Paper ID: MS-28

Influence of Lanthanum doping on the Crystallite Growth and Dielectric Properties of Barium Titanate ($BaTiO_3$) Ceramics

Masum Billah[1*], Adnan Adib Ahamed[1], Aungkan Sen[1] and Md. Miftaur Rahman[2],
[1]Department of Materials & Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh
[2]Assistant Professor, Department of Materials & Metallurgical Engineering, Bangladesh University of Engineering and Technology, Dhaka-1000, Bangladesh
[*]*Corresponding author's E-mail address: masum.buet09@gmail.com*

Abstract

The structure-property relationship of 0.3, 0.5 and 0.7 mole% lanthanum oxide (La_2O_3) doped Barium titanate ($BaTiO_3$) ceramics prepared by solid state sintering method under different sintering conditions were investigated in this research. The raw materials were La_2O_3 (grain size=~80nm, purity=99.995%) and $BaTiO_3$ (grain size=100nm, purity=99.99%) nano powders. Field Emission Scanning Electron Microscope was used to examine grain size and surface morphology of sintered pellet. X-Ray Diffraction analysis was performed to identify crystal structure. The results for 0.5mole% La_2O_3 sintered at 1300° C for 8 hours showed significantly improved and more desired grains (size=0.8-1.3µm), high densification (>90% theoretical density) and stable dielectric constant of 12700 at room temperature (100Hz) by lowering the curie temperature around 30° C. A gradual deterioration follows with increased doping concentration. So this research revealed that proper La^{3+} concentration can inhibit grain size and lower curie temperature hence significantly improving the electrical properties of $BaTiO_3$ ceramics.

Keywords: Barium Titanate, Lanthanum oxide doping, Microstructure, Frequency, Dielectric properties.

1. Introduction

Barium titanate ($BaTiO_3$) has diversified application in the field of electro-ceramics 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 a perovskite type tetragonal lattice structure (ABO_3) with a high dielectric constant of 1500-2000 at room temperature [4] which fluctuates under different operating 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 $BaTiO_3$. 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 $BaTiO_3$ can be produced by atmospheric reduction forming oxygen vacancy or by low concentration donor doping with trivalent ions (La^{3+}, Y^{3+}, Sb^{3+}) on Ba-site or pentavalent ions (Nb^{5+},Ta^{5+}) on Ti-site [5,6,7,8]. Ionic radius is the main parameter determining the substitution site. In this case La^{3+} (1.15 Å) is exclusively incorporated at the Ba^{2+} (1.35 Å) site as its size is incompatible with that of Ti^{4+} (0.68 Å). Replacement of Ba^{2+} by La^{3+} ion produces an extra positive charge and due to electrical neutrality, an e^- is trapped by a Ti^{4+} ion followed by the equation (1) [9].

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

Various research [9,10,11] showed that small concentration of La^{3+} in $BaTiO_3$ increase grain growth, decrease phase transition temperature 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 $BaTiO_3$ ceramics with minimum porosity by solid state sintering, examine the influence of La doping on microstructure, crystalline structure and dielectric properties and determine the detailed structure-property relationship.

2. Experimental procedure

Lanthanum doped Barium Titanate samples (BTL) were prepared from $BaTiO_3$ (grain size =100nm) and La_2O_3 (grain size=~80nm) nano powders [Manufacturer: INFRAMAT (USA); Purity> 99%]. Here La_2O_3 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 500º C for 1 hour (heating rate 2º C/min). Sintering was performed at 1300º C for 2, 4, 8 hours (heating and cooling rate 3º 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 Scanning Electron Microscope (Model-JEOL JSM-7600F, Japan) and crystal structure was detected using X-ray diffractometer (Model-BRUKER D8 ADVANCE, Germany). Temperature dependent dielectric constant was measured from 30º C to 145º C at various frequencies (100, 300, 500, 1k and 10 kHz) at a heating rate of 4º C/min using an impedance analyzer (WAYNE KERR 6500B series).

