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Preparation and Characterization of La_2O_3 Doped $Ba_{0.3}Sr_{0.7}TiO_3$ Perovskite Ceramics of Varied Sintering Temperature and Doping

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Abstract

In order to explore new application opportunities of Barium Strontium Titanate (BST) ceramic composite by modifying the conventional ferroelectric properties of BST through La_2O_3 doping in BST matrix sintered at different temperature was investigated in this current study. Unadulterated $Ba_{0.3}Sr_{0.7}TiO_3$ (BST) matrix was prepared from $BaTiO_3$ (99.95%) and $SrTiO_3$ (99.95%) taken in stoichiometric extents which later doped by La_2O_3 (99.99%) in varying extents (0.05 g, 0.10 g and 0.15 g) exploiting solid state reaction route. Doping caused drag effect for the penetration of impurities and sintering temperature helped the impurities migration to BST. Dielectric constant gets lower with rising of frequency, as electrons do not get enough time to polarize at high frequency. Dielectric constant and conductance are found maximum for the sample (0.1 g La_2O_3 doped BST) sintered at 1460˚C and reverse is found in impedance analysis. These electrical properties showed visible frequency dependent response irrespective of sintering temperature and doping.

Keywords

Barium Strontium Titanate, Lanthanum Oxide, Ceramics, Dielectric Constant, Conductivity, Impedance

1. Introduction

Undoubtedly throughout the last few decades, enormous dielectric properties of several ceramic materials have been successfully utilized in designing and fabricating devices intended to consumer as well as military electronics, telecommunication, energy transmission and computers based on their applicability. Ceramic material industry plays a pivotal role as the base for many other in-

dustries. And recently high dielectric constant containing ceramics have been preferably investigated to develop efficient capacitors. One of the most crucial perovskite ferroelectrics barium strontium titanate ($Ba_xSr_{(1-x)}TiO_3$, BST) has extensively been exploited due to its high dielectric constant, high tunability, low tangent and suitable phase transition temperature [1] [2] [3] [4] [5]. It was observed that improved dielectric and structural behavior can be achieved if some additives are incorporated in a specific way for better electrical ceramics like BST [6] [7] [8] and dielectric properties of BST can be improved either by controlling Ba/Sr proportion or by partially substitute isovalent or aliovalent cations for A-sites and/or B-sites of ABO_3 perovskite system [9].

The impact of rare earth metal oxide as dopant on dielectric behaviors and structure in BST has widely been investigated in recent years. Huang *et al*. summarized that Dy_2O_3-doped BST capacitor ceramics revealed high permittivity, low dielectric loss and high DC breakdown voltage [10]. According to Zhao *et al*. comprehensive characteristics were achieved in Y_2O_3 and Dy_2O_3-doped BST ceramics [11]. Besides, Li *et al*. reported that there was a change in substitution pattern of Y^{3+} ions for the host cations in perovskite system. When the doping concentration rose up to 0.5% (mole fraction), Y^{3+} ions showed preference to grasp the B-sites, resulting to the fluctuation of dielectric constant [12]. Also, Eswaramoorthi *et al.* concluded that with rise in Ga doping in BST thin films dielectric constant and dielectric loss of the products plummeted whereas surface morphologies improved [13].

The influences of La_2O_3 doping on structure and properties of BST ceramics were also studied, Zhu *et al*. found that, crystalline phase of the BST perovskite glass-ceramics ascended with the rising of dopant (La_2O_3) concentration and microstructure showed uneven distribution of the crystals as dopant reached to a specific concentration. Conductivity and impedance both showed considerable change with change in dopant concentration [14]. In another work by Zhang *et al*. La_2O_3 incorporation in $Ba_{0.4}Sr_{0.6}TiO_3$ glass ceramics revealed that dopant had a small effect on the dielectric constant but extensively affected the microstructure of the ceramics [15]. Zhang and Qu conducted a similar research on $Ba_{0.74}Sr_{0.26}TiO_3$ where dopant La_2O_3 and Sb_2O_3 were used and results showed that dielectric constant, dielectric loss and phase transitions all were affected by dopant addition [16]. Although it was well observed that a small portion of dopant ions can surprisingly influence the dielectric behaviors of BST ceramics, La_2O_3 doped pure $Ba_{0.3}Sr_{0.7}TiO_3$ ceramics have never been studied before.

