

Physical Properties of Multiferroic Ceramic

Gaurav Verma

Sree Vidyanikethan Engineering College, Tirupati, India

Abstract: *In this work, we have synthesized the bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ (BFO9) using conventional solid state reaction technique. We present the crystallographic, microstructural, electrical, and magnetic properties of orthorhombic ($Pbam$) structured bulk BFO9. BFO9 have been investigated using a variety of complementary techniques such X-ray diffraction, Raman spectroscopy, scanning electron microscopy, dielectric as well as magnetometry. Rietveld refined X-ray diffraction data and Raman spectroscopy results clearly reveal the formation of BFO9 perovskite structure and all the peaks of BFO9 perfectly indexed in the orthorhombic ($Pbam$) structure. Raman spectrum identifies A_g , B_{2g} , and B_{3g} active optical phonon modes whereas Raman peak at 470 cm^{-1} are might have a magnetic origin. As a result, coexistence of weak ferromagnetic and antiferromagnetic orders in BFO9 ceramics with remnant magnetization and coercivity ($2M_r$ and $2H_c$) of $8.74 \times 10^{-4}\text{ emu/g}$ and 478.8 Oe , respectively, were established. We report remarkable multifarious effects in polycrystalline BFO9 ceramic. These properties make this material very useful in technical and practical applications.*

Keywords: Multiferroic; $\text{Bi}_2\text{Fe}_4\text{O}_9$; Raman spectroscopy; Magnetic measurement

I. INTRODUCTION

The materials those display more than one of the primary ferroic order in same phase simultaneously are known as multiferrois. Recently, there has been a great deal of interest in systems exhibiting coupling between magnetic, electronic, and orbital degrees of freedom. Researches based on perovskite oxides have gained popularity due to their interesting structural, magnetic, optical, and electronic properties. Bismuth iron oxide (*i.e.* $\text{Bi}_2\text{Fe}_4\text{O}_9$) is an important functional material due to its potential applications as a magnetic recording media, semiconductor gas sensor magneto-resistive devices and a promising catalyst for ammonia oxidation, photo-catalyst, which will possibly replace the high-cost, shortag and unrecoverable loss of catalysts [1-4].

Basically, $\text{Bi}_2\text{Fe}_4\text{O}_9$ crytallizes in orthorhombic ($Pbam$) phase and belongs to family of mullite-type crystal structures [5]. A unit cell of $\text{Bi}_2\text{Fe}_4\text{O}_9$ contains two formula units with evenly Fe ions distributed between octahedral (FeO_4) and tetrahedral (FeO_4) sites. In addition, Bi^{3+} ions are surrounded by eight oxygen ions. Bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ has shown an antiferromagnetic ordering at $T_N \approx 260\text{ K}$ and display ferroelectric hysteresis loops at $T \approx 250\text{ K}$ is indicating that it is a promising multiferroic material. An unexpected multiferroic effect, which is observed as a coexistence of antiferromagnetism and ferroelectric polarization, was reported in $\text{Bi}_2\text{Fe}_4\text{O}_9$, attributed to frustrated

spin system coupled with phonons [6]. Low electrical conductivity in ferrites is useful for inductor, transformer cores and in switch mode power supplies. On the other hand, studies of electric and dielectric properties are also equally important from both fundamental and application point of view. Dielectric and magnetic behavior of ferrites is greatly influenced by an order of magnitude of conductivity and is mostly dependent on preparation method and sintering conditions [7].

Here, we presents the structure and physical properties of bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic synthesized by a solid-state reaction route. One requires detailed knowledge of the crystal structure to understand the physical properties. We thus aimed to understand the crystallographic structure by X-ray powder diffraction. Additionally, $\text{Bi}_2\text{Fe}_4\text{O}_9$ was subsequently characterized using several experimental techniques such as Raman spectroscopy, SEM, dielectric, ferroelectric as well as magnetometry and discussed in details.

II. EXPERIMENTAL DETAILS

Bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic sample was synthesized by solid-state reaction technique. High purity Bi_2O_3 , Fe_2O_3 were carefully weighed and stoichiometrically mixed in an agate mortar for 5 hours. The powder was doubly calcined consecutively at 650 °C for 1 hour and 850 °C for 6 hours with intermediate grinding in between to achieve desired phase. Finally, pellets were sintered at 850 °C for 6 hours, resulting in good densification.

