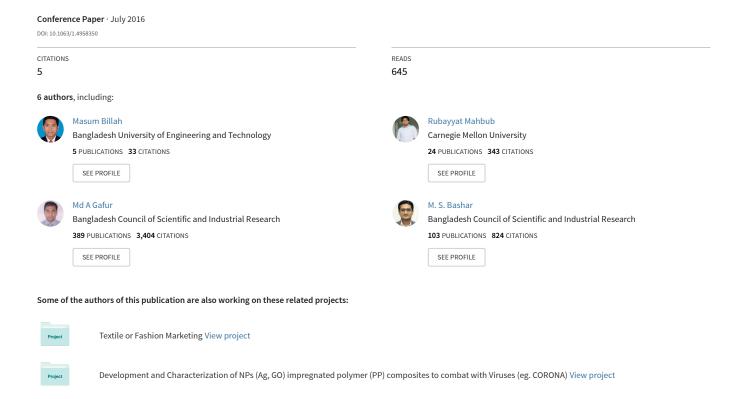
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Microstructure Evolution and Electrical Characterization of Lanthanum Doped Barium Titanate (BaTiO₃) Ceramics

Masum Billah^{1, a)}, A. Ahmed^{1, b)}, Md. Miftaur Rahman^{1, c)}, Rubbayat Mahbub^{2, d)}, M. A. Gafur^{3, e)}, M. Shahriar Bashar^{4, f)}

¹Department of Materials & Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

²Department of Glass and Ceramic Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh

³Bangladesh Council of Scientific & Industrial Research (BCSIR), Dhaka-1205, Bangladesh ⁴Institute of Fuel Research & Development, Bangladesh Council of Scientific & Industrial Research (BCSIR), Dhaka-1205, Bangladesh

a)Corresponding author: masum.buet09@gmail.com
b)jhinukbuetmme@gmail.com^{c)}miftaurrahman@mme.buet.ac.bd
d)rubayyatm@gce.buet.ac.bd^{e)}d_r_magafur@bcsir.gov.bd
f)bashar@agni.com

Abstract. In the current work, we investigated the structural and dielectric properties of Lanthanum oxide (La₂O₃) doped Barium Titanate (BaTiO₃) ceramics and established a correlation between them. Solid state sintering method was used to dope BaTiO₃ with 0.3, 0.5 and 0.7 mole% La₂O₃ under different sintering parameters. The raw materials used were La₂O₃ nano powder of ~80nm grain size and 99.995% purity and BaTiO₃ nano powder of 100nm grain size and 99.99% purity. Grain size distribution and morphology of fracture surface of sintered pellets were examined by Field Emission Scanning Electron Microscope and X-Ray Diffraction analysis was conducted to confirm the formation of desired crystal structure. The research result reveal that grain size and electrical properties of BaTiO₃ ceramic significantly enhanced for small amount of doping (up to 0.5 mole% La₂O₃) and then decreased with increasing doping concentration. Desired grain growth (0.80-1.3μm) and high densification (<90% theoretical density) were found by proper combination of temperature, sintering parameters and doping concentration. We found the resultant stable value of dielectric constant was 10000-12000 at 100-300 Hz in the temperature range of 30°-50° C for 0.5 mole% La₂O₃ with corresponding shift of curie temperature around 30° C. So overall this research showed that proper La³⁺ concentration can control the grain size, increase density, lower curie temperature and hence significantly improve the electrical properties of BaTiO₃ ceramics.

INTRODUCTION

Barium Titanate (BaTiO₃), a common versatile electro-ceramic, has a wide range of applications due to its excellent dielectric, ferroelectric and piezoelectric properties making it desirable for multilayered capacitors, positive temperature coefficient thermistors, ferroelectric thin film memories, piezoelectric transducers etc. [1,2,3]. It adopts perovskite type tetragonal lattice structure (ABO₃) with a high dielectric constant of 1500-2000 at room temperature but the dielectric constant would fluctuate [4] during operation under various conditions such as electrical field strength, operating temperature, humidity etc.

