

Capitalizing multiferroic properties of BiFeO₃ for spintronics

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Abstract: Pure BiFeO₃ ceramic was successfully synthesized by auto combustion technique. The prepared sample was characterized by X-ray diffraction (XRD), Scanning electron Microscopy (SEM), Vibrating sample magnetometer (VSM), dielectric studies and ferroelectric studies. The sample was confirmed to have perovskite type rhombohedral structure with space group R3C. The sample is found to be reasonably dense from the micrograph of BiFeO₃. Magnetic measurements showed antiferromagnetic behavior. The existence of magnetoelectric coupling was indicated by the observation of the dielectric anomaly in the dielectric constant and dielectric loss near antiferromagnetic Neel temperature. Ferroelectric polarization indicates low resistive leakage. All these properties make BiFeO₃ promising for application in the field of spintronics.

Keywords: Auto combustion, Bismuth ferrite, Multiferroic, Magnetoelectric & X-ray diffraction.

I. Introduction

Multiferroics are a class of materials which showcase exotic coupling between three different orders of parameters viz. ferromagnetism, ferroelectricity and ferroelasticity. Multiferroics are being investigated intensively since past decade on account of their potential applications right from magnetic data storage memories, sensors, actuators to spintronic devices [1-8]. As a matter of fact, there is a scarcity of materials which exhibit multiferroic nature. Fundamentally the usual atomic level mechanism propelling ferromagnetism and ferroelectricity are mutually exclusive as they stand in need of empty and partially filled transition metal orbitals respectively [9-10]. Multiferroics with perovskite structure like ABO₃ are of much significance as they contain transition metals at both A & B site. In this case ferroelectricity originates due to transition metal 'A' with empty d orbit while magnetism is produced by transition metal 'B' with partially filled d orbit. Dismally, there are very few multiferroics which exhibit this kind of atomic-level mechanism at room temperature. BiFeO₃ is considered the most assuring candidate on the grounds of ferroelectricity (T_c ≈ 1100K) and antiferromagnetism (T_N ≈ 643K) exhibited in single phase at room temperature [11]. BiFeO₃ possesses a rhombohedrally distorted perovskite structure with space group R3C at room temperature [12]. Bismuth ferrite possesses G-type antiferromagnetic ordering because of its complex cycloidal spin structure with a wavelength of 62nm with [110] spiral direction and (110) spin rotation plane [13]. A canting of the antiferromagnetic sublattice results in weak ferromagnetism due to the orientation of magnetic moment perpendicular to [111] direction [14]. However BiFeO₃ suffers from several major issues like phase defects such as oxygen vacancies and impurity, high leakage current, spiral spin structure, large difference in transition temperature (T_c & T_N). Attempts have been made to find possible structural transition, consequently to improve physical properties by partial substitution of Bi³⁺ ions with rare earth ions [15-21]. In order to reduce leakage current density efforts have been made by using different fabrication methods. Several techniques have also been recently adopted to eliminate secondary phases and oxygen vacancies [22-26]. Particle size also plays a vital role in controlling the structural and magnetic properties of BiFeO₃ [27]. In this paper, we present our work on synthesis of pure phase BiFeO₃ prepared by auto-combustion method using Urea as fuel.

II. Experimental

The BiFeO₃ ceramic was prepared by auto-combustion synthesis. The chemical Bi(NO₃)₃·5H₂O, Fe(NO₃)₃·9H₂O and Urea used were analytical reagent grade and used without further purification. Stoichiometric amount of metal nitrate (Oxidizer) and fuel when ignited undergo self propagating, gas producing combustion reaction to yield voluminous metal oxide in less than 5 min. The as synthesized samples were crushed and grinded in an agate mortar [28]. The oxidizer/fuel ratio was figured on the basis of oxidizing valencies of the metal nitrates and reducing valency of the fuel.

The sample was then characterized by using various techniques. X-ray powder diffraction data was collected using an XPERT-PRO diffractometer with Cu K α radiation ($\lambda = 0.15456\text{nm}$) at step of 0.02 in the range $2\theta = 20^\circ$ to 80° . The magnetic properties were measured by a vibrating sample magnetometer (Lakeshore VSM 7410) at room temperature. Dielectric measurements were performed on an impedance analyzer (Weynn Kerr 6500 B) for which the sintered sample was mechanically pressed in hydraulic press and an Ag paste was applied to both sides of the polished pellets.

