

CrFe₂O₄ - BiFeO₃ Perovskite Multiferroic Nanocomposites – A Review

RATNAKAR PANDU

Department of Mechanical Engineering, NRI Institute of Technology, Hyderabad, India.

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ABSTRACT

Though semiconductor technology has advanced significantly in miniaturization and processor speed the “ideal” nonvolatile memory - memory that retains information even when the power goes is still elusive. There is a large demand for non-volatile memories with the popularity of portable electronic devices like cell phones and note books. Semiconductor memories like SRAMs and DRAMs are available but, such memories are volatile. After the advent of ferroelectricity many materials with crystal structures of Perovskite, pyrochlore and tungsten bronze have been derived and studied for the applications in memory devices. Ferroelectric Random Access Memories (FeRAM) are most promising. They are nonvolatile and have the greater radiation hardness and higher speed. These devices use the switchable spontaneous polarization arising suitable positional bi-stability of constituent ions and store the information in the form of charge. This paper is focused on the synthesis and characterizations of BiFeO₃ and xCrFe₂O₄-(1-x) BiFeO₃ nanoceramics which are most promising FeRAM materials. The effect of various-dopant-induced changes in structural, dielectric, ac impedance, ferroelectric hysteresis, mechanism of the dielectric peak broadening and frequency dispersion have been addressed. It also deals with low temperature processing technique of those nanoceramics which has high dielectric and ferroelectric properties. These studies can be further extended to reinforce BiFeO₃ and CrFeO₄ materials with carbon nanotubes to obtain conductive composites using appropriate techniques.

Key words: CrFe₂O₄ and BiFeO₃ nanoceramics; FeRAM material; nanocomposites; sol-gel technique; XRD technique; perovskite materials.

INTRODUCTION

Modern engineering systems, like high-performance engines, nuclear reactors, computers and memory devices, require better and new materials than those available today. Better materials and processes have an increasing roll in efforts for environmental protection, development of information infrastructure, improvement in energy efficiency, modern and reliable transportation and civil infrastructure. In certain industries, the need for energy conversion systems, energy efficiency and materials withstanding corrosive chemical and/or thermal environments have sparked a new interest in processing of ceramic materials. Moreover, the continuing trend towards miniaturization in

the electronic industry has imposed a growing demand on preparation of semiconductors using innovative processing techniques. Ceramics have been traditionally admired for their mechanical and thermal stability and the unique electrical, optical and magnetic properties. These materials have become very important in many key technologies including communications, energy conversion and storage, electronics and automation. These materials are now classified under electro-ceramics to distinguish them from other functional ceramics like structural ceramics. Historically, developments in the various subclasses of electro-ceramics have indicated the growth of new technologies. Thus advances in materials research, represent and progress across a broad range of scientific disciplines and technological areas, with high impact on society.

The extensive research work on the solid materials during the last three decades has resulted in the understanding of the properties of solids in general. In recent times, an area of active research has been in the characterization of mixed oxide ceramic systems. These have been of particular interest because of their ease of fabrication, flexibility and the fact that a wide range of properties can be obtained by substitution of one ion for another. One of the very widely studied groups of compounds is the oxygen octahedral type ferroelectrics.

Nanomaterials and Nanocomposite Materials

Nanoscale materials are those materials which fall in between atoms/molecules and condensed matter. These materials have proportions, may be between 1 and 100nm. The nanoparticles size usually is less than 100nm. The properties of materials of these sizes have unforeseen dissimilarity from the behavior in bulk material of the same. This opens up new application areas. This change in behavior is due to increased relative surface area and also the increasing dominance of quantum effects. The physicochemical properties of nanomaterials depend on their shape and size. The interesting properties that change with size and shape are chemical reactivity, melting point, optical and magnetic properties and specific heat¹. Nanoceramic composites are multiphase solid materials where one of the phases has one, two or three dimensions of less than 100 nm, or structures having nanoscale repeat distances between the different phases that make up the material. In the broadest sense this definition can include porous media, colloids, gels and copolymers, but is more usually taken to mean the solid combination of a bulk matrix and nanodimensional phase differing in properties due to dissimilarities in structure and chemistry. The mechanical, electrical, thermal, optical, electrochemical, catalytic properties of the nanocomposite will differ significantly from that of the component materials. Size limits for these effects have been proposed, <5 nm for catalytic activity, <20 nm for making a hard magnetic material soft, <50 nm for refractive index changes, and <100 nm for achieving superparamagnetism, mechanical strengthening or restricting matrix dislocation movement. In mechanical terms, nanocomposites differ from conventional composite materials due to the exceptionally high surface

to volume ratio of the reinforcing phase and/or its exceptionally high aspect ratio. The reinforcing material can be made up of particles. The area of the interface between the matrix and reinforcement phase is typically an order of magnitude greater than for conventional composite materials. The matrix material properties are significantly affected in the vicinity of the reinforcement.

Perovskite - Ferroelectric Materials

Many oxide structures are based on close packing of cations and anions. A somewhat different structure occurs where large cations are present, which can form a close packed structure along with the oxygen ions. Calcium titanate (CaTiO_3) is the first compound to be classified as a Perovskite invented by Russian geologist Perovskiy. The commonly studied ferroelectrics have the cubic Perovskite structure (in paraelectric phase) with chemical formula ABO_3 . For convenience, the structure drawn in Fig.1 as A-site cations occupying the corners of a cube, and B-site cations on the body center. Three oxygen atoms per unit cell are on the faces. The lattice constant of these Perovskite is always close to $4a$ (where ' a ' is the lattice constant). Because, the rigidity of oxygen octahedral network and well defined oxygen ionic are having radii of 1.350 Å. The A-site cation has 12- and B-site cation has 6- coordinates. The site-A cation is generally bigger than the site-B cation. The oxygen anion has 6 as the coordination number. All the ions assumed as hard spheres, and the lattice parameter ' a ' of the cubic Perovskite is given by

$$a = 2(r_{A(12)} + r_{O(6)})/\sqrt{2} \quad \dots(1)$$

or

$$a = 2(r_{B(6)} + r_{O(6)}) \quad \dots(2)$$

as shown in Fig. 1 (a) and (b). Here, $r_{A(12)}$, $r_{B(6)}$ and $r_{O(6)}$ are the ionic radii of the 12-coordinated site-A cation, 6-coordinated site-B cation, and 6 - coordinated oxygen anion respectively. The stability of the Perovskite structure can be described geometrically as the ratio of Eq. (1) to Eq. (2), called as the tolerance factor - 't'. It is given by

$$t = \frac{r_{A(2-N)} + r_{O(6-N)}}{\sqrt{2(r_{B(6-N)} + r_{O(6-N)})}} \quad \dots(3)$$

It is advantageous if the A- and B-site cations are in contact with oxygen anions for an ABO_3 compound for forming a steady Perovskite structure. Thus, if the tolerance factor $t \gg 1.0$, then the Perovskite structure is more stable. An advantage of the Perovskite structure is that different cations could be substituted on both A and B site without any drastic change in the overall structure. Complete solid solution is easily formed between many cations, often across the entire range of composition. Simple solid solutions are basically of two types: substitutional solid solutions and interstitial solid solutions. In substitutional solid solutions, the atom that is being introduced directly replaces an atom of the same charge in the parent structure. In case of interstitial solid solutions, the introduced species occupies a site that is normally empty in the crystal structure. Even though two cations are compatible in the solution, their individual behavior can be radically different when apart. Thus, it is possible to change the properties of the materials like Curie temperature, piezoelectric coefficient etc. with a small substitution of given cation.

