

Effect of La- substitution on Structural and Dielectric Properties of Bismuth Ferrite Ceramic

Nripesh Kumar, Alok Shukla and Nitin Kumr

Department of Physics

National Institute of Technology Mizoram, Chaltlang, Aizawl-796012, Mizoram

Email: aloks.nitmz@gmail.com

Manoj Kumar Prajapati

Department of Physics

SSSVS Govt. P G College Chunar, Mirzapur-231304 (U.P.)

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Abstract: We report crystal symmetry and dielectric characteristics of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ (referred as BFLO) lead-free ceramic, synthesized by solid-state reaction technique. The XRD data supports the formation of the BFLO composite with the existence of a few impurity phase. BLFO ceramic was sintered at an optimized temperature (1123 K for 6 hrs) and shows pure orthorhombic symmetry. Structural symmetry and lattice parameters were determined and refined from the POWDMULT software of their experimental data. The dielectric parameters (dielectric constant and loss) in the high-frequency region remains unchanged. These results suggest that the BFLO composites shows potential lead-free material at room temperature. This study provides several interesting results and shows enhancement in the dielectric property may useful for device applications.

Keywords: Bismuth ferrite; Lead-free Composites; Crystal symmetry; Dielectric.

1. Introduction

Bismuth ferrite (BiFeO_3) has been subject of rigorous research with a large number of applications. Possessing a rare combination of both (anti)ferromagnetic and ferroelectric properties, coexisting at room temperature, and intercoupling between these properties, the ferrite has had an important impact in the field of multiferroics. Multiferroic materials, are being intensively studied due to their potential applications in energy

harvester, four-stage logic memory devices, magnetic field sensors, magnetoelectric random access memory (MeRAM), magnetoelectric resonator and read head¹⁻⁵. The co-occurrence of electric/magnetic ordering and adequate coupling between them deliver an extra degree of freedom in the data storage process which may either simplify the operation of currently device structure or offer new functionality into a single device. Rare-earth ferrites are among the most studied families of multiferroic materials. BiFeO₃ (BFO) is the only single-phase multiferroic material among well-studied multiferroic materials, so far exhibiting both ferroelectric ($T_c \sim 1103\text{K}$) and G-type antiferromagnetic ($T_N \sim 643\text{K}$) orderings at room temperature^{6,7}. However, bulk BFO is characterized by some inherent problems including the persistent formation of impurities phases, large leakage current, weak ferromagnetism and poor magnetoelectric coupling⁸. For bulk ceramics, two problems have puzzled researchers for a long time. First is the difficulty in the synthesis of single-phase BFO due to its metastability, non-stoichiometry, low peritectic decomposition temperature, and Bi₂O₃ evaporation. Grain size effects are a major barrier in the miniaturization and applications of ferroelectric ceramics. The ferroelectric distortion, spontaneous polarization, and Curie temperature T_c decrease with decreasing dimensions in ferroelectric ceramics. Analogously, for multiferroic materials, size effects also have a significant impact on their functional behaviour⁹⁻¹¹. It was observed that the substitution of La in BFO had significant modified electrical properties due to the reduction of oxygen ion vacancies. In addition, the substitution of La eliminates the formation of secondary phases, stabilizes the formation of La-doped BFO phase, and release the locked magnetization by suppressing the spiral spin structure of BFO. In this paper, we report on the synthesis of composition-dependent La-modified BiFeO₃ i.e., Bi(Fe_{0.7}La_{0.3})O₃ lead-free perovskite, obtained from solid-state-reaction of a stoichiometric mixture of high purity Fe₂O₃, Bi₂O₃ and La₂O₃. The investigation of the structure was carried out to optimize the calcination conditions. The effect of La doping on the elimination of the secondary phases and the dielectric properties were investigated.

