

Effects of La-Substitution on Structural and Dielectric Properties of BiFeO₃-BaTiO₃ Ceramics Compounds

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Abstract: Lanthanum (La) modified 0.56BiFeO₃- 0.44BaTiO₃ multiferroic ceramic materials were prepared by high temperature solid state reaction (mixed oxide) method. The tetragonal crystal structure of the material is confirmed from room temperature X-ray diffraction (XRD). The SEM of sintered ceramics compounds showed uniform distribution of grains by well defined boundaries and the formation of dense ceramic with average grain size in the order of 50 nm ~ 60 nm. The frequency and temperature dependence dielectric properties have shown normal behavior. Dielectric studies of the materials reveal that the dielectric constant and tangent loss decreases with doping concentrations at room temperature.

Keywords: Multiferroic Ceramic, Structural properties, Dielectric properties

1. Introduction

There has been remarkably rising interest in the multiferroic materials due coexistence of both ferroelectric and ferromagnetic properties in a single phase [1]. Today the multiferroic materials have different applications in memory devices, microelectronics mechanical systems and spintronic devices [2, 3]. Amongst the reported multiferroic ceramics, BiFeO₃ (BFO) is uniquely different because of its ferroelectric (T_c = 1143 K) and anti-ferromagnetic (T_N = 643 K) behaviour above room temperature leading to its potential applications in various multi-functional devices [4].

Besides, it has high dielectric constant, low tangent loss, and high transition temperature (120 °C). This enhanced electrical properties and high Curie temperature imply that BF-BT based piezoelectric materials have potential aeronautical applications in fuel and gas modulation, active structural control of hot sections and multifunctional active components for future aeronautic structures [5-6]. Unfortunately, most of the multiferroics have some serious inherent problems, including high-leakage current, formation of impurity phase and lack of structural stability [5, 7-10]. These defects of the materials largely affect the dielectric electrical, impedance property which limits the use of the materials. Several attempts have been made to reduce and/or remove these difficulties by which the simultaneous improvements of these multifunctional materials using of rare-earth elements (La, Sm, Dy, Nd, Gd) substitution in A- or B-site and appearance of enhanced multiferroic materials through other ABO₃-type perovskites materials [11-15]. We have attempted here, to synthesize solid solutions of 0.56BiFeO₃- 0.44BaTiO₃ and to

study the effect of La doping on its structural and dielectric properties.

2. Experimental

Lanthanum (La) modified ceramic materials of 0.56BiFeO₃-0.44BaTiO₃ was prepared by high-temperature solid-state reaction technique using high-purity (AR grade) ingredients: Bi₂O₃ (98.5% Loba-chemie), Fe₂O₃ (98.8 % CDH), BaCO₃ (99%, Finer Reagents) and TiO₂ (98.5% Loba-chemie) and La₂O₃ (99.9 % Loba-chemie). These ingredients were stoichiometrically mixed and homogenized in an agate mortar in the presence of Acetone over 2 h. This physical mixture was calcined at 840°C for 4 h in an alumina crucible in the high temperature furnace. Then Calcined powder grinding properly by agate motor for 30 minutes. The calcined powder was pelletized into small cylindrical pellets under an isostatic pressure of 5×10⁶ Nm⁻² with very small amount of polyvinyl alcohol (PVA) as the binder. The pellets were sintered at 860 °C for 3 h. PVA was burn out during high temperature sintering. The sintered pellet was polished with fine emery paper to make its surfaces flat and parallel. Then sintering pellets were finally coated with high quality conducting silver paint and dried at 80°C to remove moisture.

The crystallographic structure has been characterized by X-ray diffraction using X-ray diffractometer (RIGAKU, Japan) with Cu K_α radiation (λ = 1.5418 Å) and scanning angle 2θ between 20° and 70°. The structure, morphology and micrograph of the sample have been verified by Scanning Electron Microscope (SEM) (ZEISS, Marlin, IIT KGP) at room temperature. Measurement of electrical parameter of the sample have been carried out by a computer-controlled

frequency response analyzer (LCR 3522-50 LCR Hi TESTER, HIOKI, Japan) in the wide range of frequency (1kHz to 100kHz) at different temperature.

