

Synthesis, Structural and Dielectric Properties of La doped 95BiFeO₃-5BaTiO₃ Ceramic

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ABSTRACT: The effect of La substitution on the microstructure and electrical properties of (BLFO - BT) ceramic synthesized by the Sol-Gel method was studied. The X-ray diffraction pattern confirms the perovskite structure of ceramics with the minute traces of secondary impurity phase. The scanning electron microscopy (SEM) showed that the average grain size of sample decreases due to the addition of La₂O₃. Dielectric properties of the La doped 95BFO-5BT perovskite ceramics were studied at different frequency and temperature which shows high dielectric constant and considerably low dielectric loss.

KEYWORDS: Ceramic Material, Sol-Gel, Dielectric, XRD, SEM.

I. INTRODUCTION

Pervoskite lead based ceramics such as Pb (Ni_{1/3}Nb_{1/3})O₃ and Pb (Zr, Ti)O₃ (PZT) have received considerable attention due to their wide applications such as actuators, sensors and microelectronic devices [1, 2]. But due to harmful lead oxide content in these materials which may cause environmental damage, in recent years, researchers have moved towards lead free ceramic materials. BaTiO₃, K_{0.5}Na_{0.5}TiO₃ and Bi_{0.5}Na_{0.5}TiO₃ based lead free ceramics are some of broadly used lead-free materials [3-5]. As these materials shows fluctuation in piezoelectric properties [3-5] the other lead-free materials having high Curie temperature received a great attention.

The pervoskite multiferroic material BiFeO₃ (BF) shows a high ferroelectric Curie temperature T_C (T_C~ 830⁰C) and antiferromagnetic Neel temperature T_N (T_N ≈ 370⁰C)[6] with important multifunctional applications in various advanced devices [7-11]. However it is difficult to prepare pure BiFeO₃ due to the difficulties arises in phase stabilization and the existence of secondary impurity phases in the material [12–13]. The perovskite phase of BFO can be stabilized by doping other elements like Mn or La [14] and also some ABO₃ pervoskite phases like SrTiO₃ and PbTiO₃. Research studies shows that the addition of these impurities improved the electric, magnetic and magnetoelectric properties of BFO [15, 16]. Out of all BiFeO₃-based solid solutions, BiFeO₃-BaTiO₃ is an important and extensively discussed multiferroic material [17-22]. However, as per our knowledge, very few reports are available on the effect of La doping on the structural and dielectric properties of BFO–BT ceramics. Therefore, in this paper, we have reported the structural and dielectric properties of La-doped BiFeO₃–BaTiO₃ ceramics prepared by Sol-Gel method.

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II. EXPERIMENTAL PROCEDURE

Lead-free perovskite multiferroic ceramics of 5% La doped 95BiFeO₃ – 5BaTiO₃ (BLFO-BT) were synthesized by Sol-Gel method[23]. Primarily, BLFO is synthesized by using following raw materials: Bi₂O₃(99.99%), Fe(NO₃)₃.9H₂O (99.99%) and La₂O₃(99.99%). First Bi₂O₃ and Fe(NO₃)₃.9H₂O were mixed by adding 5% PVA solution. The solution was heated at 70⁰C with constant stirring. Concentrated HNO₃ was added to form Bi(NO₃)₃. At last, Fe(NO₃)₃.9H₂O is added in to Bi(NO₃)₃ to obtained BLFO. As prepared powders were weighed in the stoichiometric ratio of 95BLFO-5BT and mixed thoroughly in ethanol using zirconia balls for 24 h in order to get homogeneous mixture. The complex so formed was dried and calcined at 780⁰C for 4 h. After the calcinations the powder was mixed thoroughly with a poly(vinyl alcohol) binder solution and then pressed using uniaxial hydraulic press into green pallets. The binder is removed by heating and the samples were sintered at 870⁰C for 4 h in air. The X Ray Diffraction analysis was carried out to know the crystal structure of the sample using an PANalytical X'pert Pro. The microstructure of the 5% La doped 95BLFO-5BT ceramic was studied using a scanning electron microscopy (Jeol JSM-7600F). Dielectric study was done by using Novocontrol broadband dielectric spectrometer (Alpha A analyzer Novocontrol GmbH, with BDS 1200 sample holder), in the frequency and temperature range of 1 Hz to 1 MHz and 0–350⁰C.

III. RESULTS AND DISCUSSION

The XRD patterns of the 5% La doped 95BFO-5BT ceramic sintered at 870⁰C is shown in figure 1. The XRD pattern shows a number of sharp peaks which confirms the perovskite phase structure of the sample along with the minute traces of secondary impurities viz. Bi₂Fe₄O₉ and Bi₂₅Fe₄O₃₉. In addition, the XRD figure also shows that the BaTiO₃ and La with 5 wt% mixing with BiFeO₃ has resulted in forming a solid solution, as no peaks of BaTiO₃ and La appears in XRD pattern.

