

Synthesis and Characterization of Ce Incorporated BiFeO₃-BaTiO₃ Ceramic near the Morphotropic Phase Boundary

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Abstract

Cerium-doped Bismuth Ferrite- Barium Titanate ceramics were prepared using the conventional solid-state reaction method near the morphotropic phase boundary. The synthesized samples were subjected to structural, morphological and dielectric characterization. The obtained structure was distorted perovskite, without indication of any impurity phase confirmed by X-ray diffraction. Besides, modification with cerium in small scale influenced the microstructure and dielectric property remarkably. Grain growth suppression phenomenon was observed with cerium addition. Moreover, the doped samples also exhibited improved dielectric properties. The maximum dielectric constant of around 700, had been found for $x = 0.04$.

Keywords — Cerium, BiFeO₃-BaTiO₃, Donor dopant, SEM, Dielectric properties.

I. INTRODUCTION

Advanced materials that possess two of the ferroelectric, ferromagnetic and ferroelastic properties are acknowledged as multiferroic [1]. In the world of technological advancement, these materials attracted researcher's attention most, owing to their immense applicability for ultra-modern devices such as sensors, actuators, transducers, spintronics or memory devices [2],[3]. But multiferroics are rare due to the contradictory mechanisms of ferroelectricity and ferromagnetism [4].

BiFeO₃ holding rhombohedral structure at ambient condition is a well-known multiferroic due to its appreciably high Curie temperature (~830°) and Neel temperature (~370°) [5]. But its journey has restrained by some inherent limitations such as low resistivity and high leakage current, generation of secondary phase and antiferromagnetism sourced from Dzyaloshinskii-Moriya interaction [2],[6]. To suppress the aforementioned shortcomings ionic replacement (La³⁺, Nd³⁺, Eu³⁺, Mg²⁺, Ni²⁺, Sr²⁺, Al³⁺, Sc³⁺, Co³⁺, Cr³⁺) [7] and development of solid solutions with qualified perovskite structure are well-known steps undertaken by the research group [8].

Among the modified materials, BiFeO₃-BaTiO₃ (BFO-BT) has confirmed its potential by presenting enhanced resistivity and piezoelectric response in some cases [9],[10]. But still weak ferromagnetic order and rare saturated ferroelectric hysteresis remained as a key concern [11]. In this respect modification of BFO-BT with different Rare Earth (RE) (La³⁺, Sm³⁺, Y³⁺, Dy³⁺, Pr³⁺, Nd³⁺) elements have been tried recently [12].

However to the best of our knowledge Cerium (Ce) doped BFO-BT had not been stated yet. The present investigation involved preparation and characterization (structural, microstructural and dielectric) of 70BFO-30BT-Ce- x (where $x = 0, 0.02$ and 0.04) ceramics in expectation of obtaining enhanced properties necessary for multifunctional devices.

II. EXPERIMENTAL

Using conventional solid state synthesis, the composition of (Bi_{0.7}Ba_{0.3})_{1-x}Ce_x(Fe_{0.7}Ti_{0.3})O₃ was prepared from carbonate, bicarbonate, and oxides of >99% purity with appropriate stoichiometry. The Required amount of Bi₂O₃, BaCO₃, Fe₂O₃, CeO₂, and TiO₂ were mixed for 20-22 hrs in polyethylene pots with yttria-stabilized zirconia balls and then dried in the oven. The dried powder was calcined at 800°C for 3 hrs. After the calcination, the powder was crushed finely and compacted into pellets (Dia-13mm and Thickness-1.5mm) using hydraulic press (Pellet Press PP 25, Retsch) applying around 2 tons of pressure.

Finally, the samples were sintered and taken for further characterization. The cycles for sintering and calcination are shown in Figure 1 (a) and 1(b) respectively. X-ray diffractometer (Bruker D8 Advance, Germany) was used for the structural characterization. The morphological study had been conducted using a conventional Scanning Electron Microscope (SEM) (Evo-18, Carl Zeiss, Germany). Further dielectric properties were evaluated using precision impedance analyzer (Wayne Kerr 6500B).