III. Result And Discussion:

3.1 Structural Analysis

Room temperature powder x-ray diffraction was carried out on BiFeO₃. All the peaks could be indexed in the rhombohedral distorted perovskite structure with space group-R3c. In order to confirm the crystal structure, the diffraction pattern was Rietveld refined using FULLPROF program. The profile fits for the Rietveld refinement of BiFeO₃ sample is shown in fig [1]. The simulated XRD pattern of sample coincides well with measured XRD pattern. The XRD pattern of BiFeO₃ was refined with rhombohedral R3C space group with lattice parameters $a = 5.573$ & $c = 13.862$, which are in agreement with the values reported earlier [27].

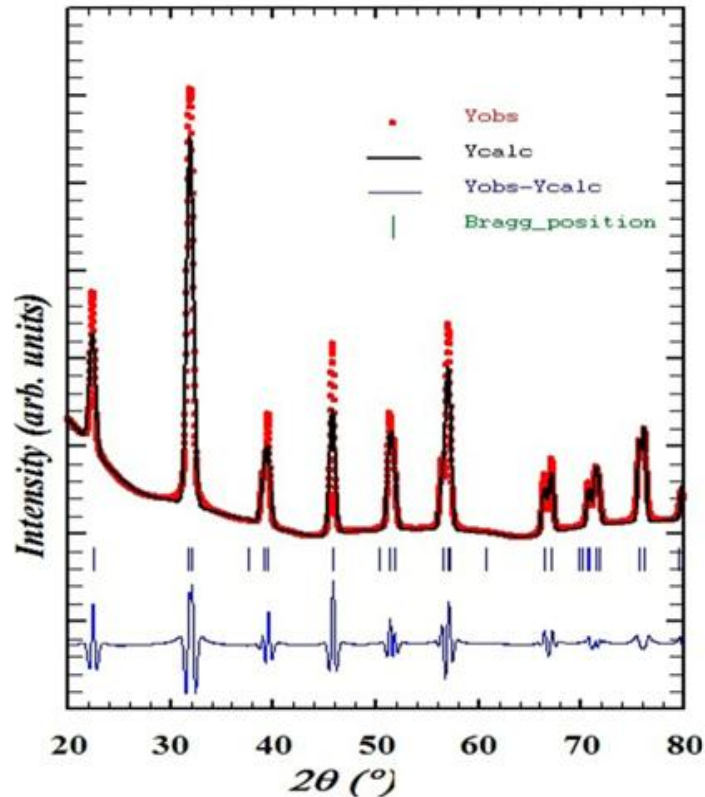


Fig [1] The XRD pattern of pure BiFeO₃

3.2 Microstructural Analysis:

Fig.[2] shows the SEM micrograph of BiFeO₃ ceramic. The micrograph reveals that the sample is reasonably dense and uniform. The grain size is found to be in the range of >500nm, which may affect the Neel temperature and in turn could affect the electrical properties.

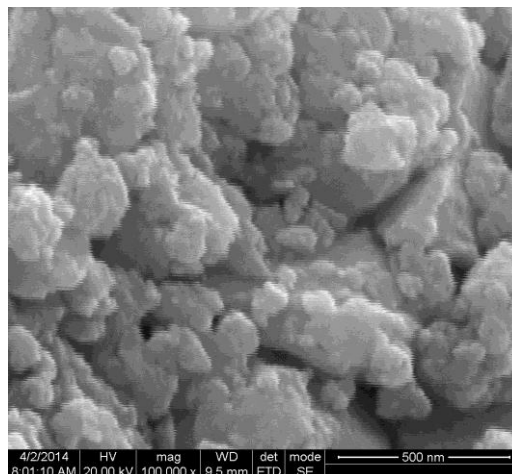


Fig [2] SEM micrograph of BiFeO₃ ceramic

3.3 Magnetic properties:

Room temperature measurement of the magnetization of pure BiFeO₃ as a function of applied magnetic field is shown in fig [3]. The pure BiFeO₃ has a linear character without any spontaneous magnetization, thereby confirming the antiferromagnetic nature of the sample. The sample exhibits very low magnetization with almost zero hysteresis. This antiferromagnetic behavior is due to two spin sublattices with ferromagnetic interaction within each sublattice and antiferromagnetic intersublattice interaction [29]. BiFeO₃ exhibits a complex magnetic configuration with antiferromagnetic spin order of G-type ordering where each Fe³⁺ with spin up is surrounded by six nearest neighbors with spin down. This kind of structure is rather spatially modulated, demonstrated by an incommensurate cycloidal structure of wavelength of nearly 62nm. The spiral spin propagation wavevector is along the [110] directions and the polarization is along the [111] directions. These two directions describe the (112) cycloidal plane where the spin rotation occurs. On account of this characteristic the antiferromagnetic vector is secured within the cycloid and gives rise to weak magnetization in BiFeO₃. The spin exchange interaction in BiFeO₃ is frustrated and can undergo a transition which provides a suitable mechanism for the magnetoelectric effect. This picture is supported by anomaly observed in temperature dependent dielectric constant measurements.

