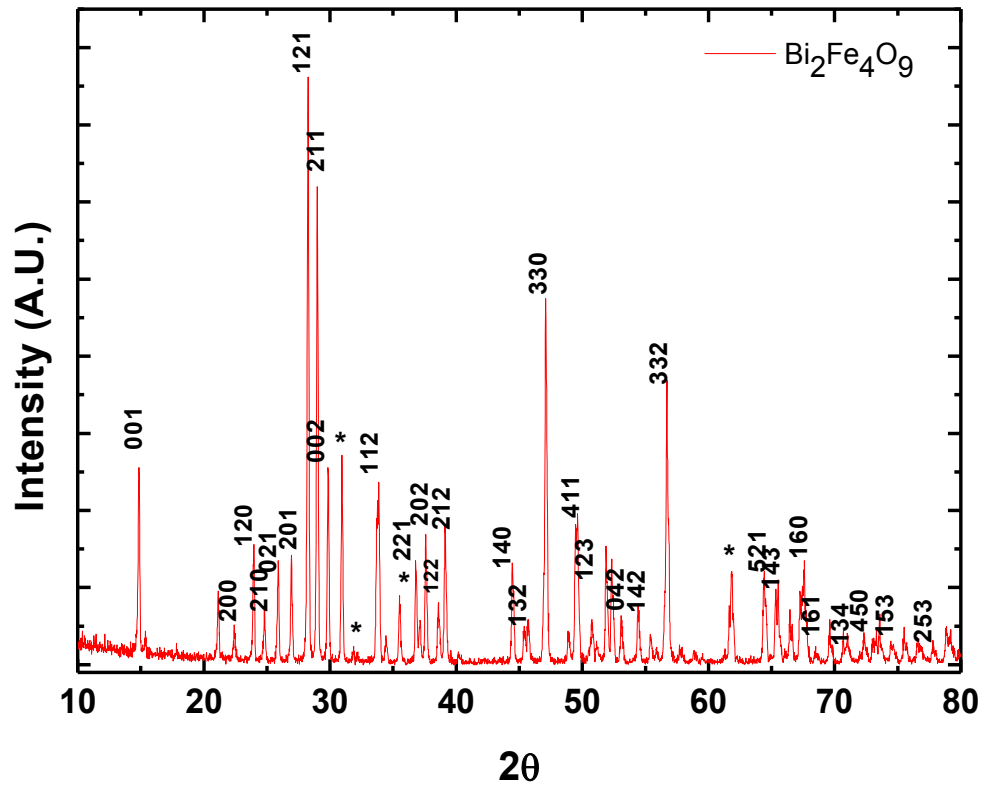


Fig.7.1: XRD patterns of $\text{Bi}_2\text{Fe}_4\text{O}_9$ samples sintered at 850°C for 12 hours using solid state reaction route.

7.2 SCANNING ELECTRON MICROSCOPY (SEM)

SEM image of $\text{Bi}_2\text{Fe}_4\text{O}_9$ sintered at 850°C for 12 hours are shown in Fig.7.2. SEM images are found to be porous and highly densified structure which was obtained by the solid state reaction route. SEM is used to determine the surface morphology of the material. From SEM photograph it is found that the pores are unevenly distributed over the bulk surface. The SEM image is taken at the resolution of $2\mu\text{m}$ and operated at 15kV .