The various applications have resulted in many different studies aiming at preparation and characterization of BaTiO₃. Among them doping with donor or acceptor ions at small concentration in the A- or B- site is the most efficient and useful process to modify electrical properties. From different researches, it is found that semiconducting

BaTiO₃ can be produced by atmospheric reduction forming oxygen vacancy or by low concentration donor doping

with trivalent ions (La³⁺, Y³⁺, Sb³⁺) on Ba-site or pentavalent ions (Nb⁵⁺, Ta⁵⁺) on Ti-site [5,6,7,8].

Ionic radius is the main parameter determining the substitution site. In this case La³⁺ (1.15 Å) is exclusively incorporated at the Ba²⁺ (1.35 Å) site as its size is incompatible with that of Ti⁴⁺ (0.68 Å). Replacement of Ba²⁺ by La³⁺ ion produces an extra positive charge and due to electrical neutrality, an e⁻ is trapped by a Ti⁴⁺ ion followed by the equation (1) [9].

$$Ba^{2+}Ti^{4+}O_3^{2-} + x La = (Ba_{1-x}^{2+}La_x^{3+}) Ti_{1-x}^{4+} (Ti^{4+}e^{1-})_x O_3^{2-}$$
(1)

Various research [9,10,11] showed that small concentration of La³⁺ in BaTiO₃ increase grain growth, decrease phase transition temperature hence enhancing dielectric properties. Adding a relatively low concentration leads to room temperature semiconducting ceramics with positive coefficient of resistivity (PTCR) effect whereas higher dopant concentration leads to insulating materials [9,10,11].

The main theme of this research was to fabricate undoped and La-doped BaTiO₃ ceramics with minimum porosity by solid state sintering, examine the influence of La doping on microstructure, crystalline structure & dielectric properties and determine the detail structure-property relationship.

EXPERIMENTAL PROCEDURE

Lanthanum doped Barium Titanate samples (BTL) were prepared from BaTiO₃ (size =100nm) and La₂O₃ (size =80nm) nano powders [Manufacturer: INFRAMAT (USA); Purity better than 99%]. Here La₂O₃ was used to dope for 0.3, 0.5, 0.7 mole% La (BTL3, BTL5 and BTL7). The powders were milled in the pot mill containing Yttria stabilized zirconia balls for 16-20 hours with a sufficient amount of acetone as the milling media. PVA (2% of sample wt.) was added as a binder after drying to remove milling media and then the mixture was stirred for 30-40 minute to ensure a homogenous binder distribution. The mixture was then dried and pressed into a disc shape (13mm diameter and 2.1mm average thickness) in a stainless steel die under the shape forming pressure of 1.5 tons. Next, the samples were placed for soaking in a box furnace (Model-NABERTHERM, HT 16/18, Germany) for binder removal at 500°C for 1 hour (heating rate 2°C/min). Sintering was performed at 1300° C for 2, 4, 8 hours (heating and cooling rate 3° C/min) in box furnace and cooled to room temperature in air atmosphere. Surface microstructure and grain size distribution of sintered pellets were examined by a Field Emission Scanning Electron Microscope, FE-SEM (Model-JEOL JSM-7600F, Japan) and crystal structure was detected using X-ray diffractometer, XRD (Model-BRUKER D8 ADVANCE, Germany). Temperature dependent dielectric constant was measured from 30° C to 145° C at various frequencies (100, 300, 500, 1k and 10 kHz) at a heating rate of 4° C/min using an Impedance Analyzer (WAYNE KERR 6500B series).

RESULTS AND DISCUSSION

The experimental results showed that better densification and moderate grain size were found when samples were sintered at a temperature of 1300°C or more. The above finding conforms to previous results performed by some other research work [11,12]. Experimental results of percent theoretical density (%TD) and grain size of La₂O₃ doped BaTiO₃ sintered at 1300°C are tabulated in Table 1. From these values, the sample sintered at 1300°C for 8 hours with a sintering rate of 3°C/min was found to yield higher density and moderate grain size for all mole% of La₂O₃ doping.