Ferroelectric And Magnetic Materials

Magnetic and Ferroelectric materials are the customary subjects of research area and have been leading the most significant technological advances in these days. These materials have several applications in modern technology. For example, the consumers' electronic products are generating huge data and are stored as regions of opposite magnetic polarization in ferromagnets. The sensors industry depends mostly on ferroelectrics materials. Many ferroelectric materials are also ferroelectric – i.e., A change in their electric polarization is accompanied by a change in shape. Consequently, they are used to convert sound waves into electrical signals in sonar detectors. In actuators they convert electrical impulses into motion. Ferro-electricity and Magnetism are concerned with off centre structural distortions of the material and local twists. These two apparently unrelated phenomena may coexist in certain odd materials. These materials are known as multiferroics²⁻¹⁴. The word “electromagnetism” derives from the fact that the magnetic and electric

fields are interdependent. A changing magnetic field produces an electric field, whereas an electric current, produces a magnetic field (Biot-Savart law). Electromagnets are coiled wire or loops, which are bulky and difficult to fabricate. The magneto-electric effect in a solid i.e., the induction of magnetization by means of an electric field and the induction of an electric polarization (P) by magnetic field are observed by Pierre Curie¹⁵. He studied the analogy of the electromagnetic phenomena in solids and in vacuum. This analogy is significant from the standpoint of applications. The efficient control of magnetism by an electric field in a solid could help the technology of spintronics used for magnetic random access memory and magnetic storage.

Ferroelectricity

Ferroelectrics are the materials that have two or more equilibrium orientations of impulsive polarization vector in the absence of an external electric field. The spontaneous polarization vector may be switched between these two orientations by an electric field¹⁶. Two main types of a ferroelectric behavior can be distinguished – displacive and order-disorder. The displacive type behavior is due to an ion getting displaced from the equilibrium position. Hence it acquires a permanent dipole moment. At high temperatures ($T > T_c$, where T_c is a ferroelectric Curie temperature), the thermal energy is sufficient to allow the ions to move randomly from one position to another, so there is no fixed asymmetry. When the temperature is below T_c , the ion is frozen in an off-center position. This gives a net dipole moment. In an order-disorder ferroelectric, a dipole exists in each unit cell. But at high temperatures, they are pointing in random directions. When the temperature is lowered, the dipoles get arranged in order and become aligned in the same direction within a single domain.

Ferroelectric polarization hysteresis loop shown in (Fig.2) is the characteristic of ferroelectric material, which arises due to the presence of ferroelectric domains in the crystal. Application of an external DC electric field, $E > E_c$ (where E_c -coercive field) to a polydomain ferroelectric crystal, causes the polarization. The vectors P , having different orientations in different domains, to align themselves parallel to the field direction via the domain wall movement. The minimum value of the DC field,

required to move the domain walls, is a measure of the coercive field. The initial value of the vector P_s in a polydomain crystal increases with increasing DC field to a maximum value which is a characteristic of the material. Reversing the electric field reintroduces movement of domain walls. This results in the vector P_s in different regions to be reversed. At zero current fields, the crystal will have a remnant polarization, which is smaller than the spontaneous polarization. At fully reversed field, the final P_s will have the same magnitude as the original P_s but with opposite sign. The hysteresis loop is a function of the work required to displace the domain walls, which is closely related to the defect distribution in the crystal and to the energy barrier separating the different orientations.

According to their symmetry, crystals can be divided into the 32 point groups with 11 of them being centrosymmetric (non-polar) and 21 lacking an inversion center (polar). Lack of inversion center is a pre-requisite for the piezoelectric behavior of the crystal. The crystal lacking a centre of symmetry will have a net displacement of the negative and positive ions with respect to each other resulting in an electric dipole. For the centrosymmetric crystals, the centers of the two opposite charges will always coincide, so that there is no electric dipole generated. Out of the twenty piezoelectric classes, only ten, possessing a unique polar axis which can be spontaneously polarized, belong to ferroelectrics. Among all the ferroelectric materials, which are studied the Perovskite ferroelectrics are the most extensively and widely used. A perfect Perovskite structure has a general formula of ABO_3 , where A represents a divalent or trivalent cation, and B is a tetravalent or trivalent cation. The origin of ferroelectricity in this class of materials can be explained using the well-known example of $BaTiO_3$. $BaTiO_3$ is a ferroelectric material with a Perovskite structure as shown in Fig.3. It is the first discovered piezoelectric ceramic¹⁷.

$BaTiO_3$ has a cubic structure above Curie temperature T_c , 120°C. Cubic $BaTiO_3$ is nonferroelectric because, the centers of negative and positive charges overlap as the ions are symmetrically prearranged in the unit cell. It has tetragonal structure below T_c , in which the O^{2-} ions in the $BaTiO_3$ crystal are shifted in the negative C-direction, while the Ti^{4+} ions are shifted in the

positive C-direction. It results in an electric dipole along the C-axis. Therefore $BaTiO_3$ is ferroelectric in tetragonal structure. The behavior of the spontaneous polarization of ferroelectrics can be explained by thermodynamic (Landau-Ginzburg-Devonshire) theory [16, 18]. In the basic Landau-Ginzburg-Devonshire theory, one assumes that the free energy may be expanded in a power series of the order parameters of the system. For a ferroelectric, the macroscopic order parameter is polarization P .

$$F(P, T, E) = -EP + a_0 + \frac{1}{2}a_1P^2 + \frac{1}{4}a_2P^4 + \frac{1}{6}a_3P^6 + \dots \quad \dots(4)$$

Where the coefficients a_n are temperature dependent. This series does not contain terms in odd powers of P if the un-polarized crystal has a center of inversion symmetry. The value of P in thermal equilibrium is given by the minimum value of F as a function of P ; differentiating the equation above with respect to P gives:

$$\frac{\partial F}{\partial P} = 0 = -E + a_1P + a_2P^3 + a_3P^5 + \dots \quad \dots(5)$$

The coefficient a_1 takes the form $a_1 = \tilde{a} (T - T_0)$, where $\tilde{a}$ is a positive constant and T_0 may be equal to or lower than the phase transition temperature, T_c . The assumed form of a_1 is a necessary result of mean field theory and its validity is supported by the experimentally observed Curie-Weiss law. A small positive value of a_1 indicates that the lattice is "soft" and close to instability. A negative value of a_1 indicates that the un-polarized state is unstable.

When a_2 is positive, we can neglect the a_3 term. The polarization for zero fields can be found from Eq.6.

$$g(T - T_0)P_s + a_2P_s^3 = 0 \quad \dots(6)$$

$$P_s^2 = \frac{g}{a_2}(T_0 - T)$$

So that either $P_s = 0$ or

For, $T > T_0$, $P_s = 0$ since $\tilde{a}$ and a_2 are positive. Therefore, T_0 is the Curie temperature. For

$T < T_0$, the minimum of the free energy in zero field is at

$$|P| = \sqrt{\frac{g}{a_2}(T_0 - T)} \quad \dots(7)$$

Which is plotted in Fig.4(a). Changes in the free energy and polarization at the transition temperature are continuous and it is a second order transition. When $\hat{a}_2$ is negative, the transition is of first order. We must retain $\hat{a}_3$ and take a positive value to ensure that F converges. The equilibrium condition for $E = 0$ in this case is:

$$g(T - T_0)P_S + a_2 P_S^3 + a_3 P_S^5 + \dots = 0 \quad \dots(8)$$

So that either $P_S = 0$ or

$$g(T - T_0) + a_2 P_S^2 + a_3 P_S^4 + \dots = 0. \quad \dots(9)$$

At the transition temperature T_C , the free energies of the paraelectric and ferroelectric phases are equal. The existence of meta-stable phases during the phase transition is characteristic of first order transitions. Correspondingly, a sudden jump in polarization occurs at T_C as shown in Fig. 2.3 (b). In the present study an attempt is made for the synthesis and characterizations of BiFeO_3 and BiFeO_3 with CrFeO_4 for different percent compositions discussed in chapters 4 and 5 respectively.