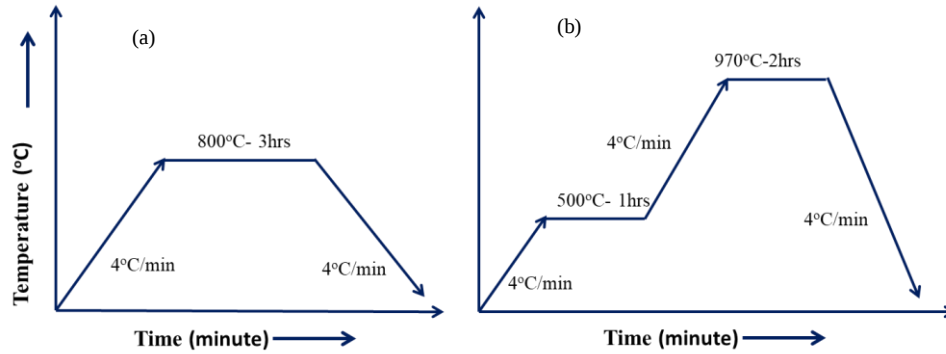


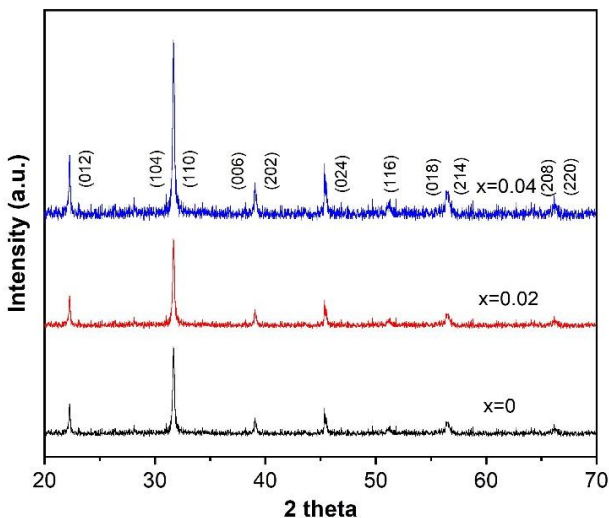
Fig 1: (a) Calcination Cycle, (b) Sintering Cycle

III. RESULTS AND DISCUSSION

A. Density Measurement

Figure 2 shows the variation of the apparent density of 70BFO-30BT-Ce- x ceramics with concentration of cerium. Dopants have a strong effect on the densification and microstructure of Bismuth Ferrite-Barium Titanate ceramic. Significant enhancement of the density was observed with increasing the mole percentage of cerium, confirmed coherency with the article of Liu et al. where a dense structure was provided by cerium doping in BFO [13].

In the crystal structure of perovskite BFO-BT, Ce was expected to replace the A- site ion Bi^{3+} and Ba^{2+} . It is well known that for lower valence dopant, the charge balance would be ensured by the formation of oxygen vacancy in consequence reduction in structural density. Notably valence of cerium ion is 4+ whereas it is 3+ and 2+ for Bi and Ba respectively; hence cerium acts as donor dopant influencing the positive densification with increasing its content.


Fig 3: XRD spectra of the BFO-BT-Ce- x ($x= 0, 0.02$ and 0.04) ceramics sintered at 970°C temperature

B. Structural Characterization

Figure 3 shows the XRD spectra of the BFO-BT-Ce- x ($x= 0, 0.02$ and 0.04) ceramics sintered at 970°C temperature, where indexing was done according to Rhombohedral symmetry ($R3c$ space group). The figure demonstrated the existence of a pure perovskite structure without any impurity phase, reflecting complete diffusion of Ce into the crystal structure due to the small radial difference between Ce^{4+} ($1.14\text{\AA}$) and Bi^{3+} ($1.17\text{\AA}$) [14].