Microstructure with lesser porosity and uniform density was found for all 0.3 mole% La₂O₃ doped samples. The average grain size of the samples sintered at 1300° C for 2 and 4 hours were in the range of 0.15-0.25 µm for both 0.5 and 0.7 mole% La₂O₃ doped samples. The effect showed an adverse effect on the electrical properties as a result of the too fine grain size. The holding time for sintering was insufficient in these cases although the slower sintering rate (3° C/min) provided longer sintering time. The micrographs of samples with different doping level of La₂O₃ mole fractions and sintered at 1300° C for 4 hours are showed in Fig. 1 while Fig. 2 shows the microstructures of samples doped with different mole fractions of La₂O₃ and sintered at 1300° C for 8 hours.

TABLE 1. Percent theoretical density (%TD) and grain size of sintered La₂O₃ doped BaTiO₃ samples

| Sample | Maximum Sintering Temp. (⁰ C) | Sintering Time (hour) | Doping mole% | % theoretical density | Average Grain Size (µm) |
|--------|---|-----------------------------|-----------------|-----------------------------|----------------------------|
| | | 2 | | 95.57 | 0.51-0.68 |
| BTL3 | 1300 | 4 | 0.3 | 95.11 | 0.67-1.07 |
| | | 8 | | 91.82 | 0.75-1.20 |
| | | 2 | | 72.77 | 0.21-0.41 |
| BTL5 | 1300 | 4 | 0.5 | 88.61 | 0.25-0.43 |
| | | 8 | | 89.43 | 0.84-1.34 |
| | | 2 | | 69.26 | 0.16-0.29 |
| BTL7 | 1300 | 4 | 0.7 | 73.40 | 0.19-0.28 |
| | | 8 | | 81.00 | 0.70-1.01 |

These results are correspond with the findings of different researchers [10,11,12] reporting the increase in boundary mobility with cation concentration for tri-valance donor cations, but it then decreases markedly above a doping threshold of 0.5 mole% which is controlled by the microstructure of doped samples. As La³⁺ ions have different valance state (+3) as compared to the Ba²⁺ or Ti⁴⁺ (+2 or +4 respectively), substitution of Ba²⁺ produce a charge imbalance which leads to charge compensation leading to excess or shortage of electrons or vacancies of cations or anions. According to the 'Doping anomaly' or 'Grain size anomaly' phenomenon [11,12] a drastic change of BaTiO₃ characteristics is found as a result of doping with higher valence donor cations compared to the host cations.

It is found that, for donor-doped BaTiO₃, a drop in resistivity is observed at first with the increase of donor concentration which is generally attributed to an electronic compensation mechanism that induces n-type semiconductor characteristics [10]. For La³⁺ ion which acts as a donor dopant, free electrons in the BaTiO₃ lattice can be generated in the grain according to equations (written in Kröger-Vink notation) bellow the doping threshold value [10,11]:

$$2La_2O_3 + 4TiO_2 = 4La_{Ba} + 4Ti_{Ti} + 12O_0 + O_2 + 4e'$$
(2)

However, when dopant concentration is higher than the threshold, the dopant can be compensated by forming cation vacancies [10,11] at grain boundaries:

$$2La_2O_3 + 6TiO_2 = 4La_{Ba}' + 6Ti_{Ti} + 18O_0 + 2V_{Ba}''$$
(3)

Or, act as acceptors to occupy the Ti-site:

$$La_2O_3 + 2e' = 2La_{Ti}'' + 3O_0 + V_0$$
(4)

At the same time, the oxygen absorption at the grain boundaries act as an oxidation reaction which gradually propagates into the grains [10]:

$$2TiO_2 + O_2 = 2Ti_{Ti} + 6O_0 + 2V_{Ba}" + 4h$$
 (5)

Above the threshold, the accumulation of Ba²⁺ vacancies in the space charge is associated with a depletion of oxygen vacancies. The diffusivity of oxygen ions across the grain boundary is expected to be slow due to their relatively large size which provides a possible mechanism for the significant reduction in grain boundary mobility yielding in finer grain. Such grain growth inhibiting mechanism has also been evident in the different research study of BaTiO₃ ceramic [10,11,12].