This current study focuses on preparing La_2O_3 doped pure $Ba_{0.3}Sr_{0.7}TiO_3$ lattice by conventional solid state reaction mechanism and characterizing its dielectric and several electrical properties against frequency and varied sintering temperature.

2. Experimental

All the samples were prepared following the convenient solid-state reaction method. $BaTiO_3$ (99.95%) and $SrTiO_3$ (99.95%) were sampled in stoichiometric

proportions to prepare a pure $Ba_{0.3}Sr_{0.7}TiO_3$ (BST) matrix and doped with La_2O_3 (99.99%) with 0.05 g, 0.1 g and 0.15 g. All powder samples were wet-milled for 24 hours in pure alcohol media in a motor driven pot mill. After mixing, the mixture was removed with the help of a strainer and subsequently dried in an oven at 100˚C for 24 hours and later calcined at 800˚C for 8 hrs with a heating rate of 10˚C/min using air atmosphere. Polyvinyl alcohol (5% PVA solution) was mixed as binder with the calcined powder to provide some green strength for subsequent handling. Then, it was dried in an oven for 24 hours to evaporate excess moisture. The pellets were prepared using press machine at 25˚C with 0.8 g of powder for every sample to maintain uniformity in thickness and then compressed at a rate of 0.2 mm/min until a desired pelletizing pressure of 10 KN was reached. The pellets made placed in a micropyretic heater (high temperature furnace) for sintering. Sintering schedule was varied from batch to batch. Here, sintering was carried out at 1460˚C, 1480˚C and 1500˚C in an air atmosphere. However, for every sintering schedule all samples with similar composition were put in the furnace at the same time. X-ray diffraction experiments were performed in order to identify the main crystalline phase of $Ba_{0.7}Sr_{0.3}TiO_3$ (BST) powders recording the diffractogram from 10˚ to 90˚ using Bruker's D8 Advance X-ray diffractometer with CuKa radiation (λ = 1.5406 Å). The microstructure of the powders was studied by a JEOL FE-SEM-7600F Scanning Electron Microscopy (SEM). Dielectric properties of perovskite were carried out by using Keithley Electrometer and Hewlett Packart Impedance Analyzer (WAYNE KERR 6500B). For dielectric measurements, the pellet shaped samples were prepared. Later on the samples were well polished to remove any roughness and the surfaces of each pellet were coated with silver paste as contact material. Dielectric measurements have been done as a function of frequency in the range of 20 Hz to 1 KHz at room temperature.

3. Results and Discussion

3.1. Grain Size

Doping and sintering are two useful processes for tuning ceramic properties [17] [18]. SEM images (**Figure 1**), with magnification × 30,000, of highest doping in

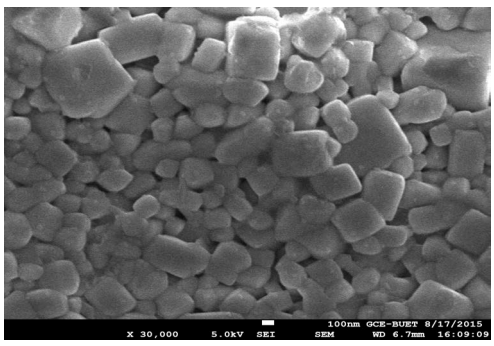

Figure 1. SEM images of 0.15 g La_2O_3 doped $Ba_{0.3}Sr_{07}TiO_3$ sintered at 1500˚C.

$Ba_{0.3}Sr_{0.7}TiO_3$ matrix at the highest sintering temperature (1500˚C) show that contraction in small grains takes place that causes movement of the grain boundary so the total boundary area decreases as the grain boundary contraction supports the grain growth [19].

Doping of La^{3+} to BST in this case act as introduction of impurities, this impurities lower the melting point of the resulting ceramic, so, grain boundary shrinkage ensued the grain growth [17]. Several research results suggested that the mobility of grain boundary is reduced by the incorporation of soluble impurities [20] [21].

