

Electrical Properties of Undoped and Lanthanum Doped $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$

M.S. Dash ^a, J. Bera ^b and S. Ghosh ^a

^aDepartment of Electrical Engineering, ^bDepartment of Ceramic Engineering
National Institute of Technology, Rourkela - 769 008, INDIA
E-mail: sghosh.ce@gmail.com

Abstract- Lanthanum doped $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ composition $x = 0.005, 0.01, 0.02, 0.05$ and 0.1 in $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{0.6[1-5x/12]}\text{Zr}_{0.4}\text{O}_3$ were prepared by modified chemical route. $(\text{COOH})_2 \cdot 2\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and La_2O_3 are used to precipitate barium oxalate hydrate, lanthanum oxalate hydrate and zirconium oxy-hydroxide from its water solution onto the surface of suspended TiO_2 particles. The lanthanum doped $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ composition was found to be cubic by XRD analysis. A gradual shift of 2θ angles to the higher angle with increasing lanthanum percentage in the BTZ reveals the contraction of perovskite lattice. The frequency dependence of dielectric permittivity and loss $\tan \delta$ of the ceramics has been investigated. It is found that dielectric permittivity (ϵ_r) decreases and loss $\tan \delta$ decreases with increase in lanthanum percentage. Neither of the samples shows semiconductivity, which is believed to be because of titanium vacancy compensation.

I. INTRODUCTION

The high dielectric constant combined with low dissipation factor makes BaSrTiO_3 (BST) one of the promising candidates for dynamic random access memory (DRAM storage capacitors), decoupling capacitors, and dielectric field tunable elements for high frequency device applications [1-3]. It is paraelectric, cubic perovskites with low leakage current, which is commonly used to replace silicon dioxide (SiO_2) as the dielectric in advanced memory devices.

The large electrical field-dependent dielectric constant can be used for devices such as tunable oscillators, filters and phase shifters. In such devices, it is desirable to have a high dielectric tunability in a certain electric field range and low dielectric loss. However, although the BST composition has been optimized, the dielectric losses are still high and its breakdown field is rather low for the production of electronic devices. In addition, for agile high frequency filters and lines, the tunability of BST is not always compatible with the low losses requirements.

New materials are then desirable to meet all these requirements. Similarly to BST, the Curie temperature of BaTiO_3 (BT) is shifted below room temperature by the addition of zirconium, a isovalent substitution. The dielectric properties thus depend on the zirconium content and have been extensively studied for the bulk ceramic.

Recently, $\text{Ba}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$ (BZT) has been chosen as an alternative to BST in the fabrication of ceramic capacitors. The

solid solution of barium titanate (BT) and barium zirconate BaZrO_3 (BZ), i.e., BZT, shows great similarity to the BST solid solution. In general Zr^{4+} is chemically more stable than Ti^{4+} , suitable for BST substitution [4 -7].

Insulating properties increases with Zr content. It is believed that the conduction by electron hopping between Ti^{+4} and Ti^{+3} , if any would be depressed by substitution of Ti with Zr.[8]. Lanthanum doping in barium titanate based perovskites exhibit semi-conducting or highly insulating properties depending on different parameters. [9-11].

In perovskites, the relaxor behavior mainly occurs in lead-based compositions (PMN, PSN, PLZT, etc.) with more than one type of ions occupying the equivalent six-coordinated crystallographic sites. Lead-free compositions could be of great interest for environmentally friendly applications (such as dielectrics for capacitors, actuators, etc.). The solid solution BT-BZ shows the highest dielectric susceptibility at room temperature for a 25% Zr substitution in the crystal structure. Therefore, $\text{BaTi}_{1-x}\text{Zr}_x\text{O}_3$ (BTZ) with $x > 0.25$ is a paraelectric material at room temperature with a high dielectric constant and low dielectric dispersion against frequency. Moreover, for the compositions between 26% and 40%, bulk ceramics display relaxor behaviour. Lanthanum doping also shows relaxor behavior. [11].