Figure 2 shows the SEM graphs of the surface microstructure of the 5% La doped 95BFO-5BT ceramic. The ceramics exhibit a dense microstructure with increased grain sized from 0.5 μm[23] to 1.5 μm with the addition of La₂O₃ impurity. This may be because the sintering performance is improved by the addition of La. As the Bi³⁺ ion is smaller [24] than that of La³⁺, the substitution of La for Bi leads to the lattice expansion of 5% La doped 95BFO-5BT ceramics.

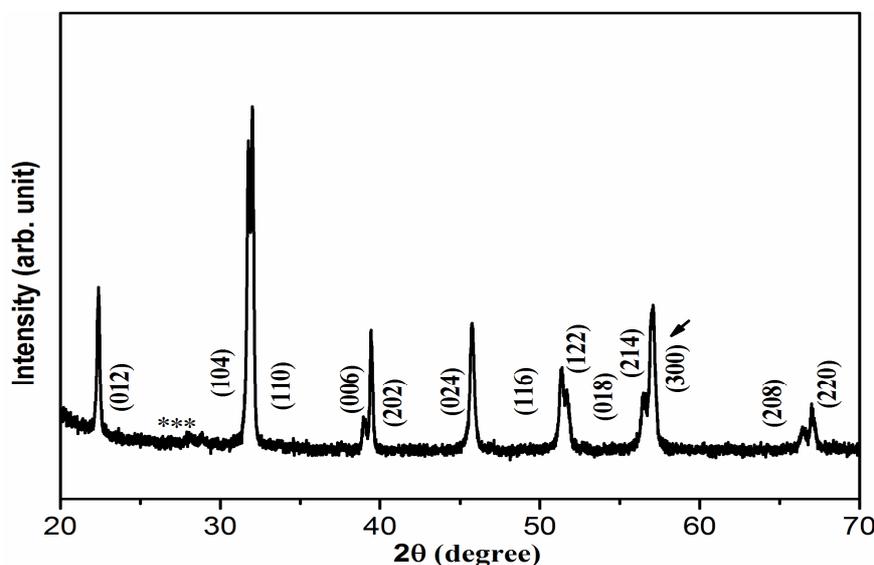


Figure 1. XRD patterns of 5% La doped 95BFO-5BT ceramics.

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The dielectric behaviour, dielectric constant (ϵ_r) and loss tangent ($\tan \delta$) of 5% La doped 95BFO-5BT with the temperature variation for different frequency viz. 1Hz, 10Hz and 100Hz is shown in figure 3. Figure 3 clearly shows that the dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) decreases with the increasing frequency, which is the characteristic of dielectric materials [25]. The gradual increase in dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) with increasing temperature is also clearly observed in figure 3. The dielectric loss $\tan \delta$ is found to be increased slowly in the low temperatures region, whereas at higher temperatures the increment is sharper. This may be due to three important reasons; first is dispersion of charge carriers at higher temperature. Second, the existence of some unknown defects including oxygen vacancies and third is due to the phases in the materials. The anomaly in the relative dielectric constant (ϵ_r) is observed at 187°C. This may be the result of electro-magnetic effect occurred in the material.