3.2. XRD

X-ray diffraction (XRD) was carried out for (Ba, Sr)TiO_3 doped with La_2O_3. Results showed that perovskite, (Ba, Sr)TiO_3 doped with 0.1 g La_2O_3 had given no extra peak at 1460˚C (**Figure 2**), indicating no phase shifting has been observed as compared to standard BST. But, one new peak was found (indicated by arrow in (**Figure 3**) for the highest doping (0.15 g La_2O_3) supported by other studies where extra peaks were found for pure La_2O_3 when doping exceeded the maximum limit [22].

3.3. Dielectric Constant

Dielectrc constant for La_2O_3 doped (0.05 gm, 0.1 gm and 0.15 gm) in 20 gm

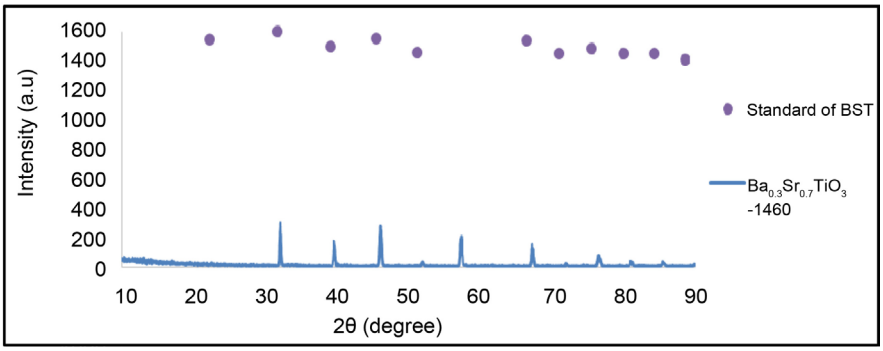

Figure 2. XRD patterns of La_2O_3 doped $Ba_{0.3}Sr_{0.7}TiO_3$ calcined at 1460˚C.

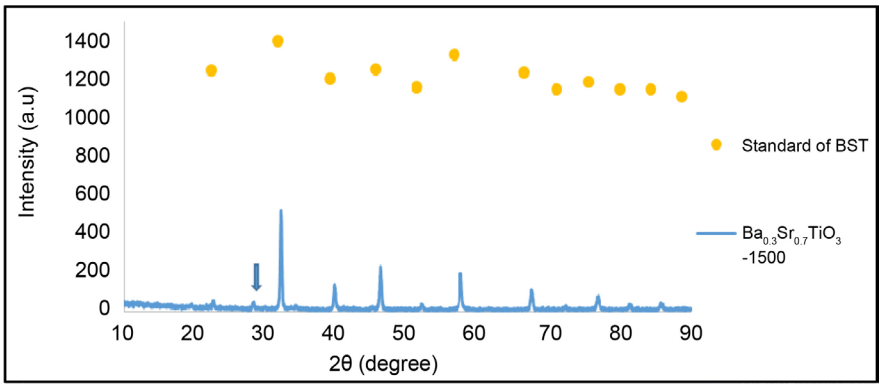

Figure 3. XRD patterns of La_2O_3 doped $Ba_{0.3}Sr_{0.7}TiO_3$ calcined at 1500˚C.

$Ba_{0.3}Sr_{0.7}TiO_3$ (BST) sample sintered at 1460˚C, 1480˚C and 1500˚C has been estimated and the result is shown in Figures 4-6.

Dielectric constant of the samples is higher at lower frequencies and decreases with increase of frequency by approaching approximately a more or less constant value. Dielectric constant is determined by the polarization of dielectric which depends on ionic, electronic and dipole polarization. Electronic polarization occurs at very short interval of time. But, when high frequency is applied electrons do not get enough time for polarization [23]. Again, dielectric constant depends on thermal motion and thermal expansion of dielectric. High temperature helps to orient the dielectrics for polarization up to an optimum temperature. On the other hand, successive increase of temperature decreases the number of dielectric in the effective length. Therefore it can be summarized as that, dielectric constant value decreases with increase of both of sintering temperature and frequency. As a consequence in the current research, dielectric constant is found maximum for the sample (0.1 gm La_2O_3 doped $Ba_{0.3}Sr_{0.7}TiO_3$) at 100 Hz sintered at 1460˚C (Figure 7).