2. Experimental Details

La-doped BiFeO₃ samples was synthesized by the conventional solid-state reaction method. Stoichiometric amounts of high purity bismuth oxide (Bi₂O₃, M/S Himedia, Purity: 99%), lanthanum oxide (La₂O₃, M/S Loba Chemie Co. Ltd, Purity: 99.9%) and iron oxide (Fe₂O₃, M/S Loba Chemie

Co. Ltd, Purity: 98%) was utilized as preliminary raw materials and they were carefully weighed and thoroughly mixed in an agate mortar for 2h. The mixtures were calcined in an alumina crucible at 850 °C for 6h in air followed by furnace cooling. The high-purity alumina crucible (cylindrical), boat and tray were utilized for preparing a BFLO ceramic compound. Phase identification and quantification of the samples was performed using Rigaku (Ultima IV) X-ray diffractometer using Cu $K\alpha_1$ radiation with a wavelength of 1.54056 Å. The experiment performs in the range of Bragg's angles ($20^\circ \leq 2\theta \leq 80^\circ$) with a scanning step of 0.02 step in 2θ . The electrical measurements were conducted on 1.5 mm thick pellets of 12 mm in diameter, fabricated by cold compaction of mixed powders in a uniaxial press followed by sintering at 875 °C for 2 h in air. Dielectric properties were recorded with a precision impedance analyzer (PSM N4L 1735) in the frequency window of 1 kHz–1000 kHz. The scanning electron microscope (Carl Zeiss) was used to investigate the surface morphology and particle size of the compound.

3. Structural Investigation

Figure 1 shows the power XRD pattern of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ at room temperature. Most of the peaks of the pattern are well defined and indexed by using POWDMULT indexing software. It is illustrated in the graph that most of the peaks have narrow and sharp intensities, which suggests a highly crystalline nature of the sample⁶. All the observed X-ray reflection (major) peaks were indexed and strongly satisfied perovskite structure with the orthorhombic symmetry.

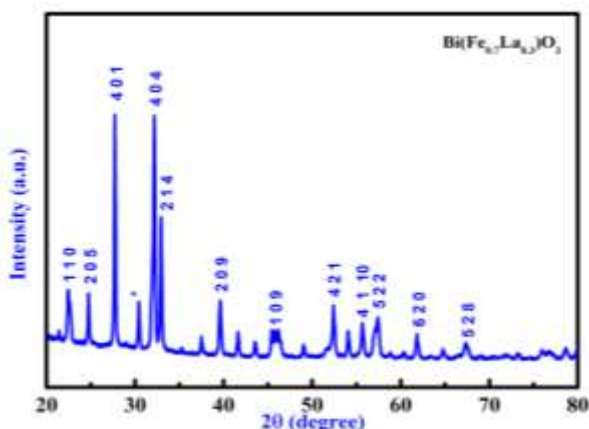


Figure 1. XRD spectra of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ ceramic

The structural stability, determined as tolerance factor (T_F) of the XYO_3 -like perovskite compounds, is based on the succeeding formalism¹²;

$$T_F = \frac{(\langle R_X \rangle + R_O)}{\sqrt{2}(\langle R_Y \rangle + R_O)}$$

Here $\langle R_X \rangle$, $\langle R_Y \rangle$ & R_O represent mean ionic radii of the X (bismuth), Y (lanthanum & iron) and O (oxygen) site(s) correspondingly. The term T_F quantifies the structural constancy of the perovskite family. For $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$, the calculated value of tolerance factor is 0.76, which proposes major distortion and deviation in said perovskite structure of the material.

4. SEM Analysis

Figure 2 represent surface morphology of the $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ compound through scanning electron microscope (SEM) at room temperature. It is clearly seen from the micrograph that the maximum grains are densely packed throughout the surface without major voids. The minor difference is in the size and shape of the grain suggests the formation of a good quality sample of BFLO. The irregularity in the grain size may persuade the structural and electrical properties of synthesized ceramic. The size and shape of grains are pretty different, which shows the existence of polycrystalline nature. Furthermore, dopant ions can be accumulated in the grain boundaries and subsequently enhance grain growth.