The BT-BZ solid solutions are conventionally synthesized through solid oxide route [12-13] and lanthanum doped BT-BZ through solid oxide route [14]. Chemical solution methods are also used to produce more homogeneous, finer particle size and low impurity level powders than that produced by the solid-oxide method [15]. On the other hand, the solid-oxide synthesis has advantages with respect to the use of relatively low-cost raw materials and simple processing steps.

In the present synthesis $\text{Ba}(\text{NO}_3)_2$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$, La_2O_3 and TiO_2 raw materials are used for the preparation of lanthanum doped BTZ to get some of the benefits of both the solid-oxide and chemical route. Use of TiO_2 and La_2O_3 instead of its organometallic salt, can effectively reduce the powder synthesis cost. Further, $\text{Ba}(\text{NO}_3)_2$, $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and La_2O_3 are used to precipitate barium oxalate hydrate, lanthanum oxalate hydrate and zirconium oxy-hydroxide from its water solution onto the surface of suspended TiO_2 particles, to get more homogeneous mixing of raw materials than that obtained in solid powder mixing. This type of powder synthesis has been

reported earlier in the literature especially for BT, BTZ and SrTiO₃ [15-17]. These reactions allow relatively phase-pure products under low temperature.

We have prepared Lead-free Ba(Zr_yTi_{1-y})O₃ ceramics through modified chemical route method. The influence of Lanthanum content on the dielectric properties and loss of the insulative Ba(Zr_yTi_{1-y})O₃ ceramics with $y = 0.4$ were examined and discussed. We investigate the system BaLaTiZrO₃ where cationic substitutions, iso-valent in octa-hedral sites (Ti⁴⁺, Zr⁴⁺), are simultaneous with off-valent ones in dodecahedral sites (Ba²⁺, La³⁺). We focused our attention on two conjugate effects which could be at the origin of the relaxor phenomena (1) the probable disorder exhibited, in appropriate scale regions, between the two tetravalent cations (2) the peculiar character of the rare-earth element which is known to induce an electronic “donor-doping” and/or an ionic compensation mechanisms.

II. EXPERIMENTAL PROCEDURE

Lanthanum doped BaTi_{0.6}Zr_{0.4}O₃ composition $x = 0.005, 0.01, 0.02, 0.05$ and 0.1 at.% in Ba_{1-x}La_xTi_{0.6[1-5x/12]}Zr_{0.4}O₃ were prepared by modified chemical route. The basic materials used in the present work include; Ba(NO₃)₂ (Assay >99%, Merck India Ltd.), TiO₂ (Anatase, Assay >99%, Merck India Ltd., particle size: $d_{10} = 0.27 \mu\text{m}$, $d_{50} = 0.35 \mu\text{m}$, $d_{90} = 0.48 \mu\text{m}$), La₂O₃ (Assay >99%, Loba Chemie Pvt. Ltd.), ZrOCl₂.8H₂O (Assay >99%, Loba Chemie Pvt. Ltd.) and (COOH)₂.2H₂O (Assay >99%, Merck India Ltd.). An aqueous solution of 0.12 M barium nitrate was prepared using deionized water. The exact molarity of the solution was determined by the chemical analysis. Lanthanum dioxide was added along with negligible amount of HNO₃, which helps in dissolving colloidal solution of lanthanum dioxide into the solution. Required amount of ZrOCl₂.8H₂O was dissolved in the above solution. Further, appropriate amount of TiO₂ was added to 0.15 M oxalic acid solution with continuous stirring to form a suspension. The suspension was treated in ultrasonic bath for 10 min to break TiO₂ agglomerates. The barium nitrate, lanthanum dioxide and zirconium oxy-chloride mixed solution was added drop-wise into the suspension of TiO₂ in oxalic acid solution under vigorous stirring. Finally, the pH of the resultant mixture was adjusted to 8 by adding ammonia solution. This process precipitates barium oxalate hydrate, lanthanum oxalate hydrate and ZrO(OH)₂ on the surface of fine TiO₂ (acting as seed) particles by heterogeneous nucleation. It is well known that heterogeneous nucleation is used in coating of ceramic particles with another ceramics. The necessary condition is that the super saturation must be controlled so that only heterogeneous nucleation on the seed takes place. If super saturation is too high, homogeneous nucleation will take place [18]. In the present case super saturation was controlled by the use of dilute solutions. The resulting precipitate was filtered

out and then washed repeatedly using deionized water & Isopropyl alcohol, followed by drying at 50 °C for 24 h.