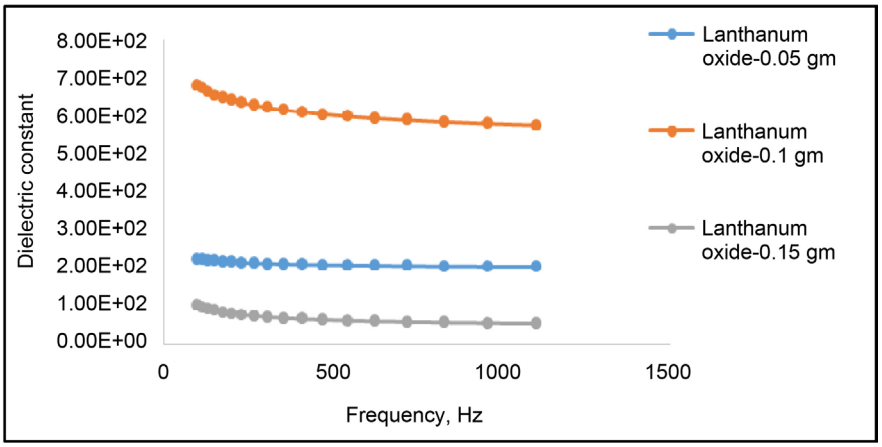

Figure 4. The variation of dielectric constant with frequency of $Ba_{0.3}Sr_{0.7}TiO_3$ doped with varying amount of La_2O_3 sintered at 1460˚C.

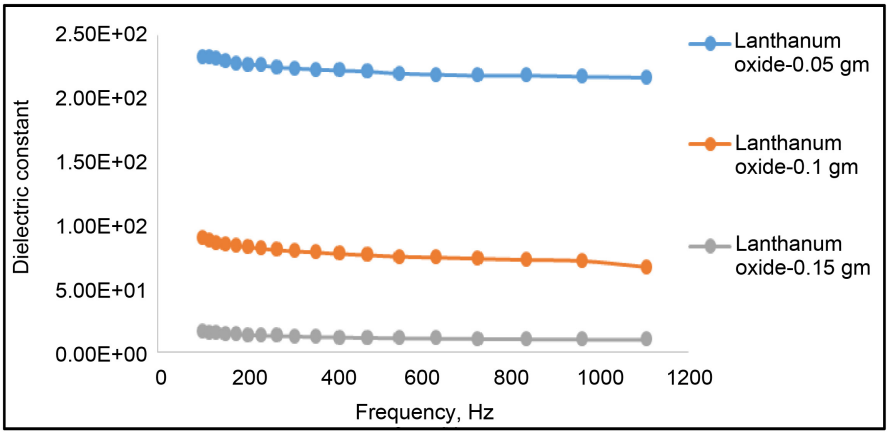

Figure 5. The variation of dielectric constant with frequency of $Ba_{0.3}Sr_{0.7}TiO_3$ doped with varying amount of La_2O_3 sintered at 1480˚C.

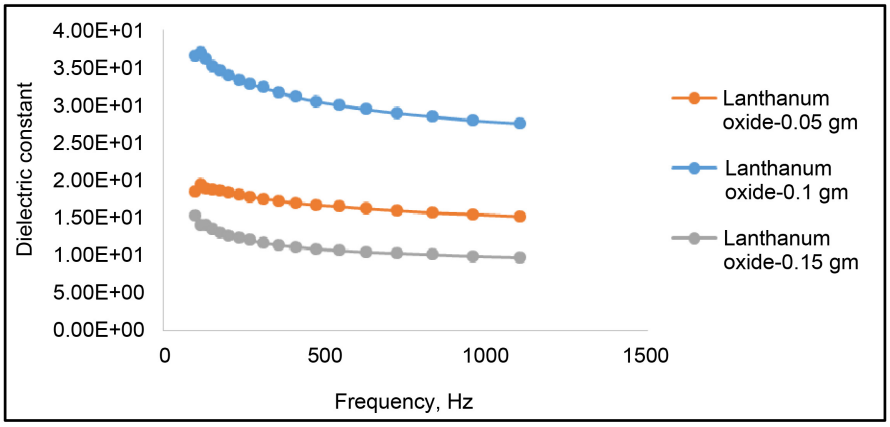

Figure 6. The variation of dielectric constant with frequency of $Ba_{0.3}Sr_{0.7}TiO_3$ doped with varying amount of La_2O_3 sintered at 1500˚C.