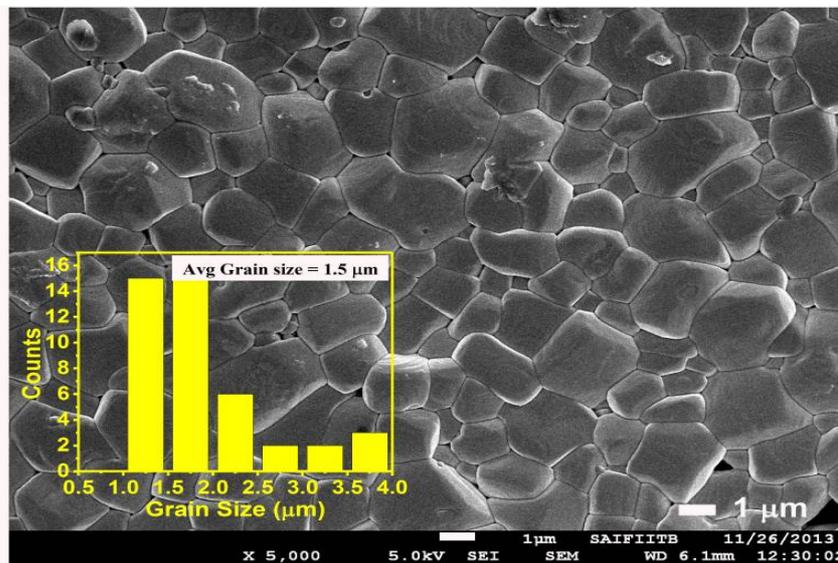


Figure 2. SEM micrographs of 5% La doped 95BFO-5BT ceramics

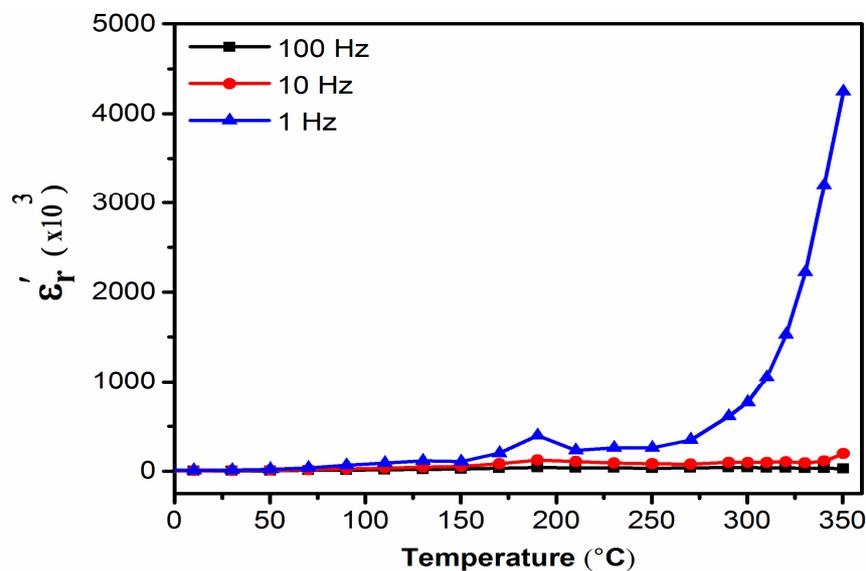


Figure 3 (a)

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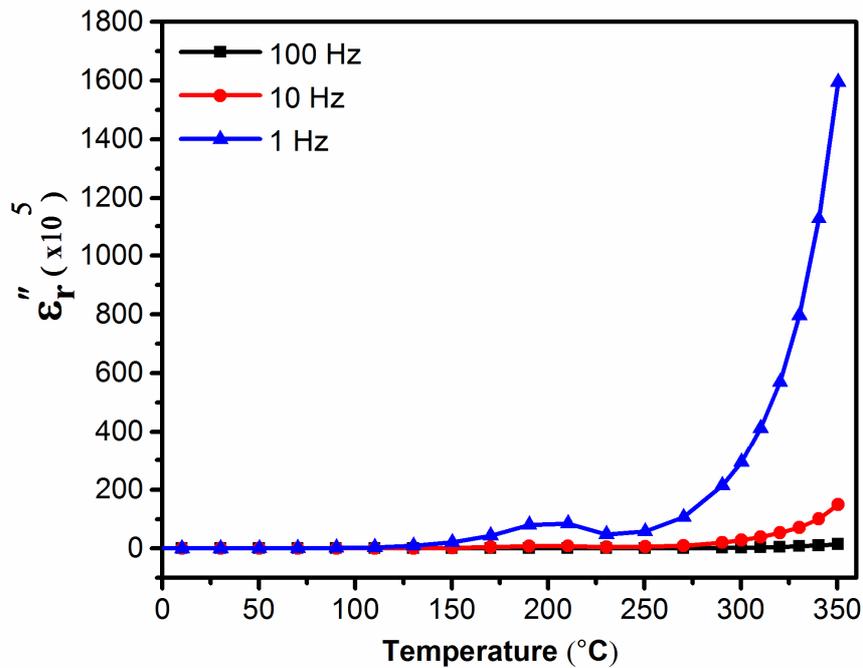


Figure 3 (b)