3. Results and Discussions

The formation of 0.56 BiFeO₃ - 0.44BaTiO₃ and La modified 0.56BiFeO₃ -0.44 BaTiO₃ compound was checked using X-ray diffraction at room temperature. Typical XRD patterns are shown in Fig 1. Sharp peaks were observed for both the samples indicating the formation good quality crystalline phase. The pattern was refined with “POWD” software package and the unit cell was found to be tetragonal. The lattice parameters were calculated using the following formula for tetragonal structure

$$\frac{1}{d^2} = \frac{(h^2 + k^2)}{a^2} + \frac{l^2}{c^2} \tag{1}$$

For the (100) plane

$$a = \frac{\lambda}{2\text{Sin}\theta} \tag{2}$$

For (002) plane

$$a = \frac{\lambda}{\text{Sin}\theta} \tag{3}$$

Crystallite size of the ceramic compounds was calculated using Debye-Scherrer’s equation

$$D = \frac{0.89\lambda}{\beta\text{Cos}\theta} \tag{4}$$

Where, θ implies the half of the glancing angle and β is FWHM of the reflection peaks.

The average crystallite size was found to be 50 nm. The particle size of sample decreases with increasing doping concentration of Sm as it is seen from the broadening of XRD peaks (increasing with doping concentration). The lattice parameters were found to be 3.9915Å for undoped and 3.9805Å for La doped sample.

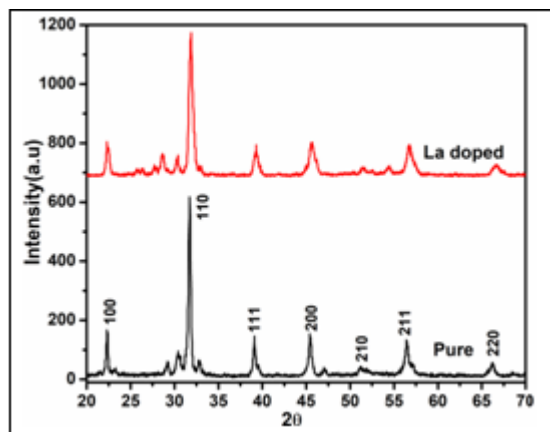


Figure 1: XRD pattern of 0.56BiFeO₃-0.44BaTiO₃ with La doped compounds

To study the surface morphology and micro-structural properties of the samples scanning electron microscopy was

carried out. Typical SEM images of undoped and doped ceramics are shown in Fig. 2 and 3 respectively. The shape and size of grains with grain boundaries show very compact and clear in both the compounds. It has been also observed that the grain size has decreased with increasing La content as estimated from the particle size calculation through XRD for as prepared samples. Very small number of pores has been identified with insignificant size which may grow at the time of grain growth in the sintering process at high temperatures [16]. There is also absence of any cracks or voids as observed in SEM micrographs. The larger grain size and compact grain boundaries depict the samples are highly dense and perfectly polycrystalline ceramics. It is worthy to mention that the high-density of the ceramic samples are very much responsible to enhance the dielectric and magnetic properties.