Multiferroic Materials & Magneto-electric Effect

As per definition, a single-phase Multiferroic⁵ material is one, which consists of 2 or all 3 of the 'ferroic' properties: i.e., ferroelectricity, ferroelasticity and ferromagnetism. On the other hand, the current tendency is to eliminate the requirement of ferroelasticity, but to include the possibility of ferrotoroidic order. Furthermore, the classification of a Multiferroic is widening to include antiferroic order. The magneto-electric effect is defined as the induction of polarization by means of a magnetic field and induction of magnetization by an electric field. Magneto-electric coupling may exist, whatever be the nature of magnetic and electrical order parameters. For example this occurs in paramagnetic ferroelectrics¹⁴. Magneto-electric coupling may

occur directly between the two order parameters, or indirectly via strain. The nontrivial spin-lattice coupling in these multiferroics has been manifested through various forms, like linear and bilinear magneto-electric effects^{19, 20}, polarization change through field-induced phase transition^{21, 22}, magneto-dielectric effect^{8, 10}, and dielectric anomalies at magnetic transition temperatures^{11, 12}.

Magnetoelectric multiferroics have all the potential applications of both their parent ferroelectric and ferromagnetic materials²³. Specific applications, that have been proposed for such materials include multiple-state memory elements, magnetic field sensors, electric-field-controlled ferromagnetic resonance devices, and transducers with magnetically modulated piezoelectricity. The ability to couple with either the magnetic or the electric polarization offers an extra degree of freedom in the design of conventional devices. It was initially proposed that both magnetization and polarization could independently encode information in a single multi-ferroic bit. Four-state memory has recently been demonstrated²⁴, but in practice, it is likely that the two order parameters are coupled^{20, 9}. Coupling could permit data to be written electrically and read magnetically. This is attractive, since it would use the best aspects of magnetic data storage and FeRAM.

In the early 1894, Curie¹⁵ claimed that symmetry conditions enable the bodies containing asymmetric molecules to be polarized in a magnetic field and, magnetized in an electric field. The existence of magneto-electric materials was first experimentally observed in an un-oriented Cr_2O_3 crystal by Astrov in 1960²⁵. Rado and Folen then revealed the anisotropic nature of the magneto-electric effect in oriented Cr_2O_3 crystals^{26, 27}. Smolensky *et al*²⁸ experimentally proved the existence of magneto-electric effect in a solid solution of $\text{PbFe}_{2/3}\text{W}_{1/3}\text{O}_3$ - Pb_2MgWO_6 . Zhdanov *et al.* independently confirmed the existence of magneto-electric Perovskite materials based on a study on the PbTiO_3 - BiFeO_3 and BiFeO_3 ²⁹⁻³¹ systems. Later, a magneto-electric effect was revealed in other structures and more and more systematic studies were undertaken^{7, 34, 32}.

BiFeO_3 , with its magnetic and electrical properties has created interest as the material with

many applications. It was expected to form a new type memory by the combination of ferromagnetic and ferroelectric properties. Tabares-Munoz *et al*³³, observed the ferroelectric/ferroelastic single domain using polarized light microscopy. After this observation, the controversy surrounding the ferroelectric nature in BiFeO₃ was solved. BiFeO₃ is reported to exhibit about a weak ferromagnetic ordering and eight structural transitions^{34, 35}. The neutron diffraction studies are conducted at room temperature. This revealed that BiFeO₃ has compensated anti-ferromagnetic ordering ($T_N \sim 397^\circ\text{C}$) with a cycloidal spin arrangement, which is disproportionate with its lattice³⁶. In BiFeO₃, the ferroelectric phase is stable up to 836°C . It is very difficult to observe ferroelectric loop at room temperature because of the low resistivity of the sample. The measurements are done at 80KV by Teague *et al*³⁷, to enhance the resistivity and observe a hysteresis loop. They obtained a loop on a single crystal, with a spontaneous polarization of 3.5 mC/cm² in the (100) direction. The existence of Bi₂Fe₄O₉ as an additional impurity phase in spite of adopting the improvised method suggested by Sosnowska *et al*³⁷ and Achenbach *et al*³⁸ is represented by several investigations. Synthesis by microwave-hydrothermal technique is reported to give rise to pure binary oxide³⁹. Forming a solid solution of BiFeO₃ with other ABO₃ type of Perovskite helps to reduce the impurity and enhances the resistivity^{40, 41}. This enables the study of physical properties of BiFeO₃ rich phases and extrapolation of the data to the pure compound. In present work, an attempt is made to study the effect of sintering temperature on electrical and structural properties of BiFeO₃ ceramics, prepared using sol-gel technique.

CRFe₂O₄ - BiFeO₃ Perovskite Multiferroic Materials

It is emphasized that the Multiferroics are a rare class of materials, since ferroelectricity and ferromagnetism make them an exclusive group. Presently, they are a hot research area in view of the many novel applications. Equilibrium contributions of the two phases like ferrite and ferroelectric form magneto-electric composites. These materials are used in sensors, transducers, switching devices and data storage⁴². In addition to the potential application as magneto-electric devices, they are likely to find applications as microwave absorption

materials also due to magneto-electric coupling⁴³. Perovskite-type BiFeO₃ is one of the multiferroics with both ferroelectric ($T_c=1103\text{K}$) and G-Type anti-ferromagnetic ($T_N=643\text{ K}$) nature⁴⁴⁻⁴⁷. In BiFeO₃, Bi-O orbital hybridization due to Bi 6s² lone pair is responsible for the ferroelectric instability, while Fe-O-Fe anti-symmetric Dzyaloshinskii-Moriya exchange gives rise to a complicated magnetic order⁴⁸. The low resistivity of the BiFeO₃ ceramics is mainly caused by existence of Fe²⁺ and oxygen deficiency⁴⁹. The selection of ferrite and ferroelectric materials depends on factors like high magnetostriction coefficient, piezoelectric coefficient, high dielectric permeability and poling strength. CrFe₂O₄ is an IIB-type half-metal material. Its molecular magnetic moments are about 5.6 μ_B which is higher than that of Fe₃O₄, 4.0 μ_B ⁵⁰.

From a theoretical study of cat-ion distribution of CrFe₂O₄, it is observed that it has Fe³⁺ at tetrahedral site, Fe²⁺ and Cr³⁺ at octahedral site⁵¹. Till now, scholars have synthesized nanocomposites of ferrites (CuFe₂O₄, CoFe₂O₄ and ZnFe₂O₄) with PZT/BaTiO₃/BiFeO₃ both in bulk and thin films in order to enhance the Multiferroic properties⁵²⁻⁵⁴. An important property is the coupling between electrical and magnetic dipole. The coupling can be induced by magneto-electric effect. Understanding the coupling between the magnetic and dielectric properties of nanocomposites is a hot area of research. The ultimate goal of controlling the magnetic/dielectric state using electrical/magnetic field requires that both these properties are coupled. The magneto-electric couplings of most of the materials are normally weak at room temperature. Hence, it is difficult to find a material with a large magneto-electric effect at room temperature. To find out the materials which have large magneto-electric effect at room temperature a lot of research is started now^{55, 56}. Very few papers have been reported on CrFe₂O₄-BiFeO₃ spinel-perovskite nanocomposite. Therefore in the present a systematic study is carried out on structural, dielectric, magnetic and magneto-electric properties of nanocomposites $x\text{CrFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ with $x = 0.0, 0.1, 0.2, 0.3$ and 0.4 synthesized by sol gel technique.