In our work, above the threshold value of 0.5 mole% doping, the grain size reduced prominently (<0.50 µm) which can be due to the pinning effect of excessive La₂O₃ [10,11,13]. A high concentration of La³⁺ ions at or near grain boundaries restricted grain growth during sintering and promoted fine grains which result in unfavorable dielectric

properties. Although very insignificant energy is needed for the dopant to concentrate at the grain boundaries more energy is needed to incorporate a dopant ion into an individual lattice site in complex oxides which is related to

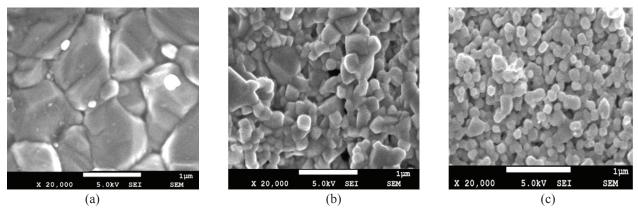


FIGURE 1. SEM micrograph of barium titanate samples sintered at 1300°C for 4 hours holding (a) BTL3 (b) BTL5 (c) BTL7

distortions, i.e. difference in ionic radii, and the formation of compensating defects during the incorporation of aliovalentions that have different valence states [11]. Thus, more energy was required in our research for the dopants to move inwards from the grain boundary by diffusion and thus reduce the pinning effect.

The required energy was provided by increasing the holding time to 8 hours at the maximum sintering temperature of 1300° C for all dopant concentration. So the average grain size of doped samples was about 1-1.2 μ m, favorable for obtaining good electrical properties.

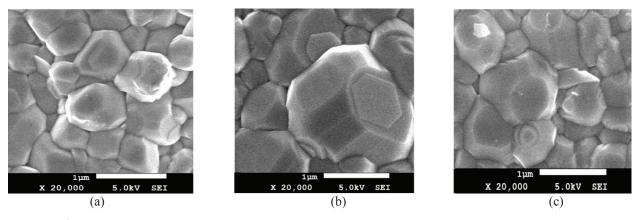


FIGURE 2.SEM micrograph of barium titanate samples sintered at 1300° C for 8 hours holding (a) BTL3 (b) BTL5 (c) BTL7.

The XRD results of lattice parameter in Table 2 showed that the tetragonality of $BaTiO_3$ crystal was reduced as the La_2O_3 doping level exceeds 0.5 mole% and at 0.7 mole % La_2O_3 doped Barium Titanate, the structure might retain the cubic phase to a greater degree. The corresponding changes in dielectric properties shown in Table 3 confirms the decrease of tetragonality as shifting the curie temperature from 100° C to 96° C when the La2O3 doping level increases from 0.5 mole% to 0.7 mole %. Moreover no trace of second phase appeared in the XRD analysis, which suggests that under the best sintering cycle (1300° C and 8 hours holding) almost all the La^{3+} ions were well diffused into the crystal structure of $BaTiO_3$ and reduced the pinning effect.