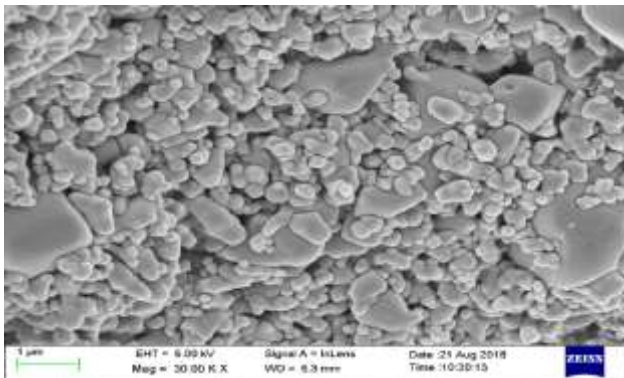


Figure 2. SEM image of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$

5. Temperature Dependence Dielectric Study

Figures 3 and 4 depicts the distinction between dielectric constant (ϵ_r) and tangent loss factor ($\tan \delta$) of the prepared compound. The dielectric graphs demonstrate that the compound possesses temperature dependent dielectric constant. Figure 3 shows the temperature dependent dielectric constant characteristics of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ at some selected frequencies. At low frequencies, all types of polarization (i.e., interfacial, ionic, atomic, dipole and so on) occur in dielectrics. Such type of polarization gradually disappears with increment in frequencies, consequently, the dielectric constant reduces. Figure 4 displays the temperature dependence tangent loss ($\tan \delta$) of $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ at some selected frequencies. The tangent loss graphs demonstrate the dependency of compounds on temperature. From the figure, we can see that lanthanum doping on Fe-site of BFO results in a lesser tangent loss. The tangent loss ($\tan \delta$) decreases with a rise in frequency for all the compositions in the entire temperature range. With the increase in frequency the position of the anomaly shifts to a higher temperature side. Both these features point to the existence of a thermally activated Debye like dipolar relaxation in the samples and is likely to be associated with the relaxation processes associated with domain reorientation, domain wall motion and the dipolar orientations of the ferroelectric materials¹³. As a consequence, the electron phonon interaction may be the main reason for increasing dielectric constant with the rise in temperature¹⁴. In addition, thermally activated scattering of charge carriers and the occurrence of oxygen vacancies may be the cause for sharp rise in the loss factor value at higher temperatures for the BFLO compound.

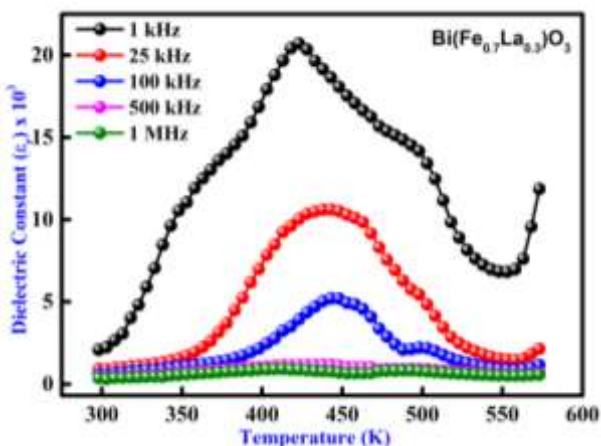


Figure 3. Temperature dependent dielectric constant

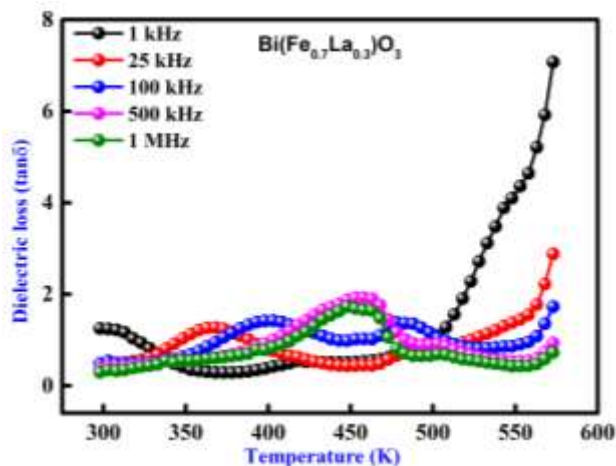


Figure 4. Temperature dependent dielectric loss

6. Conclusion

The polycrystalline sample of lead-free $\text{Bi}(\text{Fe}_{0.7}\text{La}_{0.3})\text{O}_3$ was prepared using a high-temperature solid-state reaction technique. Preliminary structural analysis and indexing of most of the reflections confirmed the formation of the material in a single phase. The FE-SEM morphology shows the uniform grain-distribution of a different dimension. The grain size of the sample was found to be of a few μm . Moreover, as prepared material shows frequency and temperature dependent dielectric nature useful for potential applications.

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