Also, the peak intensities were seemed to increase significantly with the cerium introduction, indicating substantial development of the degree of crystallinity in the BFO-BT-Ce- x structure as shown in Figure 4. The degree of crystallinity improved by 38.78% as the % mole of cerium increased from 0 to 0.04. Crystallite size (shown in Figure 4) was calculated by using Debye – Scherrer formula [13] considering all the peaks in the measurable domain. The equation is given as follows

$$D = \frac{K\lambda}{\beta \cos \theta} \text{----- (1)}$$

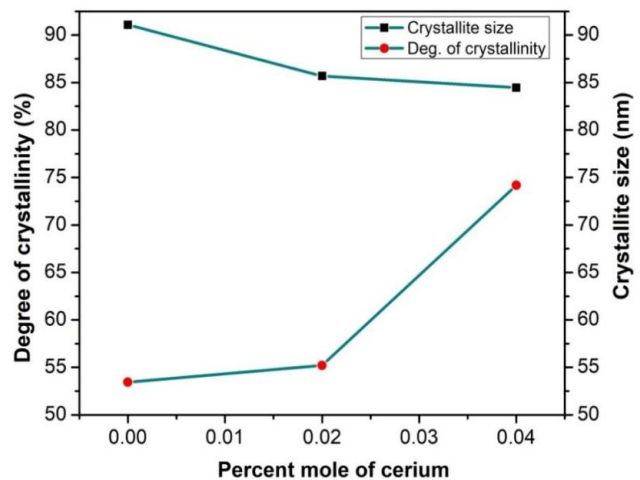


Fig 4: Effects of doping on the 'degree of crystallinity' and 'crystallite size'

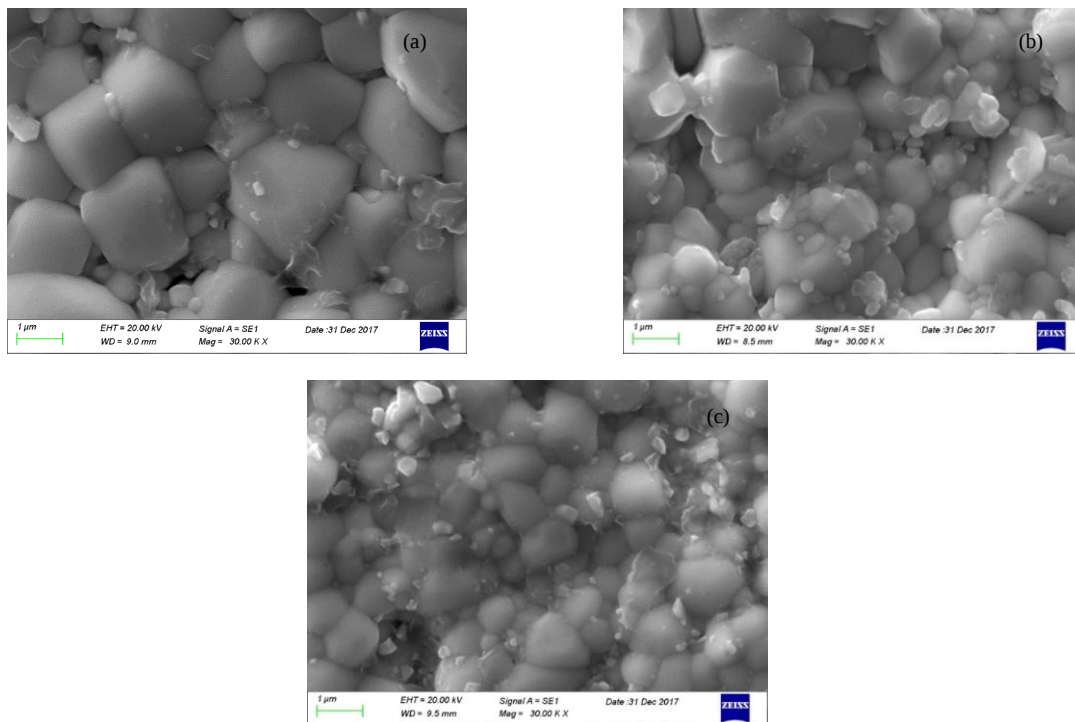
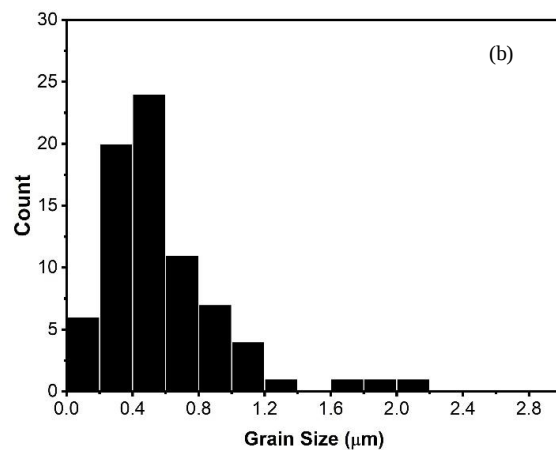
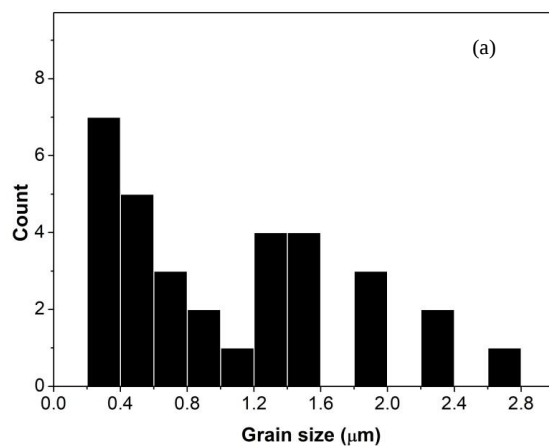