For crystallinity and phase identification X-ray diffraction (XRD) pattern were taken using $\text{CuK}\alpha 1$ radiation ($\lambda = 1.5406 \text{ \AA}$) of a Bruker D8 Advance X-ray diffractometer. Crystal structure characterization of synthesized sample was performed by employing Rietveld whole profile fitting method using FullPROF software [22]. The sample morphology was investigated with a scanning electron microscope (JEOL, JSM-5600). Raman measurements on as synthesized sample was carried out on Jobin-Yovn Horiba LABRAM spectrometer with a 632.8 nm excitation source. Dielectric measurements were made as a function of frequency in the range of 100 Hz - 1 MHz on Novocontrol alpha-ANB impedance analyzer at room temperature. Ferroelectric measurement was carried out using a ferroelectric loop tracer based on Sawyer-Tower circuit. The $M-H$ curve was performed using a Lakeshore VSM.

III. RESULTS AND DISCUSSION

3.1 Crystal Structure Analysis

Room temperature XRD pattern of bulk $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample is shown in Fig. 1(a). From the XRD pattern we can indexed the data in orthorhombic phase as shown in Fig. 1(a). The present XRD patterns match well with JCPDS card No. 74-1098 ($\text{Bi}_2\text{Fe}_4\text{O}_9$) [8]. The occurrence of BiFeO_3 secondary phase peaks was generally observed in pure $\text{Bi}_2\text{Fe}_4\text{O}_9$. In order to further confirm structural data the Rietveld refinement of the XRD pattern for $\text{Bi}_2\text{Fe}_4\text{O}_9$ sample were performed using FullPROF program and shown in Fig. 1(b). The XRD pattern of parent $\text{Bi}_2\text{Fe}_4\text{O}_9$ was refined with orthorhombic ($Pbam$) structure with lattice parameters $a = 7.941(4) \text{ \AA}$, $b = 8.420(4) \text{ \AA}$ and $c = 5.986(4) \text{ \AA}$. The obtained lattice parameters are consistent with earlier reported data [9]. The Rietveld refined calculated parameters of $\text{Bi}_2\text{Fe}_4\text{O}_9$ are documented in Table 1. We have illustrated

structural parameters for $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic, and also identify the residuals for weighted pattern R_{wp} , the expected weighted profile factor R_{exp} , and goodness of fit χ^2 . The selected bond lengths and bond angles are mentioned in Table 1. The average value of the Bi-O bond is 2.482 Å. The generated orthorhombic structure of $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramics is depicted in Fig. 1(c). In the crystal structure, chains of FeO_6 octahedra parallel to the c axis are connected *via* FeO_4 tetrahedra alternating with bismuth atoms along the c axis.

3.2 SEM Analysis

The surface morphological and microstructural properties of $\text{Bi}_2\text{Fe}_4\text{O}_9$ compound was investigated using scanning electron microscopy (SEM). Fig. 2. (upper part) shows the SEM micrograph of pristine $\text{Bi}_2\text{Fe}_4\text{O}_9$ sintered at 850 °C for 10 Hours. The typical SEM image reveals that microstructures are dense comprising of non-uniform grains with varying submicron-sized particles with an average particle size of 1.0 to 3.0 μm indicating polycrystalline nature of as prepared samples. The SEM image also shows that some porosity existed among the loosely connected grains in the sample.

3.3 Raman Scattering Analysis

Raman scattering spectroscopy has been extensively utilized to study the crystal lattice vibrations. Raman scattering spectroscopy would also offer a distinctive potential as a sensitive probe for the spin dynamics and studying the effect of magnetic ordering. Raman spectrum of $\text{Bi}_2\text{Fe}_4\text{O}_9$ at room temperature is depicted in lower part of Fig. 2. The Raman active modes of the structure can be summarized using the irreducible representation $12A_g + 12B_{1g} + 9B_{2g} + 9B_{3g}$, which is employed to describe Raman modes of orthorhombic ($Pbam$ space group) [4]. In the measured Raman spectra all are the A_g modes (85, 93, 114, 210, 227, 280, 331, 366, 436, 465, 561, and 648 cm^{-1}) accept modes in attendance at 164 (B_{2g}) and 189 (B_{3g}) cm^{-1} . The agreement between experimental and predicted values is relatively good for the all frequency modes, dominated by Bi vibrations. The Raman peak centered at 470 cm^{-1} is might be attributed to magnetic ordering effect on phonon line width consistent with earlier observation of bands at ~ 260 and 472 cm^{-1} due to magnon scattering [4]. It would be more practical to study the magnetic excitations in $\text{Bi}_2\text{Fe}_4\text{O}_9$ under the assumption that they involve two-magnon processes, like in the well-known cases of ferrites [10] or cuprates [11, 12]. At higher frequency ($> 250 \text{ cm}^{-1}$), it is unlikely the magnetic-order-induced bands correspond to one-magnon excitations but in rare-earth orthoferrites ($R\text{FeO}_3$; $R = \text{Dy, Ho, Er, Sm}$ etc.) have frequencies below 25 cm^{-1} for comparison the zone-center magnons [13].