3. Results and discussion

The experimental results showed that better densification and moderate grain size were found when samples were sintered at a temperature of 1300º 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 La_2O_3 doped $BaTiO_3$ sintered at 1300º C are tabulated in Table 1.

Table 1. Percent theoretical density (%TD) and grain size of sintered La_2O_3 doped $BaTiO_3$ samples

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

From these values, the sample sintered at 1300º C for 8 hours with a sintering rate of 3º C/min was found to yield higher density and moderate grain size for all mole% of La_2O_3 doping.

The micrographs of samples with different doping level of La_2O_3 mole fractions, sintered at 1300º C for 2 and 4 hours are shown in Fig. 1 and Fig. 2, while Fig. 3 shows the microstructures of samples doped with different mole fractions of La_2O_3, sintered at 1300º C for 8 hours. Microstructure with lesser porosity was found for all 0.3 mole% La_2O_3 doped samples but when sintered at 1300º C for 2 hours, the grain growth was insufficient resulting in non-uniform grain size as shown in Fig.1. Moreover the average grain size of the samples sintered at 1300º C for 2 and 4 hours were in the range of 0.15-0.25 µm for both 0.5 and 0.7 mole% La_2O_3 doped samples and showed an adverse effect on the electrical properties as a result of too fine grain size. The holding time for sintering was insufficient in these cases although the slower sintering rate (3º C/min) provided longer sintering time. However the sample sintered for 8 hours indicated better grain size with enhanced dielectric properties.

These results correspond with the findings of different researchers [10,11,12] reporting the increase in boundary mobility with cation concentration for tri-valent donor cations, but it then decreases markedly above a doping threshold of 0.5 mole% which is controlled by the microstructure of doped samples. When La^{3+} substitutes Ba^{2+} ion, it produces a charge imbalance. As a result a charge compensation occurs 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 $BaTiO_3$ 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 $BaTiO_3$, 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].

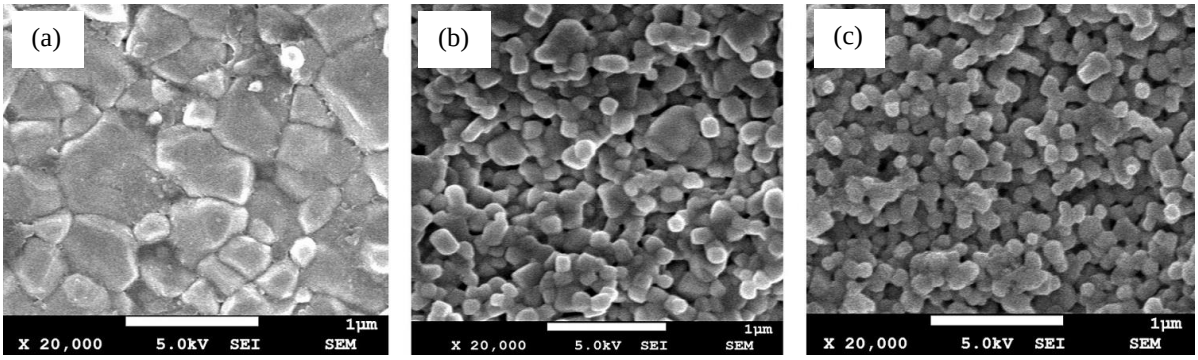

Fig. 1. SEM micrograph of $BaTiO_3$ samples sintered at 1300° C for 2 hrs. holding (a) BTL3 (b) BTL5 (c) BTL7

During this distinct process, free electrons in the $BaTiO_3$ lattice can be generated in the grain according to the equation (written in Kröger-Vink notation) bellow the doping threshold value [10,11]:

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

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

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

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

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

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

$$2TiO_2 + O_2 = 2Ti_{Ti} + 6O_0 + 2V_{Ba}'' + 4h^{\cdot} \quad (4)$$

Above the threshold values, accumulation of Ba^{2+} 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. It provides a possible mechanism for the reduction in grain boundary mobility to yield finer grains. Such grain growth inhibiting mechanism has been evident in the different research on $BaTiO_3$ [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 La_2O_3 [10,11,13]. A high concentration of La^{3+} ions at or near grain boundaries restricted grain growth during sintering and promoted fine grains which resulted in unfavorable dielectric properties.