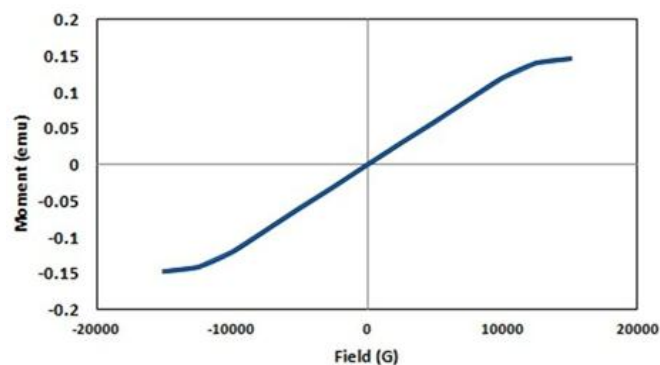


Fig [3] The M-H plot of BiFeO₃ at 300k.

3.4 Dielectric properties:

Fig [4 & 5] shows the temperature dependence of the dielectric constant and dielectric loss at zero bias field and frequency of 100Hz. The dielectric constant is found to be strongly influenced by Maxwell –Wagner relaxation, which is usually observed in transition metal oxides [30]. The dielectric constant exhibits continuous increase in temperature with an explicit anomaly observed in the vicinity of Neel temperature in BiFeO₃ samples. This anomaly specifies a phase transition from antiferromagnetic to paramagnetic phase of BiFeO₃ and also manifests a possible coupling between electric and magnetic dipole of BiFeO₃ which is a signature of magnetoelectric coupling where the coupling is between two ising type orders, namely the ferroelectric order and the coupled magnetic order of antiferromagnetic chains and makes BiFeO₃ a promising material for spintronics[31].

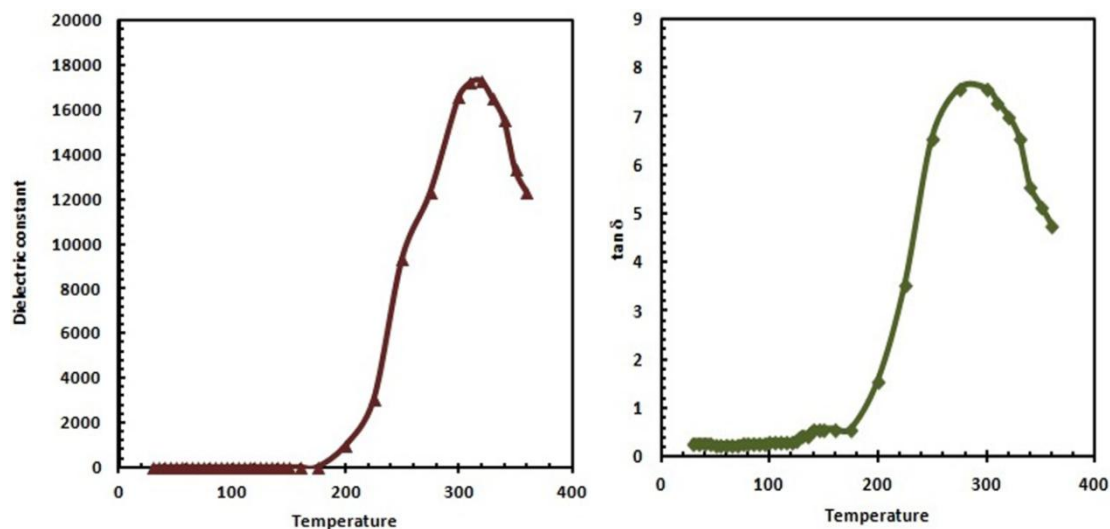


Fig [4 & 5] Temperature dependent dielectric constant and tanδ of BiFeO₃ at 100Hz