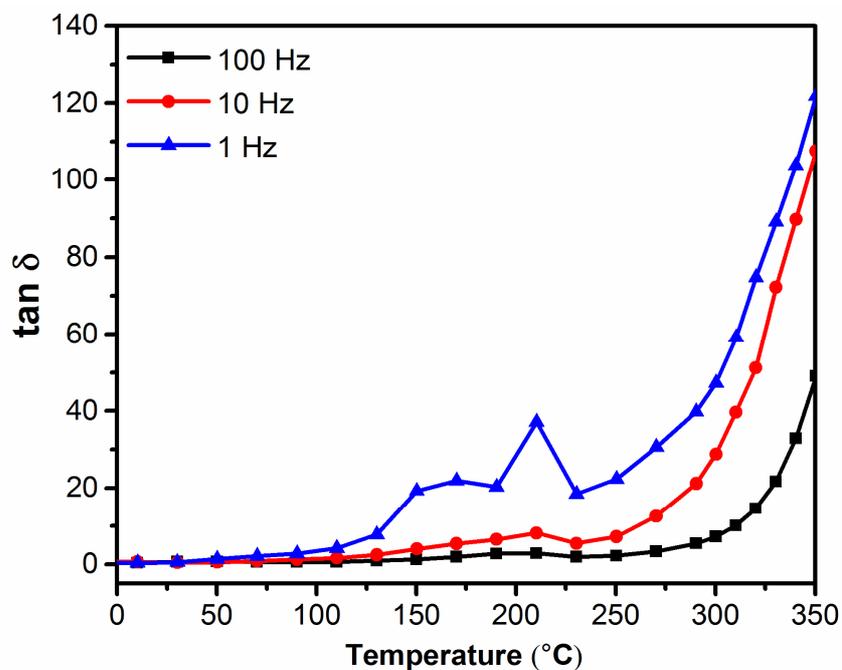


Figure 3 (c)

Figure 3. Temperature dependent dielectric constant and dielectric loss of La doped BFO-BT ceramics

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Figure 4 shows the frequency dependent dielectric constant (ϵ_r) and dielectric loss ($\tan \delta$) of 5% La doped 95BFO-5BT at 300C temperature. The value of dielectric constant decreases with rise of frequency at 300C which is a

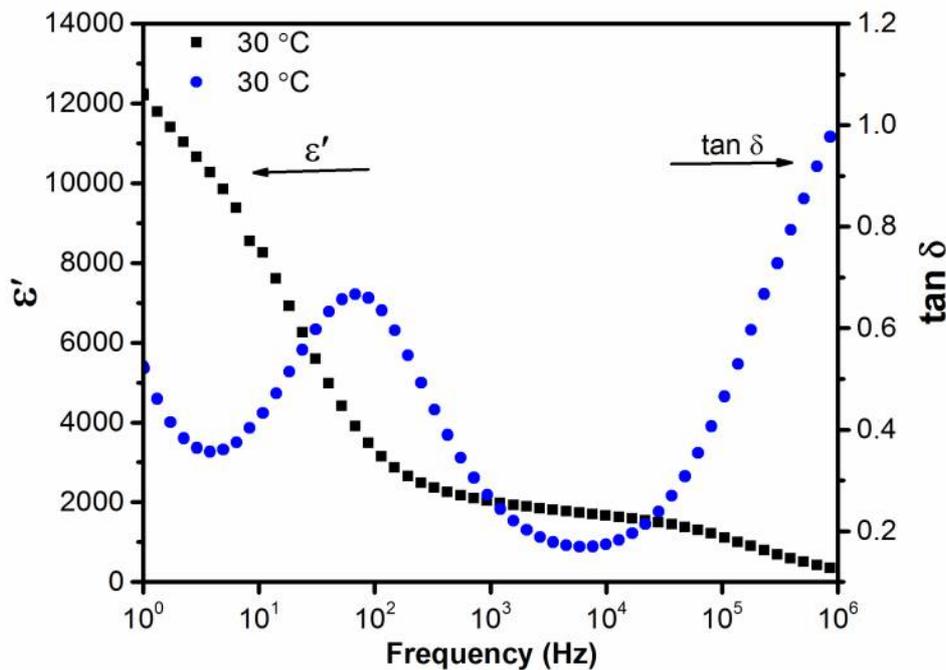


Figure 4. Frequency dependent dielectric constant and dielectric loss of La doped BFO-BT ceramics

general characteristic of most of ceramic material. The frequency dependence dielectric characteristics of the material can be explained by the Maxwell–Wagner model [26].

The low $\tan \delta$ values (0.1) is observed at 10 kHz as BFO has lower $\tan \delta$ values than BT. It is reported in research literature that dielectric constant and $\tan d$ values of some dielectric materials depend on defects and on the high sintering temperature which in turn produces defects like oxygen vacancies in sample.[27–28]

IV. CONCLUSION

In summary, an effect of addition of La_2O_3 in 95BFO-5BT ceramics is presented in this article. The sample was synthesized via Sol-Gel method. The structural analysis using XRD pattern suggests that the 5% La doped 95BFO-5BT ceramic exhibited pure perovskite crystal structure with minute traces of secondary impurity phase. A SEM image suggests that the doping of La impurity produced changes in ceramic microstructure and increases the grain size up to 1.5 μm . The high dielectric constants and lowest dielectric loss ($\tan \delta \approx 0.1$ at 10 kHz can be explained with the help of Maxwell–Wagner models&existence of defects in sample.

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