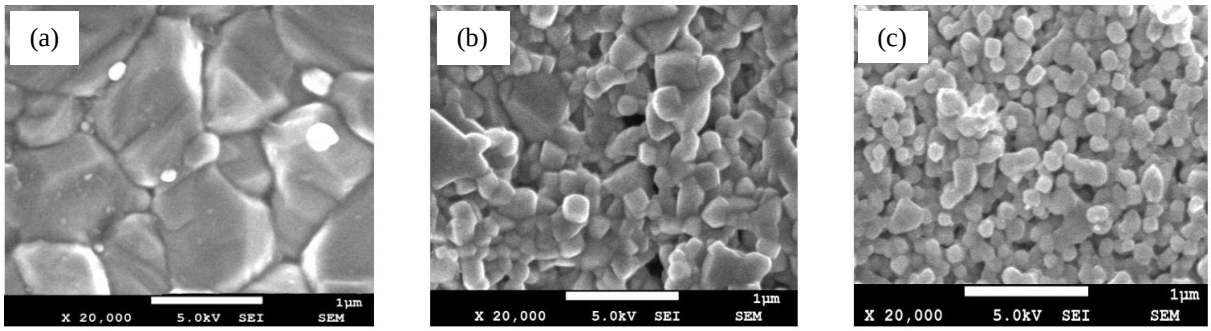

Fig. 2. SEM micrograph of $BaTiO_3$ samples sintered at 1300° C for 4 hrs. holding (a) BTL3 (b) BTL5 (c) BTL7

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

distortions, i.e. difference in ionic radii, and the formation of compensating defects during the incorporation of aliovalent ions 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.

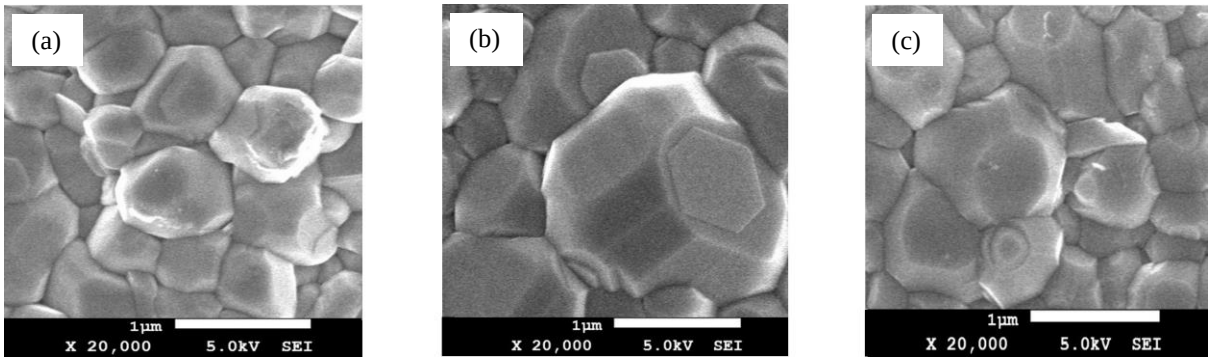

Fig. 3. SEM micrograph of $BaTiO_3$ samples sintered at 1300º C for 8 hrs. holding (a) BTL3 (b) BTL5 (c) BTL7

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% in $BaTiO_3$, 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 100º C to 96º C when the La_2O_3 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 (1300º C and 8 hours holding time) almost all the La^{3+} ions were well diffused into the crystal structure of $BaTiO_3$ and reduced the pinning effect.