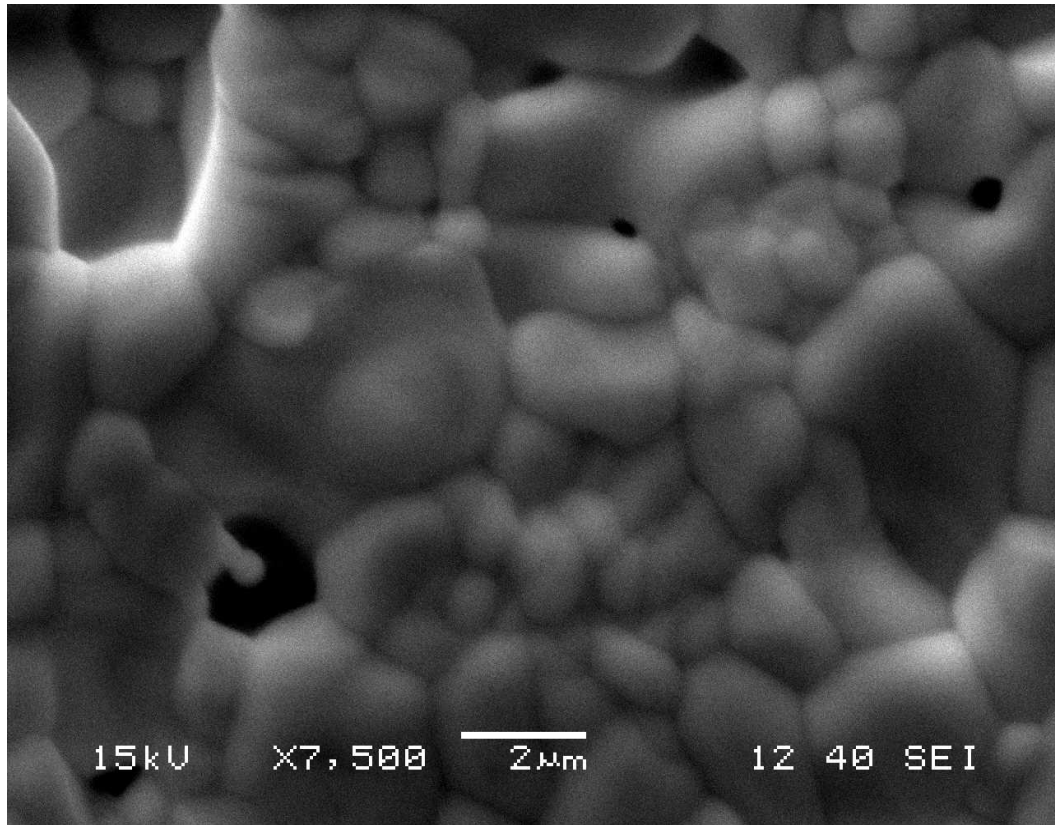


Fig. 7.2: SEM image of Bi₂Fe₄O₉ sintered at 850°C for 12 hours.

7.3 DIELECTRIC SPECTROSCOPY ANALYSIS

Dielectric constant and different dielectric properties of the materials are determined by dielectric spectroscopy analysis technique. Dielectric loss or tangent loss of Bi₂Fe₄O₉ decreases with increase in frequency. Dielectric loss becomes zero in the frequency range of 100 to 1000 Hz. Impedance of Bi₂Fe₄O₉ is constant upto 1000Hz frequency after that the increase in the frequency impedance decreases. Dielectric constant decreases with increase in frequency.