The dry powder was then annealed at 1200 °C for 2-16 hours depending upon composition to get phase pure product. The annealed powder was ball milled for 24 hours using zirconia balls with acetone as medium. The milled powder was then uniaxially pressed to disk-shaped pellet (15 mm Φ) at 3.5 tonne pressure with 0.5 wt% PVA as binder. The pellets were heated at the rate of 2 °C/min till 500 °C (2h) for binder burnout and sintered at 1300 °C -1400 °C depending upon the composition, at the rate of 2 °C/min and slowly cooled in the furnace. The bulk densities of sintered samples were measured by Archimedes method using distilled water as medium. Silver paste was coated, fired on at 700 °C for 10min, to form electrodes on both sides of sintered ceramic specimen for dielectric measurement.

X-ray diffraction measurements were done by using Cu (K_α) X-ray Diffractometer (PW-1830, Philips, Netherlands). The phases present in the sintered samples were identified by comparison of the diffraction patterns with the reference cards of JCPDS Powder Diffraction File. The lattice parameters were measured using check cell software. The measurement on the bulk densities of the BLTZ specimens shows the densities of the ceramics are as high as 90% of the theoretical density. The capacitance and loss tan δ of the samples were measured using an HP-4192A impedance analyzer. The relative permittivity of the dielectric (ϵ_r) was calculated using the formula $\epsilon_r = c d / \epsilon_0 A$, where ϵ_0 is the permittivity of free space, c the capacitance, d the thickness and A the capacitor area.

III. RESULTS AND DISCUSSIONS

Fig.1. shows the X-ray diffraction pattern (XRD) of different at.% lanthanum doped BaTi_{0.6}Zr_{0.4}O₃. Perovskite peaks were observed for all the lanthanum percentages without existence of any secondary phases. A gradual shift of 2θ angles to the higher angle with increasing lanthanum percentage in the BTZ reveals the contraction of perovskite lattice. A rather long sintering time was adopted to ensure a homogeneous dopant distribution in the final material and determination of meaningful lattice parameter.

The usually adopted sintering times do not always guarantees the attainment of uniform distribution of temperature. Different sintering times were required to obtain a homogeneous single phase perovskite solid solution as discussed in the previous section. Less sintering times indicates non-equilibrium and highly distorted states within the ceramic samples. Reduced lattice parameter is obtained for higher substitution of lanthanum.

For many years, A and B site dopants have been used to modify the electrical properties of BaTiO₃, many cases the doping mechanism(s) and defect chemistry remain poorly understood and/or controversial. Undoped BaTiO₃ and BaTi_{0.6}Zr_{0.4}O₃ is electrically insulating, but oxygen deficiency can occur at high temperatures.

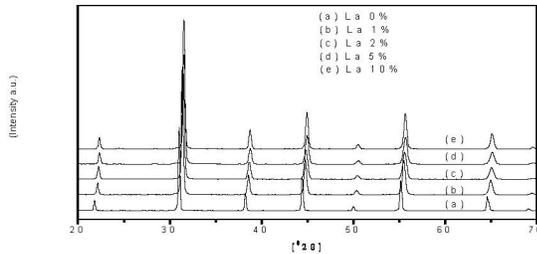


Fig.1. XRD patterns for different lanthanum doped Ba (Ti_{0.6}Zr_{0.4})O₃ at room temperature.