Table 2. Crystal parameters from XRD patterns of La_2O_3 doped $BaTiO_3$ samples

$Ba_{1-x}La_xTiO_3$	Sintering time (hr)	*a* (Å)	*c* (Å)	*c/a*	Cell Volume (Å^3)
$BaTiO_3$ (1300ºC)	8	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 1300º C have been studied. The temperature dependence of dielectric constant and dielectric loss as a function of donor concentration is presented in Fig. 4. 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 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

$Ba_{1-x}La_xTiO_3$	Maximum Sintering Temp. (ºC)	Sintering Time (hour)	Doping mole %	% theoretical density	Average Grain Size (µm)	T_C (ºC)	Dielectric Constant at room temperature 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 Figure 5(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 $BaTiO_3$ doped with different mole percentage of La_2O_3 and sintered at 1300º C for 8 hours are shown in Figure 5. 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 Figure 4(d) and Figure 5(b).

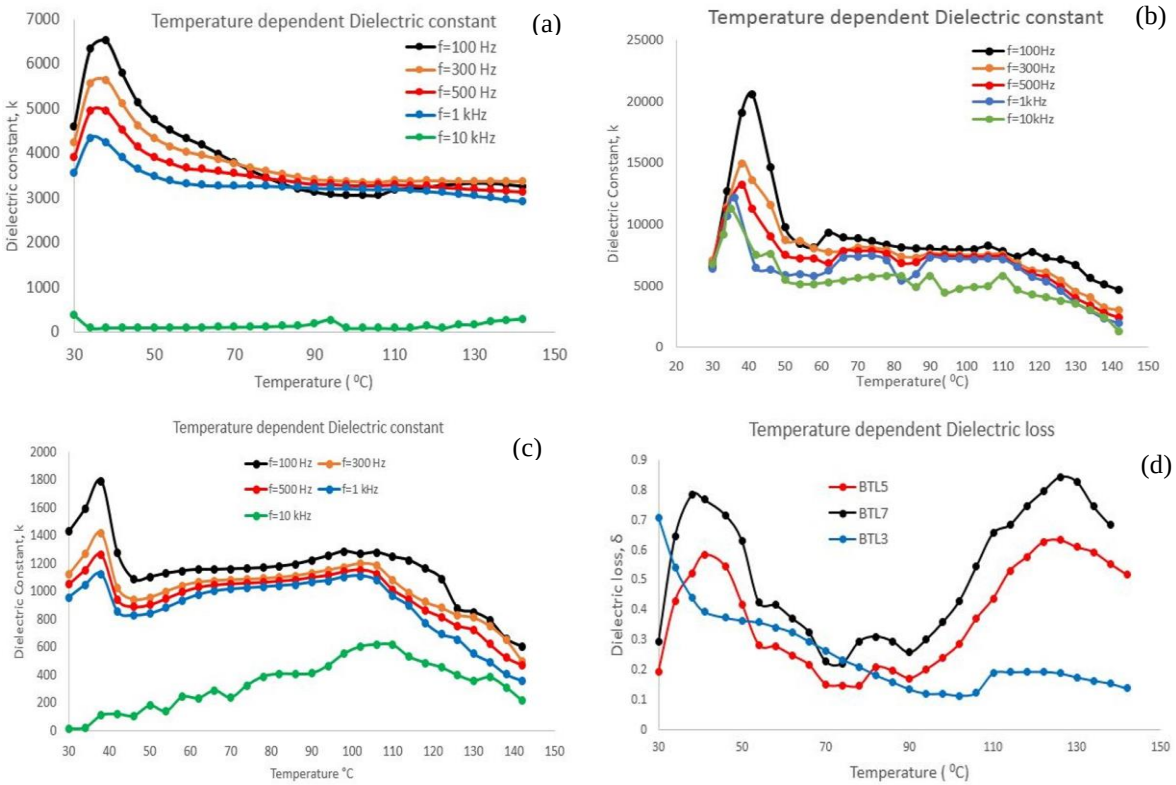

Fig. 4. (a) Temperature dependent dielectric constant at different frequencies for 0.3 mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8hrs, (b) temperature dependent dielectric constant at different frequencies for 0.5 mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8hrs, (c) temperature dependent dielectric constant at different frequencies for 0.7mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8hrs, (d) temperature dependent dielectric loss at f=100 Hz for 0.3, 0.5 and 0.7mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8hrs.