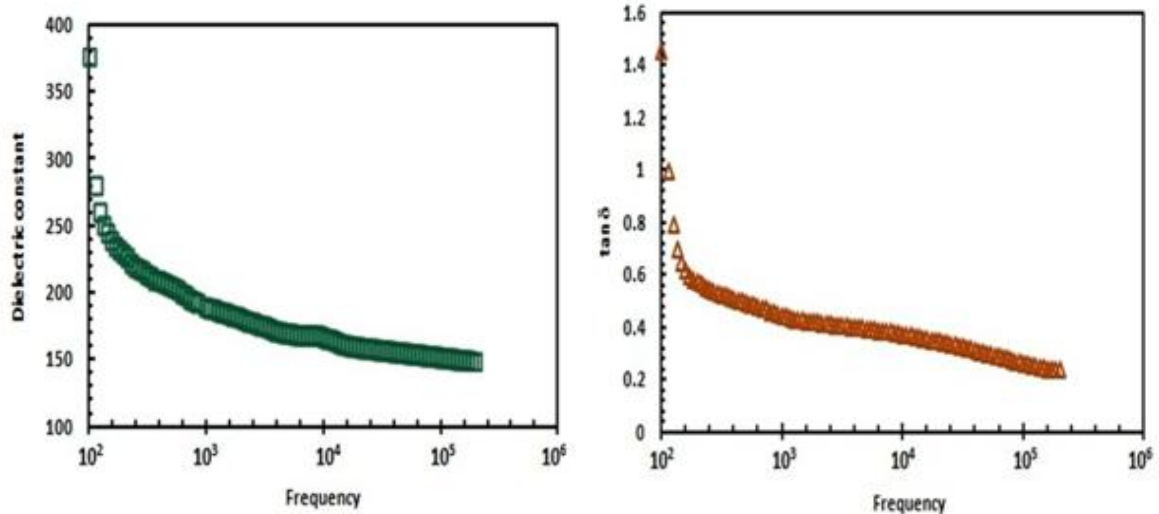


Fig [6 & 7] Frequency dependent dielectric loss of BiFeO₃ at 300K

Fig [6 & 7] shows the dielectric constant and dielectric loss as function of frequency of BiFeO₃ at room temperature. Both dielectric constant & loss are found to decrease with increase in frequency in lower frequency range. In this particular range of frequencies all polarizations are present, however the space charge polarization is noticeable according to the theory of dielectric polarization. On increasing the frequency further, both dielectric constant and loss become almost constant. The initial decrease in the values with increasing frequency demonstrates the dispersion due to Maxwell-Wegner type interfacial polarization which goes along with Koop's phenomenological theory [32]. The value of dielectric constant is quite higher for our sample compared to some of the BiFeO₃ prepared by other synthesis techniques [33 & 27]. The enhanced value of dielectric constant may be attributed to dense microstructure with distinct grain and grain boundary structures.

1.5 Ferroelectric properties:

The polarization versus electric field (P-E) hysteresis loop of BiFeO₃ ceramic at room temperature with different applied field is shown in figure [8] at frequency of 50Hz. The P-E loop is not saturated for our measurement system. The loop is quite narrow indicating low resistive leakage. From the P-E loop it can be predicted that dielectric loss or leakage current is imperceptible, which is in good agreement with our dielectric results.

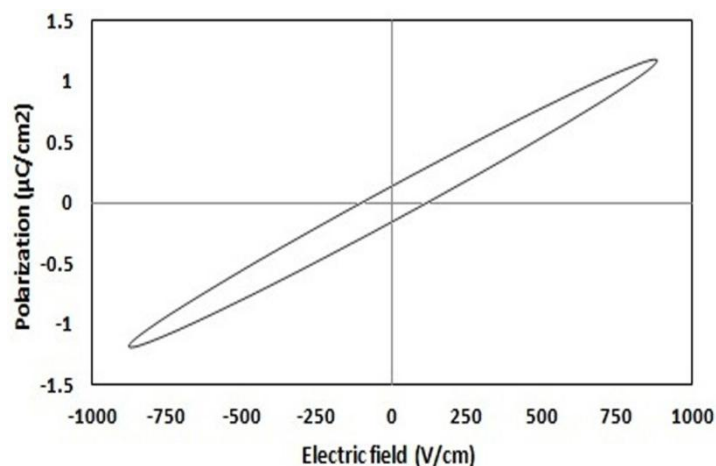


Fig [8] Ferroelectric hysteresis loop of BiFeO₃ at 50Hz.

IV. Conclusion:

BiFeO₃ ceramic was successfully synthesized using Auto-combustion technique. The X-ray diffraction spectrum reveals rhombohedral perovskite structure of sample. Magnetic measurement confirms the antiferromagnetic nature of Bismuth ferrite. A noticeable change in the dielectric constant near Neel temperature showed the magnetoelectric coupling between electric and magnetic orders. P-E loop indicates fairly good

ferroelectric properties for our sample, which makes BiFeO₃ a potential candidate for application in the field of spintronics.

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