TABLE 2. Lattice parameters from XRD patterns of La₂O₃ doped BaTiO₃ samples

| Ba _{1-x} La _x TiO ₃ | Sintering time (hr) | a (Å) | c (Å) | c/a | Cell Volume (ų) |
|--|------------------------|--------------------|--------------------|--------|--------------------|
| BaTiO ₃ (powder) | 0 | 3.9993±0.002 | 4.0135±0.013 | 1.0035 | 64.20 |
| $Ba_{0.997}La_{0.003}TiO_{3}$ | 8 | 4.0254 ± 0.013 | 4.0032 ± 0.004 | 1.0055 | 64.86 |
| $Ba_{0.995}La_{0.005}TiO_{3}$ | 8 | 4.0061 ± 0.003 | 4.0352 ± 0.004 | 1.0073 | 64.76 |
| $Ba_{0.993}La_{0.007}TiO_{3}$ | 8 | 4.0087 ± 0.003 | 4.0038 ± 0.002 | 1.0012 | 64.34 |

Dielectric Properties

The enhanced dielectric properties of BTL3, BTL5 and BTL7 ceramics obtained by solid state sintering for 8 hours at 1300° C have been studied. The temperature dependence of dielectric constant and dielectric loss as a function of donor concentration is presented in Fig 3. Dielectric dissimilarities were detected for the samples corresponding to tetragonal to cubic phase transition. The peak positions of all structural transitions were shifted to lower temperatures. The peaks became broadened and the peak position went higher (up to threshold doping %) as the lanthanum concentration increased. These plots also point out that up to 5 mole% addition of lanthanum leads to increase of dielectric constant. The observed peak temperatures corresponding to all structural transformation and dielectric constant values at 100 Hz for the samples are tabulated in Table 3.

TABLE 3. Theoretical density, grain size, curie temperature (T_C) and dielectric constant of best sintering cycles

| Ba _{1-x} La _x TiO ₃ | Max. Sintering Temp. (°C) | Sintering Time (hour) | Doping mole% | % theoretical density | Average Grain Size (μm) | T _C (°C) | Dielectric Constant at room temp. and 100 Hz | Dielectric constant at T _C and 100 Hz |
|--|------------------------------------|-----------------------------|-----------------|-----------------------------|-------------------------------|---------------------|--|---|
| Ba _{0.997} La _{0.003} TiO ₃ | 1300 | 8 | 0.3 | 91.82 | 0.75-1.20 | 110 | 6000 | 3200 |
| $Ba_{0.995}La_{0.005}TiO_{3}$ | 1300 | 8 | 0.5 | 89.43 | 0.84-1.34 | 100 | 12700 | 8000 |
| $Ba_{0.993}La_{0.007}TiO_{3}$ | 1300 | 8 | 0.7 | 81.00 | 0.70-1.01 | 96 | 1600 | 1200 |

According to the literature [15,16,17], for a particular temperature it is apparent that there is a decrease in dielectric constant with an increase of frequency and Fig. 4(a) conforms to this. It can be noted that dielectric constant for doped samples decreases rapidly with the increase of frequency and then stabilizes at a constant value. Therefore, addition of different concentration of lanthanum can be an effective way to control grain size and adjust the dielectric behavior.

Frequency dependent dielectric constant and dielectric loss of BaTiO₃ doped with different mole percentage of La₂O₃ and sintered at 1300°C for 8 hours are shown in Fig. 4. Dielectric losses of all samples followed a similar pattern, they decreased with increase of temperature up to certain limit and increased as concentration of lanthanum became higher as shown in Fig. 3 and Fig. 4(b).

M.M. Vijatovic, B.D. Stojanovic [13] proposed two factors that can be responsible for this behavior. Lowering of Tc with lanthanum concentration may be due to size of La^{3+} (1.15 Å) which is smaller compared to Ba^{2+} (1.35 Å) and making the tetragonal phase unstable or due to creation of titanium vacancies destroying Ti–O–Ti linkages, responsible for ferroelectricity.

The pinning effect or influence of defect structure on doping level was found to affect grain size and grain size affects dielectric properties. Average grain size around 1 µm normally provides a good condition for dielectric properties of doped BaTiO₃. In this research, grain sizes in the range of 0.85-1.34 µm showed high dielectric constant, while increasing grain size deteriorated its property. The best stable value of dielectric constant as a function of temperature was obtained in the range 10000-12000 for 0.5 mole % La₂O₃ doped BaTiO₃ as shown in Fig. 3(b). It is evident from the figure that the curie point was shifted to about 100° C for BTL5 and to about 96° C for BTL7.