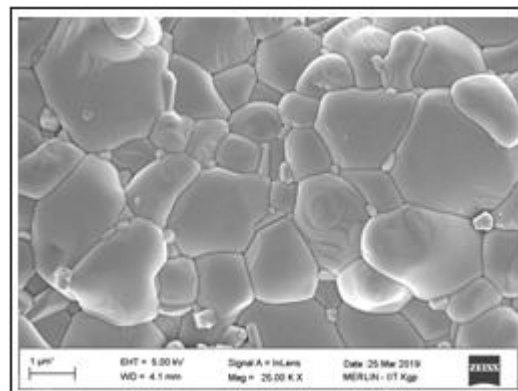


Figure 2: SEM image of 0.56BiFeO₃-0.44BaTiO₃ compounds

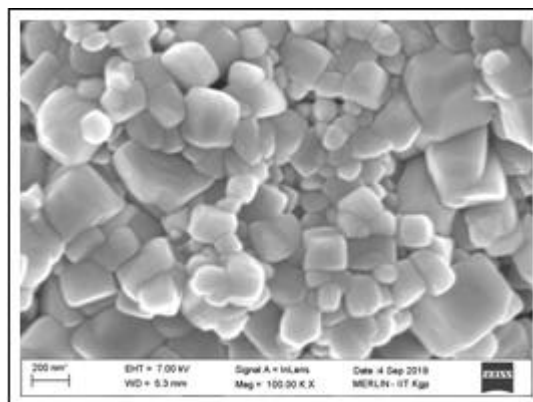


Figure 3: SEM image of La doped 0.56BiFeO₃-0.44BaTiO₃ compounds

Fig. 4 and Fig. 5 shows the temperature dependence of relative dielectric permittivity (ϵ_r) and loss tangent ($\tan \delta$) in the frequencies range (1 kHz to 100 kHz) for the 0.56BiFeO₃-0.44BaTiO₃ ceramic respectively. It is found that both (ϵ_r) and $\tan \delta$ decrease with increase in frequency. This implies that usual behavior of a dielectric or ferroelectric material. The variation of dielectric constant with temperature for different frequencies gradually increases with the increase of temperature for both the samples. The dielectric constant very high at higher temperature for lower frequencies which is due to space charge polarization and it comes from mobility of ions. The value of tangent loss ($\tan \delta$) increases at higher

temperature for the La modified samples. The loss is quite higher for doped samples in the high temperature compared to undoped. This effect arises because of the presence of thermally activated relaxation process in the La-doped materials. The tangent loss has high value at low frequency region at a particular temperature due to large value of resistance at grain boundary region which may be the additional energy to be supplied to drift the charge carriers. So, the dielectric constant ϵ_r and loss tangent shows regular behaviour of increasing with temperature for a ferroelectric material.

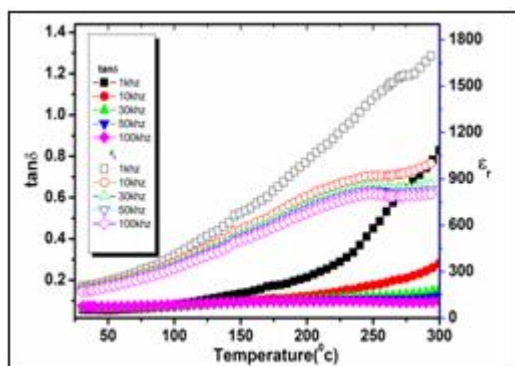


Figure 4: Dielectric constant (ϵ_r) of $0.56\text{BiFeO}_3\text{-}0.44\text{BaTiO}_3$ compounds

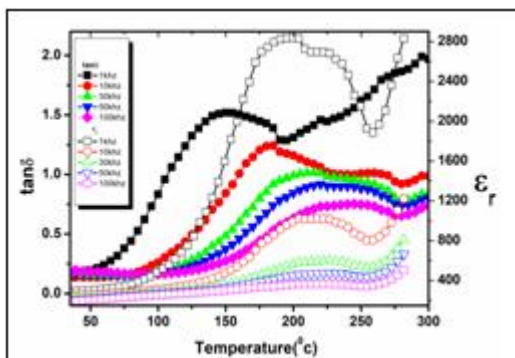


Figure 5: Loss tangent ($\tan\delta$) of $0.56\text{BiFeO}_3\text{-}0.44\text{BaTiO}_3$ with La doped compounds

4. Conclusions

In conclusion, the ceramics material has been prepared through high temperature solid state reaction technique. The detailed analysis of X-ray diffraction (XRD) data confirmed that the prepared compounds have tetragonal crystal structure with small distortion at room temperature. SEM micrographs depict the surface of the sintered samples with high density homogenous grain growth with few scattered pores. The grain distributions have been found uniform from the surface morphology of the sintered compounds. The average grain size of the annealed compounds has been calculated and found to be 50 nm. The temperature dependence dielectric study, i.e., ϵ_r and $\tan\delta$ versus temperature of the compound has shown the usual characteristic of dielectric materials. Frequency dependent loss tangent is decreased with increasing frequency

which makes the material for potential of elegant material for device application.

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