3.4 Dielectric and PE Loop Studies

The real part of permittivity (ϵ') and loss tangent ($\tan\delta$) as a function of frequency of $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramics at room temperature is shown in Fig 3(a) and (b). The value of ϵ' and $\tan\delta$ for $\text{Bi}_2\text{Fe}_4\text{O}_9$ are about 21.57 and 0.05, respectively at frequency 10 Hz. At higher frequency ($\approx 1 \text{ MHz}$) the value of ϵ' and $\tan\delta$ are 18.59 and 0.006, respectively. Dielectric behavior (*i.e.* ϵ' and $\tan\delta$) decreases with increase in frequency and it is constant at higher frequency region. From Fig 3(a)

and (b) we have found that the value of dielectric constant in the whole frequency range (10 Hz– 1 MHz) is nearly constant representing the low loss in the prepared ceramic. This result appears to be consistent with our previous empirical analysis using the Maxwell–Wagner model with thermal activation across multiple band gaps in isolated impurities [14]. Fig 3(c) shows the semilog plot of conductivity (σ) at room temperature with frequency. The study of the frequency dependence of the conductivity is a deep-rooted method for describing the hopping dynamics of the charge carrier. The conductivity plot exhibits both low and high frequency dispersion phenomena [15-18]. The low-frequency region corresponds to the *dc* conductivity (σ_{dc}), which is due to the band conduction, and it is frequency independent. The high-frequency region corresponds to the *ac* conductivity (σ_{ac}), which is frequency dependant. To conclude, the electrical conductivity σ for $\text{Bi}_2\text{Fe}_4\text{O}_9$ follows the Jonscher power law [18]: $\sigma_{ac}(\omega) = \sigma_{dc} + A(T)\omega^n$. Here, A is the pre exponential factor and n is the power law exponent. The exponent n can have a value between zero to one. This parameter is frequency independent but temperature and material dependent.

The polarization-electric field (P - E) hysteresis loop of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic at room temperature represented in Fig. 4(a). The obtained loop indicates the paraelectric behavior in as prepared sample. Under a maximum applied field 10 kV/cm, the remnant polarization ($2P_r$) of the $\text{Bi}_2\text{Fe}_4\text{O}_9$ was found to be $0.006 \mu\text{C}/\text{cm}^2$. It may be possible after substitution of some rare earth ion it may become a ferroelectric.

3.5 Magnetic (M-H curve) Analysis

From the measured M - H hysteresis loop (Fig. 4(b)) of $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic, we deduce the magnetic parameters as remnant magnetization, coercivity and saturation magnetization as ($M_r = 4.37 \times 10^{-4}$ emu/gm, $H_c = 239.4$ Oe and $M_s = 0.024$ emu/gm, respectively). In our $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic, the coexistence of antiferromagnetic and weak ferromagnetic interactions simultaneously is consistent with the earlier published data for the $\text{Bi}_{0.75}\text{Sr}_{0.25}\text{FeO}_{3-x}$ [19, 20]. A weak ferromagnetic order is seen in the low magnetic field region. The weak ferromagnetic order itself can be understood as a result of canted spin arrangements in two sublattices [21]. As the magnetic field increases, the ferromagnetic order saturates and the antiferromagnetic component dominates. There is not even any evidence of saturation. It is obvious that the little bit nonzero values of M_r and M_s are achieved in the prepared ceramic. We may note that the measured hysteresis curve confirm that the relationship between the applied field and the magnetization does not evidence a linear behavior and shows the weak ferromagnetism. In future, through the compatible doping or preparation technique we can improve the magnetization value of prepared ceramics.

IV. CONCLUSION

In summary, polycrystalline sample of pure $\text{Bi}_2\text{Fe}_4\text{O}_9$ was successfully prepared using conventional solid-state reaction route. X-ray diffraction shows that this compound has an orthorhombic ($Pbam$) symmetry. The room temperature Raman peak at 470 cm^{-1} is might be due to the magnetic origin of the material and may be related to Magnon scattering. The value of dielectric constant seems to be non-variable in the whole frequency region. Ferroelectric hysteresis as revealed in the P - E loop

measurement that the material is in paraelectric phase. Conclusively, we report remarkable multiferroic effects in polycrystalline $\text{Bi}_2\text{Fe}_4\text{O}_9$ ceramic with coexistence of antiferromagnetic and weak ferromagnetic interactions simultaneously. These obtained properties shows the potentiality of $\text{Bi}_2\text{Fe}_4\text{O}_9$ compound to use in advanced technical and practical applications.

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