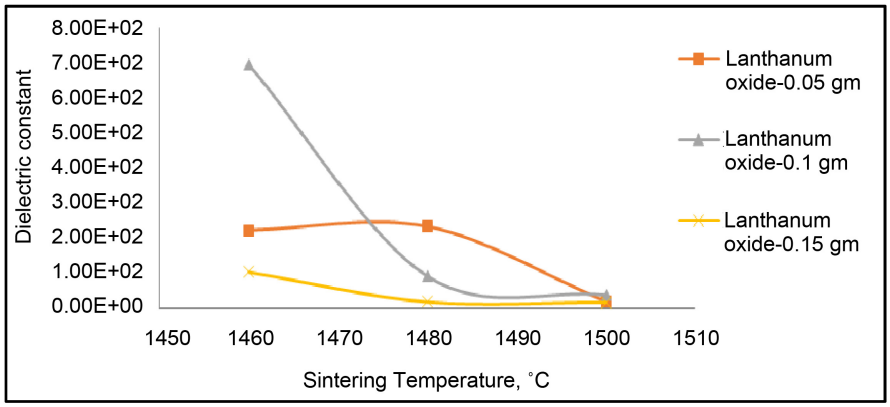

Figure 7. Variation of dielectric constant with Sintering temperature of $Ba_{0.3}Sr_{0.7}TiO_3$ with varying amount of La_2O_3 at frequency 100 Hz.

3.4. AC Conductivity

The electrical conductivity in dielectric materials is primarily due to hopping of electrons. Also, it is between ions within a same element present above monovalent state [24]. The charges tend to relocate under the impact of the field resulting in conductivity [25]. In our research, the ac conductivity may be ascribed to formation of Ti^{3+} ions which are generated due to partial reduction of Ti^{4+} ions during the sintering process. Conductivity is found maximum at lowest sintering temperature (1460˚C) and optimum doping (0.1 g) and decreases with rising sintering temperature **Figure 8**. This is because of densification of Perovskite increases with sintering temperature and that consequently lower the conductance [26].

3.5. Impedance Analysis

The sophisticated impedance mechanism grants us to differentiate between the attribution of intra-grain (bulk), inter-grain (grain boundary) and the electrode effect to conduction [27]. Impedance plots show expected result that supports the conduction property of the composites. From **Figure 9**, it is visible that the

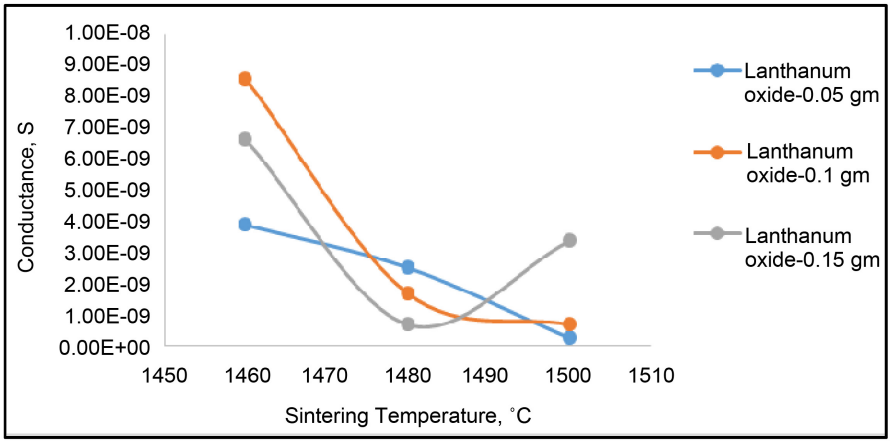

Figure 8. Temperature dependent conductance of $Ba_{0.3}Sr_{0.7}TiO_3$ with varying amount of La_2O_3 at frequency 100 Hz.