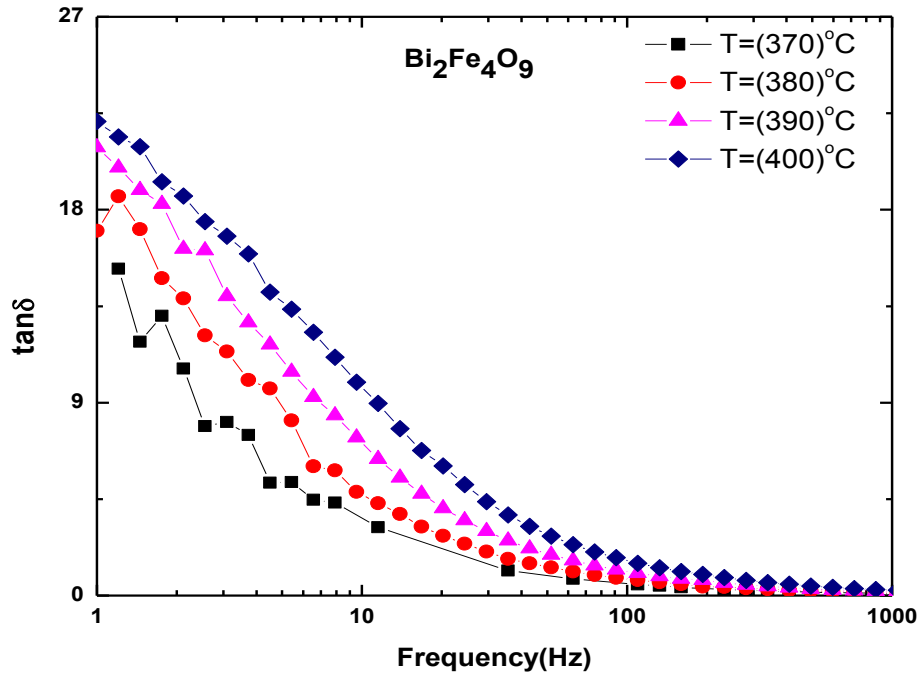


Fig 7.3.1: Dielectric loss verses frequency.