The electrons generated reduce Ti⁺⁴ ion to Ti⁺³ and makes it semiconducting. Small addition of lanthanum (<1 at.%) also induces n-type semiconductivity, which has been widely believed to occur via an electronic compensation mechanism. This phenomenon is commonly referred to as lanthanum “donor-doping” mechanism and gives general formula Ba_{1-x}La_xTiO₃. F. D. Morrison *et. al* [10] confirmed that lanthanum doped BaTiO₃ forms primarily according to an ionic, titanium-vacancy compensation mechanism leading to a general formula Ba_{1-x}La_xTi_{1-x/4}O₃. Detailed electrical-properties measurement shows smooth variation of dielectric properties from classical first order ferroelectric to paraelectric phase transition for x<0.1. However heating the samples in air >1350 °C causes a change to semiconducting or leaky dielectric behavior attributed to oxygen loss. Despite extensive studies, the electrical properties of lanthanum doping in BaTiO₃ ceramics heated in air is poorly understood.

The amount of oxygen loss in the undoped of lanthanum doped BaTiO₃ is very small and difficult to control specially heating in air >1350 °C. The electrical properties are very sensitive to oxygen nonstoichiometry, and room temperature resistance is heavily dependent on degree of reoxidation that occurs during cooling, on kinetic variables, such as cooling rate. Thus semiconductivity can be obtained only by rapid quenching of samples from high temperature, where as slow cooled samples exhibit much higher room temperature resistance.

In this study, we have taken minimum lanthanum percentage to 0.5% and maximum to 10% and the samples were heated between 1300 °C to 1400 °C in the furnace. Cooling was controlled to be slow. We did not find semiconductivity in any sample starting from 0.5% to 10%. Samples had been prepared according to titanium vacancy mechanism, which is used to make insulative ceramic bodies.

Literature says [10], rare earth doped BaTiO₃ ceramic shows two unusual electrical properties, neither of which has been fully explained. First, the resistance passes through a minimum with increasing rare earth content; the minimum supposedly coincides with a change in doping mechanism from an electronic or donor doping mechanism to small rare earth contents, which leads to reduction in resistance, to an ionic compensation mechanism confirmed to be titanium vacancy mechanism.

Fig.2 shows relative dielectric permittivity (ε_r) as a function of frequency at room temperature. Result shows a broad ε_r with frequency. It's value decreases with increasing lanthanum percentage. Permittivity of undoped sample was found to be 700 where as for 10% lanthanum doped it is around 100.

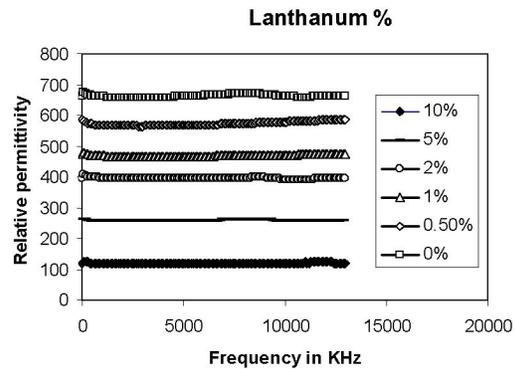


Fig. 2. Relative permittivity of different lanthanum doped Ba(Ti_{0.6}Zr_{0.4})O₃ at room temperature.

Fig.3 shows the variation of Tan δ as a function of frequency. In the frequency range 1 MHz to 7 MHz loss tangent obeys a decreasing tendency with increasing lanthanum percentage. However below 1 MHz the response is quite irregular. Above 7 MHz we have erroneous result because of instrument contacts. We got tan δ as low as 0.003 with lanthanum 10% doping. Un doped sample shows around 0.035 loss tan δ. All of a sudden, there is decrease in loss tan δ from undoped to 0.5% doping of lanthanum, which suggest decrease in tan δ with lanthanum doping.

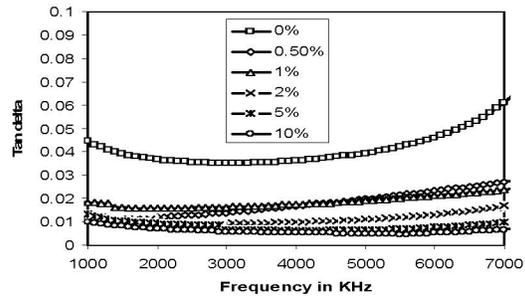


Fig. 3. Loss tan delta of different lanthanum doped Ba(Ti_{0.6}Zr_{0.4})O₃ at room temperature.