Fig 5: Microstructural (SEM) image (30000x) for different concentrations of cerium- (a) $x=0$, (b) $x=0.02$ and (c) $x=0.04$

Where D represents the crystallite size, β stands for the Full Width at half Maxima (FWHM), K is the dimensionless constant having a value of 0.90, λ is the wavelength of $\text{CuK}\alpha$ beam and lastly,

θ corresponds to the Bragg angle. The measured crystallite sizes were 91.08, 85.68 and 84.45 nm correspondingly from the undoped to maximum doped ceramics.



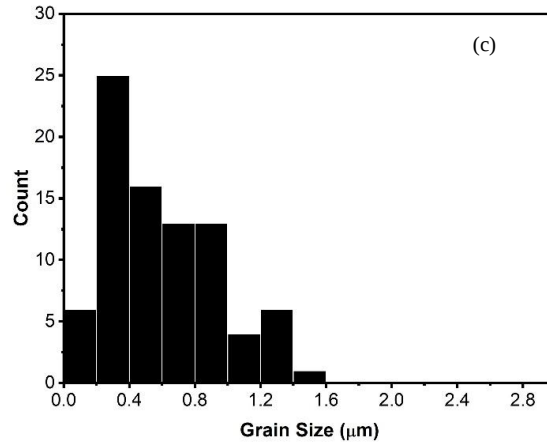


Fig 6: Variation of grain size distribution with dopant concentration-- (a) $x=0$, (b) $x=0.02$ and (c) $x=0.04$