Experimental Procedure

As discussed in the above sections, the properties of BiFeO₃ phases are studies and

extrapolated to set the properties of the pure compound. An attempt is made to estimate the effect of sintering temperature on electrical and structural properties of BiFeO_3 ceramics prepared using sol-gel technique by Ratnakar Pandu *et al*⁶⁷. In their experiment, BiFeO_3 is made by sol-gel technique. All reagents are in the analytical grade. $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, citric acid and ethylene glycol are used as starting materials. In the first step, in the distilled water, an aqueous solution of citric acid is made. Then bismuth and ferric nitrates are added

to this solution with thoroughly mixing at 60-70°C. This is mention to get a homogeneous mixture and to avoid precipitation. Thus a brown color citrate mixture is obtained with clear solution and without precipitation. Then the citric acid/ethylene glycol in the ratio of 60:40 is added to the solution. Subsequently the solution is heated at 600°C for 5 hours. Initially this solution was started to swell and filled the beaker by producing a foamy precursor. This foam contains light and homogeneous flakes of tiny particles. The formation of BiFeO_3 is checked by XRD technique with Cu K_α radiation ($\lambda=0.15418$ nm), using a BRUKER D8 XRD spectroscope. The surface grain distribution and composition analysis of BiFeO_3 samples were studied using Field Emission Scanning electron micrographs (FESEM), Quanta 200 attached with Energy dispersion X-ray spectrometer (EDAX). Thermo-gravimetric (TG) and differential thermal gravimetric analysis are conducted and checked the stability and phase transformation in the samples. To study ferroelectric hysteresis behavior, a modified Sawyer–Tower circuit is used.

Similarly, Spinel-perovskite nano-composites of $x\text{CrFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ with x values taken as 0.0, 0.1, 0.2, 0.3 and 0.4 are synthesized by sol-gel process (synthesized samples are shown in Fig.5). All reagents are taken on the basis of analytical grade, $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, ethylene glycol and citric acid are used as starting materials. Suitable molar metal nitrates are fixed at the proportions of Cr: Fe: Bi, ratios of 1:11:9, 2:12:8, 3:13:7, 4:14:6 for x values 0.1, 0.2, 0.3, and 0.4 respectively. Hydraulic press, Weighing balance and hot air oven are used for preparation of these samples. An aqueous solution

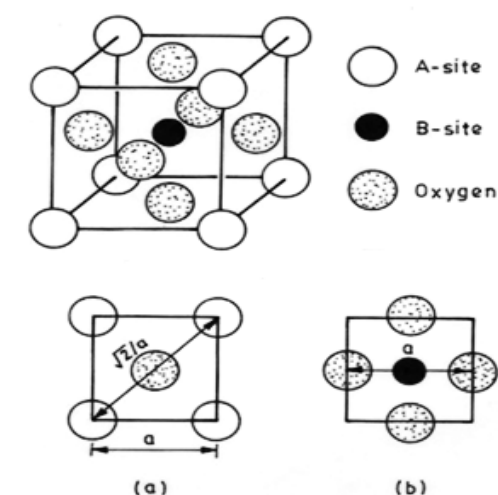


Fig. 1: Structure and geometrical details of Cubic ABO_3 Perovskite for Lattice Parameter 'a'.

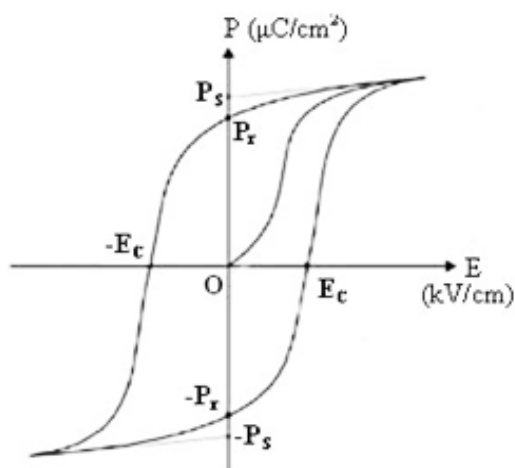


Fig. 2: Hysteresis loop showing polarization switching in Ferroelectric materials

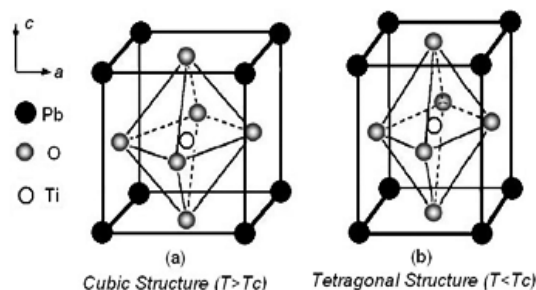


Fig. 3: Perovskite structure

of citric acid is made in the distilled water. Then chromium nitrate, bismuth nitrate and ferric nitrate are added to this solution by continuous stirring at 60-70°C. This keeps with no precipitation and obtained a homogeneous mixture. A clear solution of brown color of the citrate mixture thus obtained without precipitation. Then ethylene glycol is added to this solution, with ethylene glycol/ citric acid in the ratio of 40:60. On complete evaporation of water by heating the solution on a hot plate, a gel is formed. Then the gel is decomposed at different temperatures in the range of 400°C - 700°C. The gel initially started to swell and filled the beaker producing a foamy precursor consisting of very light and homogeneous flakes of very small particle size. Structural characterization and particle morphology study of the synthesized powder is conducted using XRD by monochromatic Cu K α radiation and TEM respectively. The dielectric measurements are

carried out on silver coated pellets using HIKOI-3532 LCR Hi-Tester. Magnetic measurements are carried out at room temperature using a VSM (vibrating sample magnetometer) with a maximum magnetic field of 5kOe. Variations of dielectric constant as a function of magnetic field are also studied.

RESULTS AND DISCUSSIONS

BiFeO₃ is the rhombohedrally indistinct perovskite material. This belongs to the space class $R3c$, with rhombohedral lattice parameters $a_R=5.63$ Å and $\alpha_R=59.35^\circ$. In other words it has hexagonal parameters $a_{\text{hex}} = 5.58$ Å, $c_{\text{hex}} = 13.87$ Å⁵⁹⁻⁶¹. Preparation of phase-pure BiFeO₃ is difficult because of its narrow temperature range of phase stabilization. Different impurity phases are reported, mainly Bi₂Fe₄O₉, Bi₁₂(Bi_{0.5}Fe_{0.5})O_{19.5} and Bi₂₅FeO₄₀,

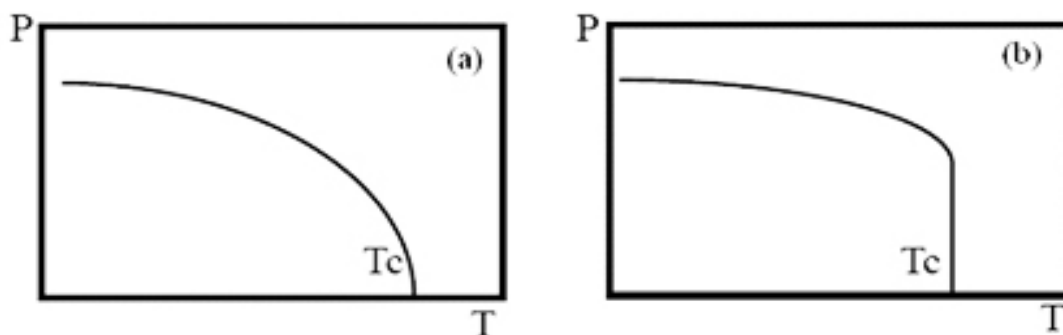


Fig. 4: Polarization vs. temperature plot for (a) second order and (b) first order phase transitions.