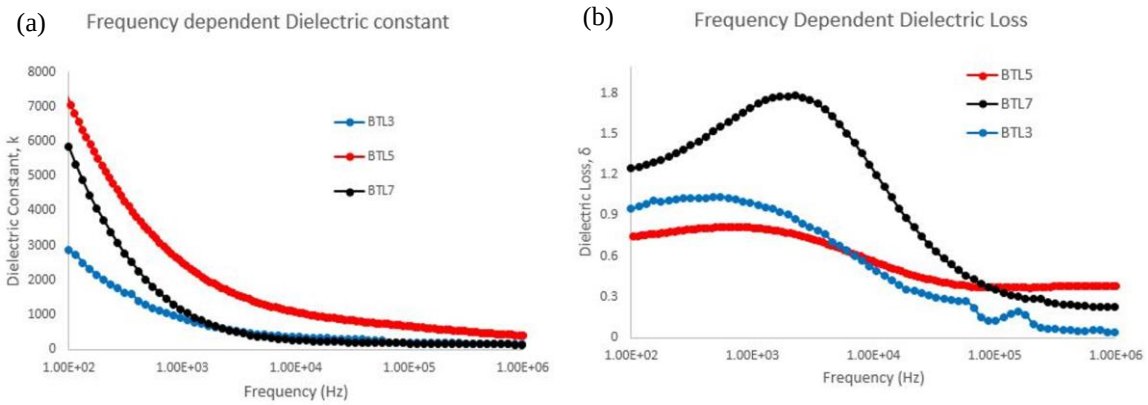

Fig. 5. (a) Frequency dependent dielectric constant of 0.3, 0.5 and 0.7 mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8 hours, (b) frequency dependent dielectric loss of 0.3,0.5 and 0.7 mole% La_2O_3 doped $BaTiO_3$ sintered at 1300º C for 8 hours (determined at T=22º C)

M.M. Vijatovic, B.D. Stojanovic [13] proposed two factors that can be responsible for this behavior. Lowering of T_c 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 $BaTiO_3$. In this research, grain sizes in the range of 0.85-1.2 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 12000-14000 for 0.5 mole % La_2O_3 doped $BaTiO_3$ as shown in Figure 4(b). It is evident from the figure that the curie point was shifted to lower value i.e. 110º C, 100º C and 96º C for 0.3, 0.5 and 0.7 mole% respectively. These results indicate at the influence of grain size on dielectric constant as well. As grain size of samples becomes smaller (~1/1.2 µm) by the influence of lanthanum concentration, dielectric constant becomes higher as noticed in the previous papers [12,13] as well.

Further research should be conducted of different ranges of intermediate mole percentage between 0.3, 0.5 and 0.7 mole% by the polymeric precursor method which is more acceptable to form denser product for identifying detailed and better properties of lanthanum doped barium titanate ceramics.

4. Conclusion

In this work, moderate grain size of La doped $BaTiO_3$ was formed from starting materials of 80-100 nm 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 and most stable temperature dependent dielectric constant was found to be 12700 for 0.5 mole% doping of La_2O_3 with average grain size of 0.84-1.34 µm. It was also found that, dielectric constant decreased with increasing applied frequency for a particular temperature.

5. Acknowledgement

The author gratefully acknowledge the Glass and Ceramic Engineering Department, BUET and Bangladesh Council of Scientific and Industrial Research (BCSIR) for their consistent technical support.