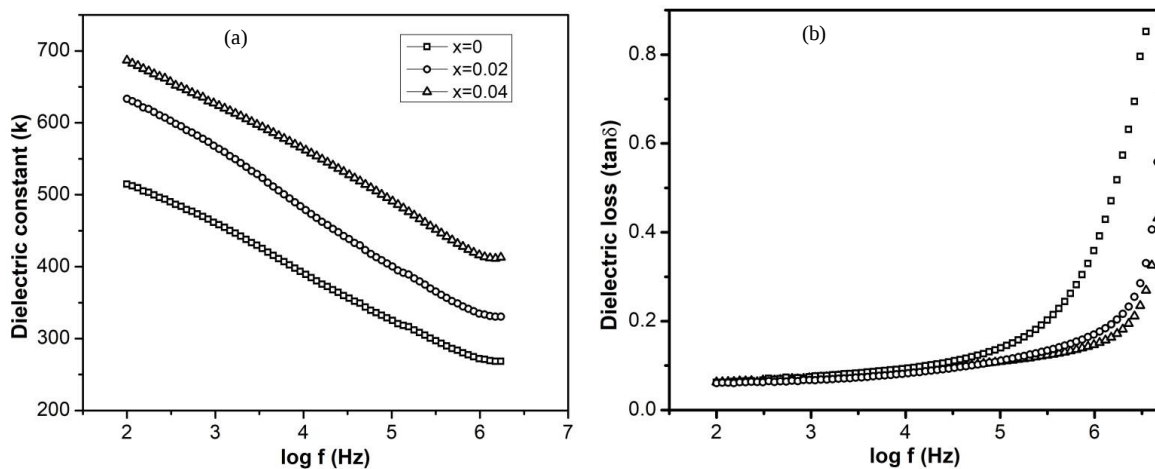


Fig 7: Change of (a) Dielectric constant and (b) dielectric loss with frequency

C. SEM Analysis

Microstructural image (30000x) portrayed in Figure 5-(a), (b) and (c) reveals a compact and homogeneous structure with the presence of trace porosity. The microstructure seemed to comprise of more or less polygonal grains with few round shaped. It is quite evident that with increasing the mole% of dopant the grain size of the ceramics decreased. This grain growth suppression phenomenon was also observed in the previous report for other RE (La^{3+} , Gd^{3+}) [12],[15] doped BFO-BT composition. The average grain size was measured using the linear intercept method, provided that 1.24, 0.711 and 0.602 μm for $x=0$, 0.02 and 0.04 respectively.

The measured grain size distribution (GSD) is shown in Figure 6(a) $x=0$, (b) $x=0.02$ and (c) $x=0.04$. The obtained GSD for $x=0$ appeared to be less symmetrical than the counterparts. The majority of the grains are positioned in the domain of 0.2-0.4, 0.4-0.6 and 0.2-0.4 μm for $x=0$, 0.02 and 0.04 respectively. Besides BFO-BT-Ce-0.04 ceramic reveals the least content of porosity compared to others, established suppression of pore and subsequently better

densification with cerium modification. Accordingly, the morphological features of the samples showed harmony with the density data explained earlier.

D. Dielectric Analysis

The variation of dielectric constant (k) and dielectric loss ($\tan\delta$) with frequency is shown in Figure 7. It is evident from the figure that k shows a decreasing tendency with frequency. This can be attributed by the cumulative contribution of all polarization mechanisms such as electronic, ionic, dipolar and space charge polarization, at low frequency [16],[17]. While with an increment of frequency mechanisms fail in altering alignment with the alternating electric field. On the contrary improved k and reduced dielectric loss were attained with Ce introduction, k increased from 515 to 687 as x changed from 0 to 0.04. So, BFO-BT-Ce-0.04 showed maximum density and high k , demonstrating a strong dependency of dielectric constant on density [18]. As reported earlier [8], the dielectric constant for BFO-BT close to the morphotropic composition found ~ 350 , confirming the effectiveness of the processing routes followed in this investigation. RE element such as La-doped BFO-BT presented $k < 500$, at 0.1 %mole [19]. This

data attests that cerium is a good choice for the property enhancement of bismuth ferrite- barium titanate based materials.

IV. CONCLUSION

Ce doped BFO-BT ceramic, near the morphotropic phase boundary prepared successfully using solid state reaction method. The ceramics exhibited a distorted perovskite structure in nature. Enhanced densification and grain growth retardation scenario were observed for the doped samples. The highest apparent density of $6.977 \times 10^3 \text{ Kg/m}^3$ had been exhibited by BFO-BT-Ce-0.04. Additionally, the grain size suppression from 1.24 to $0.602 \mu\text{m}$ had been observed as x increased from 0 to 0.04. Moreover, the ceramic containing 0.04 mole% cerium was found to pose a higher dielectric constant of 687, compared to other counterparts. So, increasing the content of cerium further would possibly enhance the properties of the base material significantly. Thus this investigation could be considered as the foundation for the detailed study of Ce doped BFO-BT in the whole composition range to ensure its applicability for multifunctional devices.

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