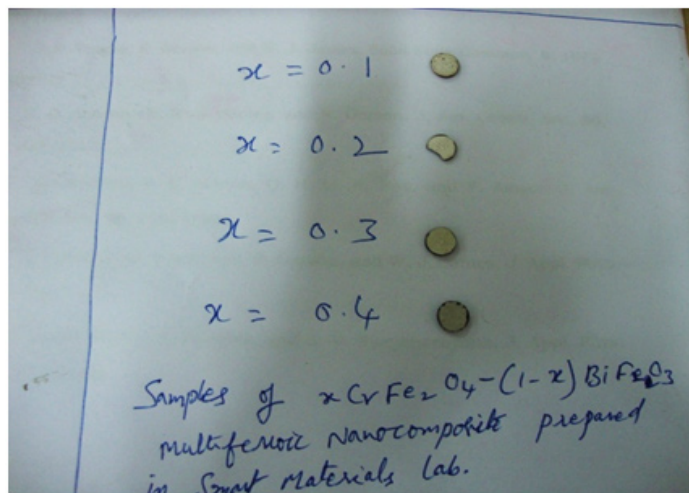


Fig. 5: Samples of $x\text{CrFe}_2\text{O}_4-(1-x)\text{BiFe}_2\text{O}_3$ Multi-ferroic Nanocomposite

since BiFeO_3 is metastable with respect to $\text{Bi}_2\text{Fe}_4\text{O}_9$ (mullite phase) and $\text{Bi}_{25}\text{FeO}_{39}$ (sillenite phase)^{62, 63}. The presence of these impurities results in leakage current in BiFeO_3 . It results in poor ferroelectric property and thus causes to be this material is not suitable for practical applications. The available methods, for formation of phase-pure BiFeO_3 with improved multi-ferroic properties are (a) forming solid solution of BiFeO_3 with other ABO_3 type of perovskites like PbTiO_3 ^{64,65} (b) calcinations of stoichiometric mixture of Bi_2O_3 and Fe_2O_3 followed by discharging with nitric acid [66] and (c) rapid liquid phase sintering of BiFeO_3 ^{67, 68}.

Selbach *et al.*, on the basis of thermodynamics have suggested that isovalent substitution with a larger cat-ion on the A site or a smaller cation on the B site would increase the stability of BiFeO_3 relating to the binary oxides and

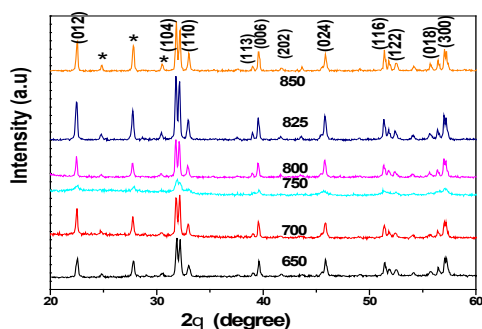


Fig. 6: XRD patterns for BiFeO_3 at different sintering temperature [where (*) Bi_2O_3]

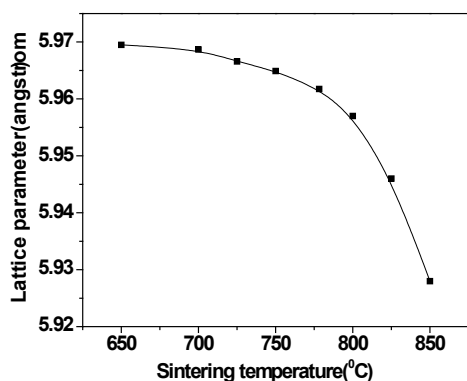


Fig. 7: Variation of Lattice parameter ' a_R ' with sintering temperature plot for BiFeO_3 .

possibly also relating to the $\text{Bi}_2\text{Fe}_4\text{O}_9$ mullite and $\text{Bi}_{25}\text{FeO}_{39}$ sillenite phase^{69, 70}. Substitution of a more acidic cation on the B site or a more basic cation on the A site is also expected to stabilize the perovskite phase. They also reported that La^{3+} is about the same size as Bi^{3+} , and although the space group changes with high substitution levels, perovskite phase is obtained with up to 40% La^{3+} . Rare earth ions are smaller than Bi^{3+} , but more basic cat-ions, hence the stable solid solutions prepared at ambient pressure have been reported up to 15-20% substitution⁷¹⁻⁷⁴. Fig.6. shows the XRD patterns of BiFeO_3 , sintered at 650, 700, 750, 800, 825 and 850°C. From the XRD pattern, it is noted that the major peaks of all sintered samples belong to rhombohedrally fuzzy perovskite BiFeO_3 (R-phase), although tiny amounts of Bi_2O_3 were detected due to excessive Bi used for compensating volatilization during synthesis. Moreover, the formation of BFO (R-phase), the formation of the minor impure phases, like $\text{Bi}_{46}\text{Fe}_2\text{O}_{72}$ (non perovskite paramagnetic phase shown by * symbol) was detected from the XRD analysis. BiFeO_3 is a metastable composite and because of its chemical kinetics of formation. It is always associated with some impurities which do not contribute for the observed magnetic and dielectric properties, as reported by several research scholars^{75, 76}. The phase analysis is carried out by taking into account the hexagonal BFO unit cell. This unit cell of BFO system consist two formula pseudocubic units cells of BiFeO_3 . The lattice parameters for rhombohedral unit cell of BiFeO_3 are calculated from the indexed XRD pattern for BFO samples sintered at 850°C

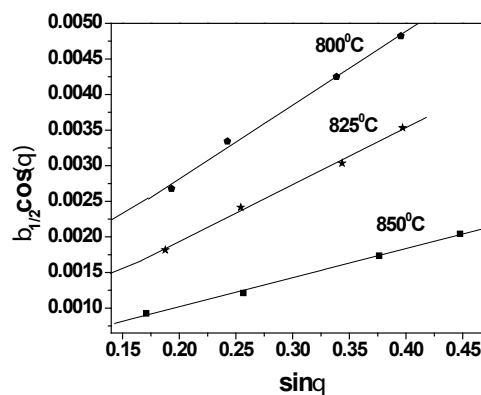


Fig. 8: $\beta_{1/2} \cos q$ vs. $\sin q$ plot for BiFeO_3 .

as shown in Fig.6. Using 2θ values from the XRD graph and (hkl) values from the standard JCPD-86-1518 card the lattice parameters for the unit cell are generated. The calculated values of the lattice parameters for the hexagonal unit cell of BiFeO_3 matched well with the values reported in the literature [60, 61] which is in the range of which is in the range of 5.5575 – 13.861 Å.

The variation of lattice parameter ' a_R ' with sintering temperature is given in Fig.7. From the plot of lattice parameter, it is found that with increasing sintering temperature the lattice parameter ' a_R ' decreases for BiFeO_3 . In this research work the Williamson–Hall approach is used for de-convoluting crystallite size and strain contribution to the X-ray line broadening ($\hat{a}_{1/2}$) in the present materials since the Scherrer's formula does not take the strain contribution into account. According to this approach,

the X-ray line broadening is a sum of the contribution from small crystallite size and the broadening caused by the lattice strain present in the material⁷⁷, i.e.

$$\beta_{1/2} = \beta_{\text{size}} + \beta_{\text{strain}} \quad \dots(10)$$

where $\beta_{\text{size}} = \lambda/L \cos\theta$ (from Scherrer's formula) and $\beta_{\text{strain}} = 4\eta \tan\theta$; where η is strain

$$\text{Therefore Eq.10 becomes } \beta_{1/2} = \lambda/L \cos\theta + 4\eta \tan\theta \quad \dots(11)$$

$\beta_{1/2} \cos\theta/\lambda = 1/L + T \sin\theta/\lambda$, where $T = 4\eta$, is a measure of strain present in the lattice. Hence by plotting $\hat{a}_{1/2} \cos\theta$ vs. $\sin\theta$, it is found that the crystallite size from the intercept of the line at $x = 0$. The lattice strain and crystallite size is calculated from Fig.8. using the above explained expression