These results indicate at the influence of grain size on dielectric constant as well. As grain size of samples becomes smaller (\sim 1/1.2 μ m) by the influence of lanthanum concentration, dielectric constant becomes higher as noticed in the previous papers [12,13] as well.

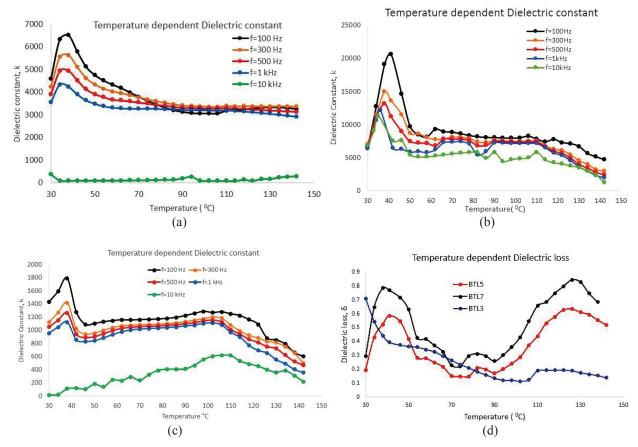


FIGURE 3. (a) Temperature dependent dielectric constant at different frequencies for 0.3 mole% La₂O₃ doped BaTiO₃ sintered at 1300° C for 8 hours, (b) temperature dependent dielectric constant at different frequencies for 0.5 mole% La₂O₃ doped BaTiO₃ sintered at 1300°C for 8 hours, (c) temperature dependent dielectric constant at different frequencies for 0.7 mole% La₂O₃ doped BaTiO₃ sintered at 1300°C for 8 hours, (d) temperature dependent dielectric loss at f=100 Hz for 0.3, 0.5 and 0.7 mole% La₂O₃ doped BaTiO₃ sintered at 1300° C for 8 hours.

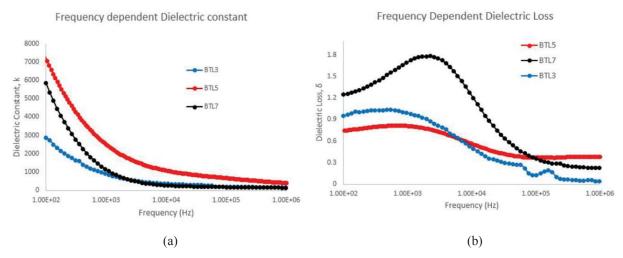


FIGURE 4. (a) Frequency dependent dielectric constant of 0.3, 0.5 and 0.7 mole% La₂O₃ doped BaTiO₃ sintered at 1300° C for 8 hours, (b) frequency dependent dielectric loss of 0.3,0.5 and 0.7 mole% La₂O₃ doped BaTiO₃ sintered at 1300°C for 8 hours (determined at T=22° C)

Further research should be conducted of different ranges of intermediate mole percentage between 0.3, 0.5 and 0.7 mole% by polymeric precursor method for identifying detailed properties of lanthanum doped barium titanate.

CONCLUSIONS

In this work, moderate grain size of La doped BaTiO₃ was formed from sintering materials of 80-100nm size particles by conventional ball milling mixing process and solid state sintering method. The method appeared to be quite appropriate for the current work. By altering sintering temperature and holding time, grain size could be modified and hence the electrical properties were enhanced which also depended on dopant concentration.

Doping of La_2O_3 lowered the curie temperature by acting as a peak suppressor. Attractive dielectric constant was found with 1.0 - 1.2 μm grain size. The best stable of temperature dependent dielectric constant was found to be 13000 for 0.5 mole% doping of La_2O_3 with average 0.84-1.34 μm grain size. It was also found that, dielectric constant decreased with increasing applied frequency for a particular temperature.

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