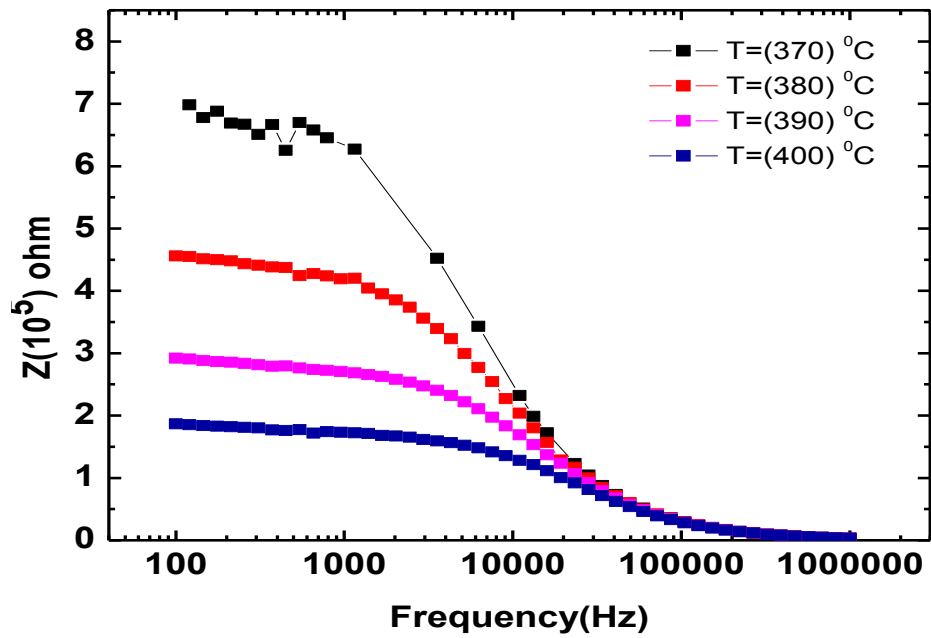


Fig 7.3.2: Impedance verses frequency

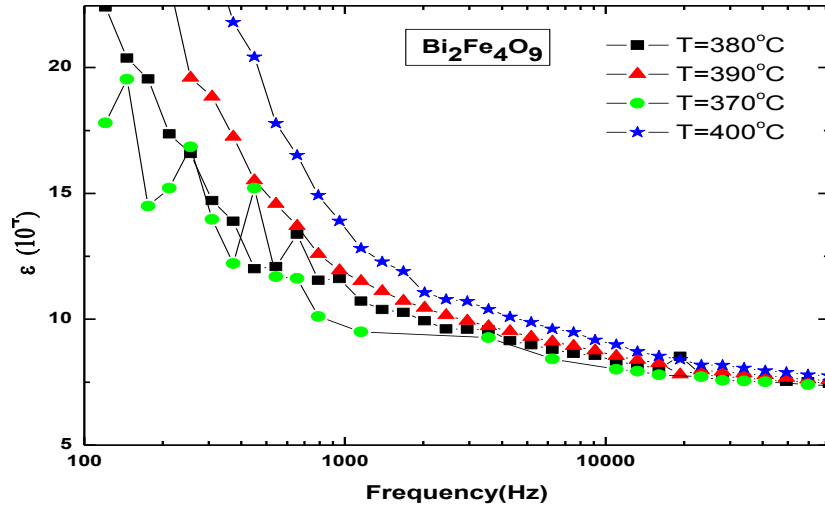


Fig 7.3.3: Dielectric constant verses frequency

7.4 UV-VISIBLE SPECTROSCOPY

UV-Visible spectroscopy is used to determine the band gap (E_g) of the material. Absorption coefficient increases with increase in frequency. From the below graph the band gap of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is found to be 4.6 eV, which shows that $\text{Bi}_2\text{Fe}_4\text{O}_9$ is an insulator.

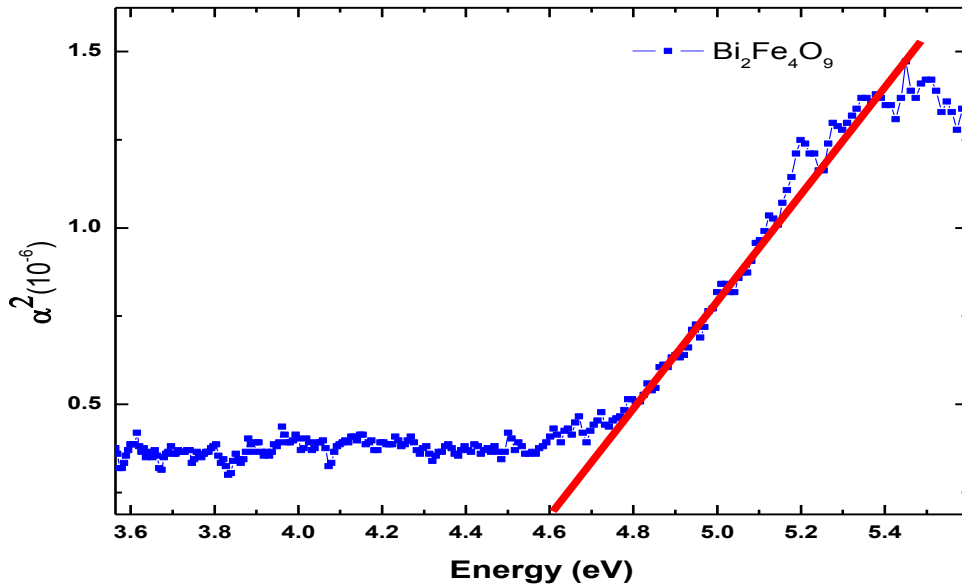


Fig 7.4: Absorption coefficient verses Energy.

8. CONCLUSION

We have prepared $\text{Bi}_2\text{Fe}_4\text{O}_9$ using solid state reaction technique. Our X-ray diffraction analysis confirms the formation of orthorhombic crystal with space group $Pbam$. Using Scherer's formula, the crystallite size of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is calculated to be 51.62nm. SEM data suggests porous nature of the sample. From dielectric spectroscopy, we concluded that dielectric loss of $\text{Bi}_2\text{Fe}_4\text{O}_9$ decreases with increase in frequency. Dielectric constant of $\text{Bi}_2\text{Fe}_4\text{O}_9$ also decreases with increase in frequency. Impedance of $\text{Bi}_2\text{Fe}_4\text{O}_9$ decreases with increase in frequency but from 100-1000Hz frequency impedance is constant. From UV-Visible spectroscopy, We calculate the band gap of $\text{Bi}_2\text{Fe}_4\text{O}_9$ is 4.6 eV.

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