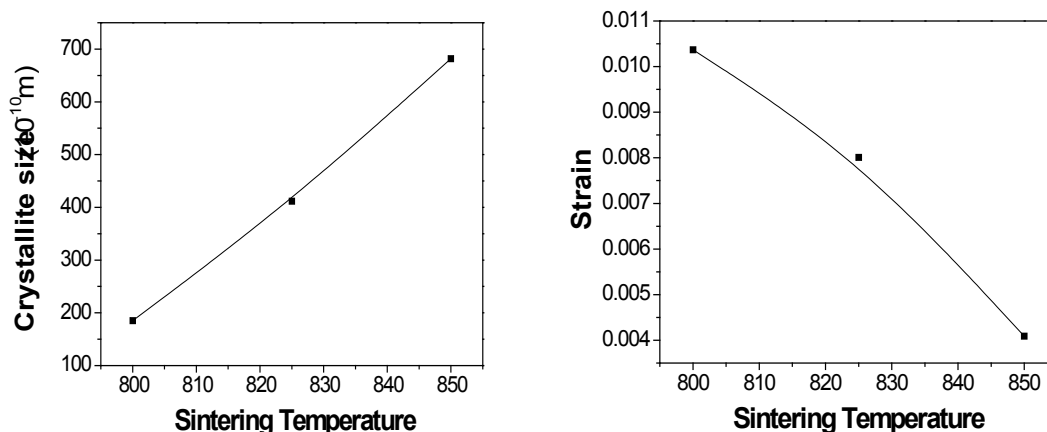


Fig. 9: (a) variation of Crystallite size with temperature and (b) Variation of Strain with sintering temperature plot for BiFeO_3

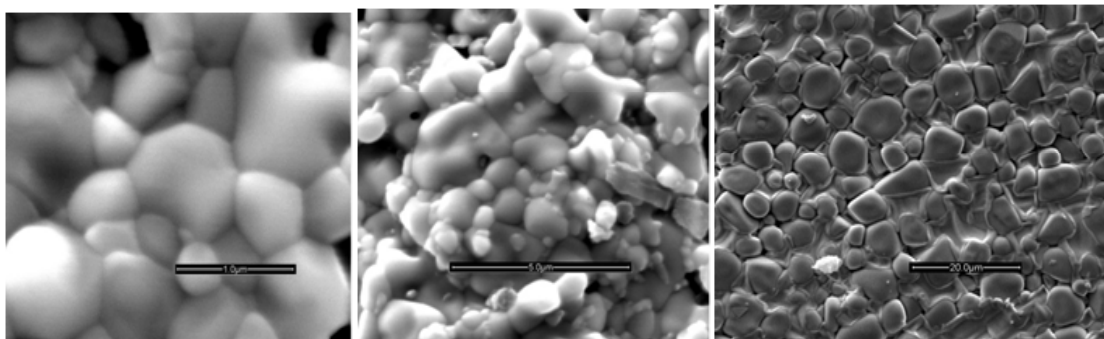


Fig. 10: SEM images of BiFeO_3 sintered pellets (a) 800°C, (b) 825°C and (c) 850°C

(eq.11) for BiFeO_3 sintered at different temperatures. The variation of crystallite size and strain with different temperature are plotted in Fig.9. (a) and (b) respectively.

From the plot of crystallite size verses sintering temperature, it is found that with increasing sintering temperature crystallite size increases and strain decreases. Fig.10. shows the FESEM micrographs of BiFeO_3 sintered at different temperature. The microstructures of the sintered BiFeO_3 pellets specified spherical grains, which are uniformly and homogeneously distributed. These microstructures also reveal that the sintered pellets are reasonably dense. Also, it was found that the edges of the grains are not sharp, which shows melting like behavior resembling liquid phase sintering.

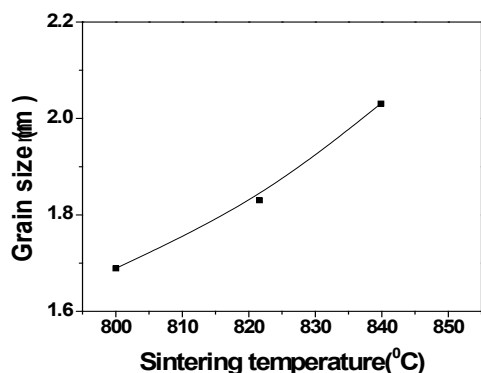


Fig. 11: Variation of Grain size with temperature plot for BiFeO_3

The Fig.11 is shown the variation of grain size with sintering temperature. Grain size measurement is complicated by a number of factors. First, the three-dimensional size of the grains is not constant and the sectioning plane will cut through the grains at random. Thus, on a cross-section it is observed a range of sizes, none larger than the cross section of the largest grain sampled. Grain shape also varies, particularly as a function of grain size. So the intercept approach is applied for measuring grain size. In this method, one or more lines are superimposed over the structure at a known magnification. The true line length is divided by the number of grains intercepted by the line. This gives the average length of the line within the intercepted grains. This average intercept length will be less than the average grain diameter but the two are interrelated. Grain size was observed to increase

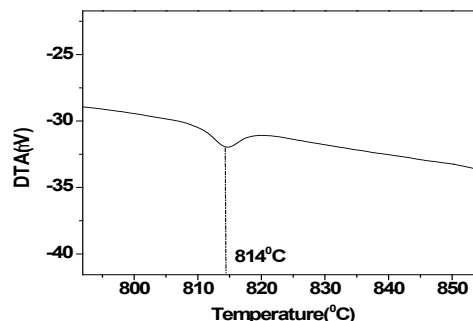


Fig. 12: DTA analysis curve

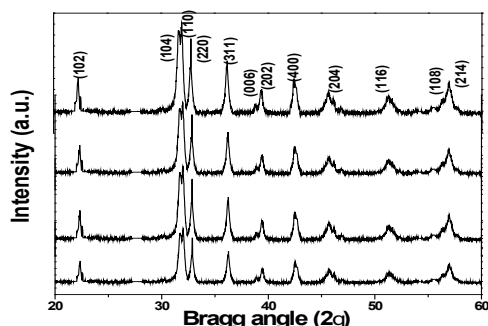


Fig. 13(a) X-ray diffraction for nanocomposites of $x\text{CrFe}_2\text{O}_4 - (1-x)\text{BiFeO}_3$ for $x=0.1, 0.2, 0.3$ and 0.4

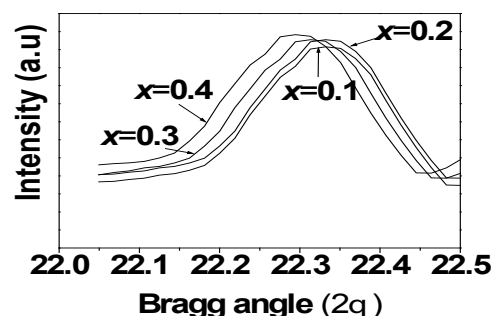


Fig. 14(b) XRD patterns for nanocomposites of $x\text{CrFe}_2\text{O}_4 - (1-x)\text{BiFeO}_3$ for $x=0.10, 0.20, 0.30, 0.40$. Showing peak shift as concentration of CrFe_2O_4 is increased indicating lattice distortion.

with increase in sintering temperature. This happens because as the sintering process continues at higher temperatures, the individual powder particles lose their identity completely and grain boundaries move across prior particle boundaries. Larger grains replace the original fine particle structure which influences the dielectric and electrical properties of the samples. In order to observe the phase transition temperature, the DTA curve of BFO is shown in Fig.12. Ferroelectric to paraelectric transition temperature (T_c) was detected by DTA analysis, which shows that the Curie temperature of pure BiFeO₃ is 814°C which is very close to the ideal value (827°C) found by dielectric measurement⁷⁸.