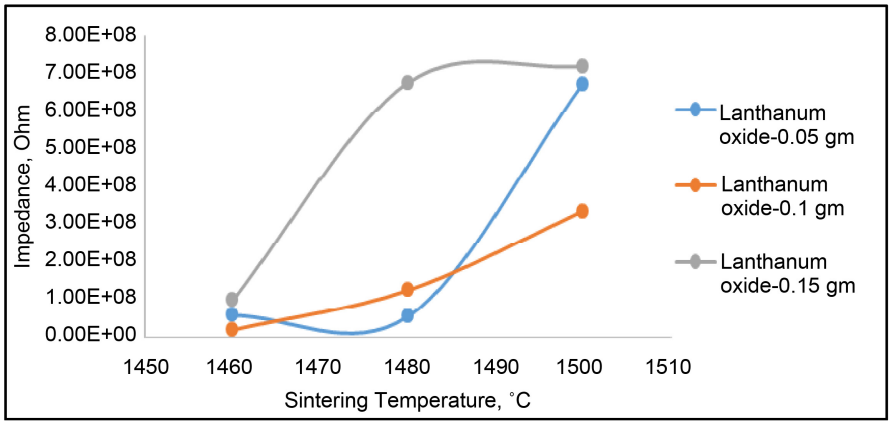

Figure 9. Temperature dependent impedance of $Ba_{0.3}Sr_{0.7}TiO_3$ with varying amount of La_2O_3 at frequency 100 Hz.

lowest impedance is found for optimum doping (0.1 g) which showed the highest conductance.

3.6. Capacitance Analysis

From Figure 10, it can be seen that the highest amount of capacitance is obtained for 0.1 gm La_2O_3 doped $Ba_{0.3}Sr_{0.7}TiO_3$ sintered at 1460˚C. Here, capacitance went down with rising sintering temperature for all doping. That is in similar trend as AC conductivity and follows the same principle as mentioned [26].

4. Conclusion

Barium strontium titanate (BST), $Ba_{0.3}Sr_{0.7}TiO_3$ perovskite has been successfully synthesized by solid state reaction method. La^{3+} doped to BST and subsequently sintered at different temperatures to alter or add properties to BST. Doping and sintering helped to grain growth of perovskite. Dielectric constant gets lower with rising of frequency, as electrons do not get enough time to polarize at high frequency. In this study dielectric constant is found maximum for the sample

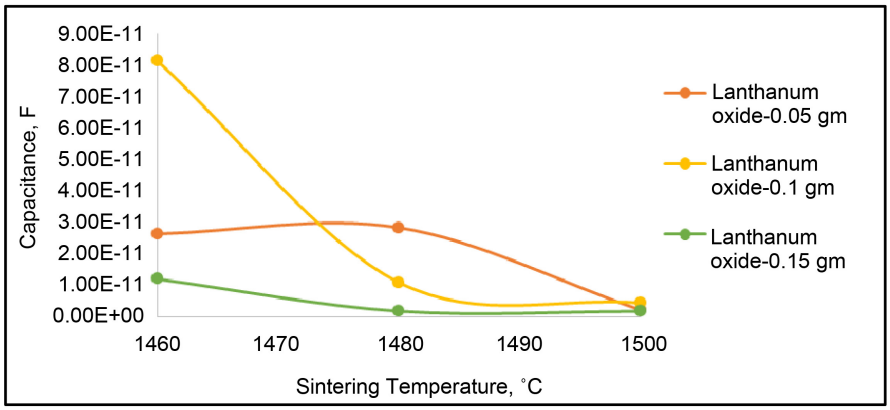

Figure 10. Temperature dependent capacitance of $Ba_{0.3}Sr_{0.7}TiO_3$ with varying amount of La_2O_3 at frequency 100 Hz.

(0.1g La_2O_3 doped $Ba_{0.3}Sr_{0.7}TiO_3$) at 100 Hz sintered at 1460˚C. The electrical conductivity, primarily for hopping of electrons between ions of the same element present above monovalent state in this studied dielectric, is found maximum for optimum doping of 0.1 g La_2O_3 and vice-versa for impedance analysis.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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