6. References

[1] J.B. Xu, J.W. Zhai, X. Yao, "Structure and dielectric nonlinear characteristics of $BaTiO_3$ thin films prepared by low temperature process", *Journal of Alloys and Compounds*, 467 pp. 567–571, 2009.

[2] H. Fan, L. Liu, "Optimizing design of the microstructure of sol-gel derived $BaTiO_3$ ceramics by artificial neural networks", *Journal of Electro-ceramic*, 22**,** pp. 291–296, 2009.

[3] F. Wan, J.G. Han, Z.Y. Zhu, "Dielectric response in ferroelectric $BaTiO_3$", *Phys. Lett. A*, 372**,** pp. 2137–2140, 2008.

[4] Arlt G, Hennings D, De-With G, "Dielectric properties of fine grained barium titanate ceramics", *Journal of Applied Physics*, Vol-58, pp. 1619, 1985.

[5] M.T. Biscaglia, V. Buscaglia, M. Viviani, P. Nanni, M. Hanuskova, "Influence of foreign ions on the crystal structure of $BaTiO_3$", *Journal of European Ceramic Society*, 20, pp.1997–2007, 2000.

[6] F.D. Morrison, D.C. Sinclair, A.R. West, "Doping mechanisms and electrical properties of La-doped $BaTiO_3$ ceramics", *Int. J .Inorg. Mater*., 3, pp.1205–1210, 2001.

[7] Rubayyat Mahbub, Md. Sazzad Hossain, Md. Fakhrul Islam, "Structural Characteristics and Dielectric Properties of Tantalum Oxide Doped Barium Titanate Based Materials", *Materiálové inžinierstvo (MEMI) Journal*, 20, pp.45-53, 2013.

[8] Rajendra N. Basu, H. S. Maiti, "Materials Research Bulletine" 21(9), pp. 1107, 1986.

[9] B. Wodecka-Dus, D. Czekaj, "Fabrication and Dielectric Properties of Donor Doped $BaTiO_3$ Ceramics", *Archives of Metallurgy and Materials*, Vol. 54, Issue 4, 2009.

[10] Zhi Cheng Li, Bill Bergman, "Electrical properties and ageing characteristics of $BaTiO_3$ ceramics doped by single dopants", *Journal of European Ceramic Society*, 25, pp. 441-445, 2005.

[11] Yoeng Jung Kim, June Won Hyun, HeeSoo Kim. Joo Ho Lee, Mi Young Yun. S.J. Noh and Yong Hyun Ahn, "Microstructural characterization and dielectric properties of barium titanate solid solution with donor dopants", Bulletin of Korean Chemical Society, Vol. 30, No. 6, pp.1268-1273, 2009.

[12] Helen M.Chan, Martin P. Harmer and Donald M. Smyth, "Compensating Defects in Highly Donor-Doped $BaTiO_3$", *Journal of American Ceramic Society*, Vol. 69[6], pp.507-10, 1986.

[13] M.M. Vijatovic´, B.D. Stojanovic´, J.D. Bobic´, T. Ramoska , P. Bowen, "Properties of lanthanum doped BaTiO3 produced from nanopowders", *Ceramics International*, Vol.36, pp. 1817, 2010.

[14] Tadas Ramoška, J. Banys, R. Sobiestianskas, M. V. Petrovic, J. Bobic, B. Stojanovic, "Dielectric Investigation of La-doped barium titanate", *Processing and Application of Ceramics* 4 [3], pp.193–198, 2010.

[15] C. Barry Carter, M. Grant Norton, Ceramic Materials Science and Engineering, *Springer*, 3rd edition, pp.556-574.

[16] Kingery, Bowen, Uhlman: Introduction to Ceramics, *John Willey & Sons*, second edition, Singapore, 1976.

[17] David W. Richerson, Modern Ceramic Engineering, 2nd edition, Marcel Dekker, pp.204-312, 1992.