Fig: 13(a) shows XRD pattern of nanocomposites of $x\text{CrFe}_2\text{O}_4 - (1-x)\text{BiFeO}_3$ with $x=0.1, 0.2, 0.3, 0.4$ (samples in Fig.5) powder annealed at 700°C for two hours. At 700°C possible peaks of BiFeO₃ and CrFe₂O₄ have been formed. All the peaks positions are well matched in the XRD pattern of CrFe₂O₄ and BiFeO₃ which are able to be identified to appear from the spinel structure of the CrFe₂O₄ and BiFeO₃ presenting that the samples are formed in pure composite phase. Fig: 13-b shows that peaks are shifted to lower Bragg angles as concentration of CrFe₂O₄ is increased indicating lattice distortion.

Fig: 15(a) demonstrates the SEM image of Nanocomposite 0.2CrFe₂O₄-0.8BiFeO₃ which

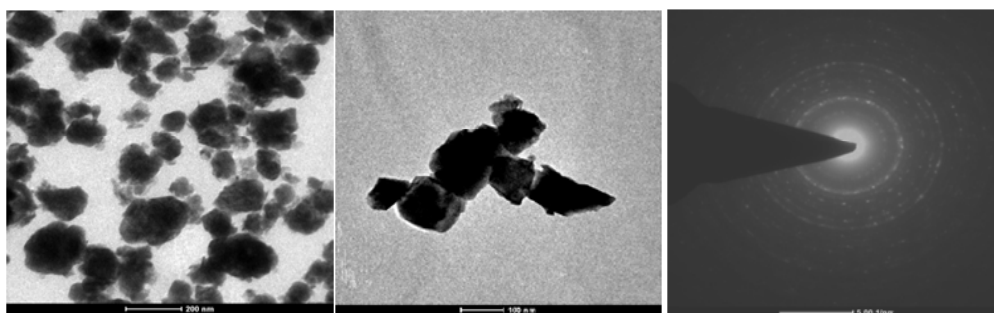


Fig. 15: (a) SEM image (b) Particle size: 100nm (c) SAED

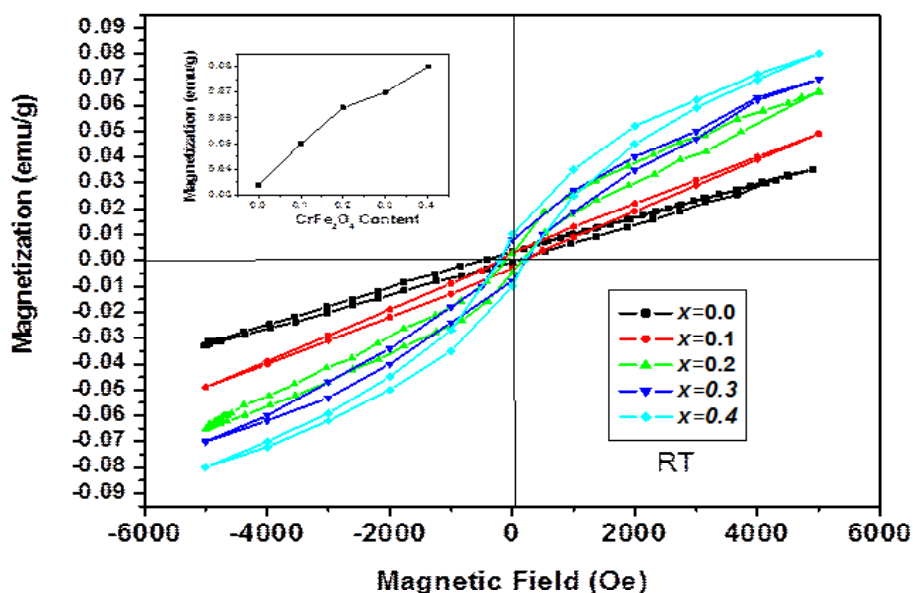


Fig. 16: Variation of magnetization with magnetic field for $x\text{CrFe}_2\text{O}_4 - (1-x)\text{BiFeO}_3$ at room temperature

is annealed at 700°C and the average particle size is found to be ~100 nm as shown in Fig: 15(b). Fig: 15(c) demonstrates the SAED pattern, which are the reflections of the spinel phase of (CrFe_2O_4) and Perovskite phase (BiFeO_3). The diffuse diffraction spots confirm the nano-size of the synthesized material. Variation of magnetization of nanocomposite as a function of CrFe_2O_4 is shown in Fig: 16. The increase of CrFe_2O_4 concentration in nanocomposites shows the increase in magnetization which has also been reported for CoFe_2O_4 - BiFeO_3 nanocomposites [171].

Fig: 17 shows variation of dielectric constant (ϵ') and dielectric loss ($\tan\delta$) with frequency for the nanocomposites $x\text{CrFe}_2\text{O}_4$ -(1-x) BiFeO_3 with $x=0.00, 0.10, 0.20, 0.30$ and 0.40 . Due to Maxwell-Wagner [80, 81] type interfacial polarization the low value of the dielectric constant at high frequency and the high value of dielectric constant at low frequency indicate large dielectric dispersion. This is in agreement with Koops phenomenological theory⁸². The high values of dielectric constant at lower frequencies may be explained on the basis of space charge polarization due to inhomogeneities present in dielectric structure viz. porosity in the nanocomposite system.

Decrement of dielectric constant for nanocomposites with $x=0.10, 0.20, 0.30$ and 0.40 may be accepted on the basis of Ginzburg-Landau theory. This explains the origin of anomaly in dielectric constant (ϵ') on the magnetic order of ferroelectromagnets with $T_M \ll T_E$. The difference of the dielectric constant ($\Delta\epsilon'$) below temperature T_M will be proportional to square of the magnetic order parameter i.e., $\Delta\epsilon' \sim \tilde{a}M^2$, where M is magnetization. The sign of $\Delta\epsilon'$ depends on the sign of the constant magneto-electric interaction ($\tilde{a}$). It can be either positive or negative⁸³.

The dielectric constant variation (Fig: 18(a)) with the applied external magnetic field (0-9kOe) is found to be above 0.05% for $x=0.2, 0.3$, which is high compared to other reported values [84]. This indicates the presence of coupling effect at room temperature for nanocomposite $x\text{CrFe}_2\text{O}_4$ -(1-x) BiFeO_3 , which might have been induced by magneto-electric coupling. Magneto-capacitance is found to decrease at higher field for $x=0.2$ and 0.3 . It is low for $x=0.4$ compared with $x=0.2$ and $x=0.3$. The change of the dielectric constant (ϵ') under the variation of magnetic field can be induced by magneto-electric coupling effect as well as other factors such as magnetostriction effect. This occurs due to the

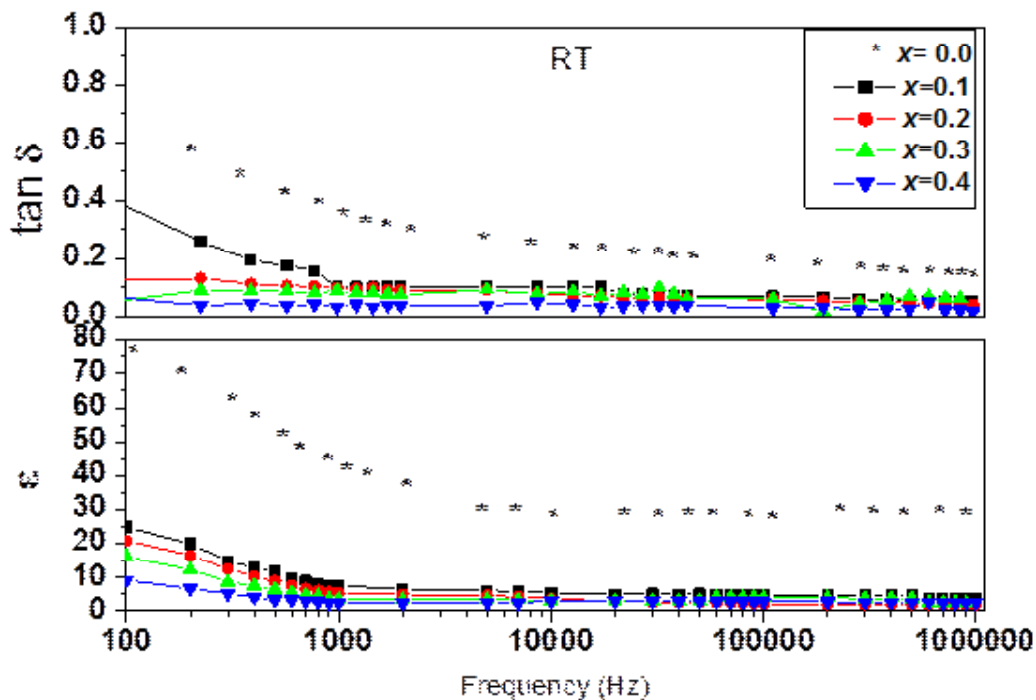


Fig. 17: Variation of Dielectric constant and Dielectric loss with frequency (at room temperature)

change in lattice parameters on applying magnetic field. The change in the sample dimension by the magnetic order, i.e., magnetostriction, might be considered as the origin of the observed magneto-capacitance. This factor may be considered for $x=0.4$. Also, It has been reported that the magnetic domain rotation least affects the dielectric constant at low temperature⁶⁵.

Fig: 18(b) and (c) illustrates the temperature dependence of dielectric loss and dielectric constant at 1 kHz frequency for nanocomposites respectively. One broad peak (!) is observed at around 180°C for $x=0.4$ nanocomposite. This peak is shifted to lower temperature as concentration of CrFe_2O_4 increased. This peak shift may be ascribed to structure distortion

due to ferrite phase. This peak could be one of the six transitions reported by Khijch *et al*⁶⁶ and Pajak *et al*⁶⁷. BiFeO_3 has the transition at $T_N = 397^\circ\text{C}$. This is not clearly evident in the Fig: 18(b) because of the high dielectric loss in the samples. These losses could be due the conducting behavior of the nanocomposites at higher temperatures, possibly due to the thermally activated conductivity. In BiFeO_3 , oxygen deficiency is an inherent problem. Hence space charge polarization is always present. However, due to the thermally activated process, there is considerable increase in space charge polarization and material conductivity at higher temperature⁶⁸. Hence, the peak at 397°C is not clearly marked in the nanocomposites with $x=0.1, 0.2, 0.3$ and 0.4 .

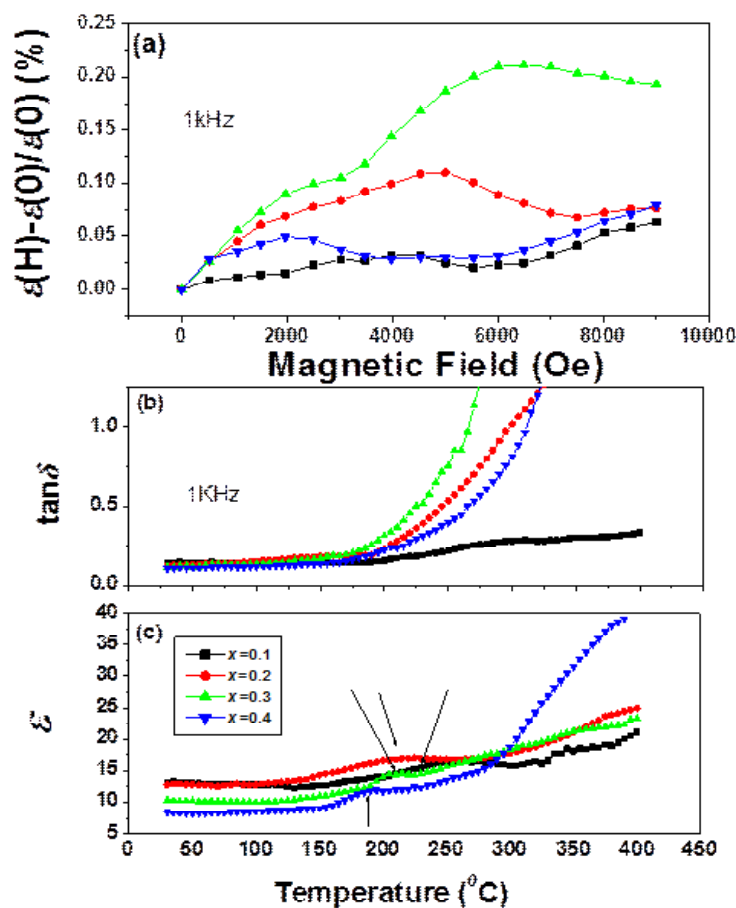


Fig. 18: Variation of magneto-capacitance (a) with magnetic field at room temperature, dielectric loss (b) and dielectric constant (c) with temperature respectively

CONCLUSIONS

The following conclusions are drawn from the present research work.

1. Synthesis of BiFeO_3 is carried out at low temperature using sol-gel method.
2. From the X-ray Diffraction pattern it is seen that
 - i) The crystallite size increases with increase in sintering temperature.
 - ii) The strain in the crystallite decreases with increase in sintering temperature.
 - iii) The crystallite size increases with increasing temperature the lattice parameter decreases.
3. From an SEM micrograph, it is shown that the samples are homogeneous and that the grain size increases with increasing sintering temperature and the particle size follows the Gaussian distribution.
4. The DTA analysis shows that the Curie temperature of pure BiFeO_3 is 814°C which is closer to that of ideal temperature 827°C .
5. In the experiment $x\text{CrFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ with $x = 0.0, 0.1, 0.2, 0.3$ and 0.4 , the XRD and thermal analysis confirmed that at 700°C the phase was formed. The particle size observed in TEM is about $\sim 100\text{nm}$.
6. The change of dielectric loss and dielectric constant with frequency confirmed distribution in the range of low frequency.
7. The Magnetization is estimated and observed the ferrite concentration and annealing

temperature. Dielectric analysis confirms the conducting behavior at high temperatures.

8. Magneto-capacitance is estimated in the prepared nano-composites. This approves the presence of magneto-electric coupling in the synthesized nano-composites at room temperature.

Scope for the Future Work

The research work reported in this paper mainly deals with the preparation by an economical methods and characterizations of some BiFeO_3 , CeFe_2O_3 - BiFeO_3 nanocomposites and Carbon Nanotubes. Multiferroics are the potential keystones in upcoming magnetic data storage and spintronics devices provided a simple and fast way can be found to turn their electric and magnetic properties on and off. The present experimental study on synthesis and characterizations of $x\text{CrFe}_2\text{O}_4-(1-x)\text{BiFeO}_3$ Multiferroic nanocomposites, with $x = 0.0, 0.1, 0.2, 0.3$ and 0.4 can be used as reference work and be extended for further studies with different 'x' values for different properties. Further, this work can be extended to study the carbon nanotubes may be reinforced into BiFeO_3 nanoceramics and convert to metallically conductive composites. By using spark-plasma-sintering method [89], we can fabricate nanocrystalline BiFeO_3 matrices that retain the integrity of SWCNT in the matrix. The conductivity of these composites increases with increasing content of CNTs.

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