We have also measured the resistivity of undoped and lanthanum doped samples. It shows resistivity increases with lanthanum percentage increase, which is in accordance with literature report. It supports titanium vacancy mechanism.

IV. CONCLUSIONS

Lanthanum doped BaTi_{0.6}Zr_{0.4}O₃ composition x = 0.005, 0.01, 0.02, 0.05 and 0.1 in Ba_{1-x}La_xTi_{0.6[1-5x/12]}Zr_{0.4}O₃ were prepared by modified chemical route. Perovskite peaks were observed for all the lanthanum percentages without existence of any secondary phases. A gradual shift of 2θ angles to the higher angle with increasing lanthanum percentage in the BTZ

reveals the contraction of perovskite lattice. The lanthanum doped $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ composition was found to be cubic by XRD analysis. The frequency dependence of dielectric permittivity and loss $\tan \delta$ of the ceramics has been investigated. It is found that dielectric permittivity (ϵ_r) decreases and loss $\tan \delta$ decreases with increase in lanthanum percentage. Neither of the samples shows semiconductivity, which is believed to be because of titanium vacancy compensation.

ACKNOWLEDGMENT

The authors acknowledge the support of the Ministry of Human Resource Department (MHRD), Government of India to carry out this work.

REFERENCES

- [1] A.K. Tagantsev, V.O. Sherman, K.F. Astafiev, J. Venkatesh and N. Setter, "Ferroelectric materials for microwave tunable applications," *J. Electroceramics*, Vol.11, No.1-2, pp.55-66, September 2003.
- [2] S. U. Adikary, A. L. Ding and H. L. W. Chan, "Preparation and characterization of compositionally graded $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films," *Applied Physics- A: Materials Science*, Vol. 75, No. 5, pp. 597-600, November 2002.
- [3] W. J. Kim, W. Chang, S.B. Qadri, J.M. Pond, S.W. Kirchoefer, D.B. Chrisey and J. S. Horwitz, "Microwave properties of tetragonally distorted $(\text{Ba}_{0.5}\text{Sr}_{0.5})\text{TiO}_3$ thin films," *Applied Physics Letters*, Vol. 76, Issue 9, pp. 1185-1187, February 2000.
- [4] X.G. Tang, H.L.W. Chan and A.L. Ding, "Structural, dielectric and optical properties of $\text{Ba}(\text{Ti}, \text{Zr})\text{O}_3$ thin films prepared by chemical solution deposition," *Thin Solid Films*, Vol. 460, pp 227-231, 2004.
- [5] U. Weber, G. Greuel, U. Boettger, S. Weber, D. Hennings and R. Waser, "Dielectric properties of $\text{Ba}(\text{Zr},\text{Ti})\text{O}_3$ -based ferroelectrics for capacitor applications," *J. American Ceramic Society*, Vol. 84, pp. 759, 2001.
- [6] T. Tsurumi, Y. Yamamoto, H. Kakemoto and S. Wada, "Dielectric properties of BaTiO_3 - BaZrO_3 ceramics under a high electric field," *J. Materials Research*, Vol. 17, pp 755-759, April 2002.
- [7] P.H. Sciau, G. Calvarin and J. Ravez, "X-ray diffraction study of $\text{BaTi}_{0.65}\text{Zr}_{0.35}\text{O}_3$ and $\text{Ba}_{0.92}\text{Ca}_{0.08}\text{Ti}_{0.75}\text{Zr}_{0.25}\text{O}_3$ compositions: influence of electric field," *J. Solid State Communication*, Vol. 113, Issue 2, pp. 77-82, November 1999.
- [8] T.B. Wu, C.M. Wu and M.L. Chen, "Highly insulative barium zirconate-titanate thin films prepared RF magnetron sputtering for dynamic random access memory applications," *Applied Physics Letters*, Vol. 69, Issue 18, pp. 2659-2662, 1996.
- [9] Hector Baltran, Eloisa Cordoncillo, Purificacion Escribano, Derek C Sinclair and Anthony R. West, "Insulating properties of lanthanum doped BaTiO_3 ceramics prepared by low temperature synthesis," *J. American Ceramic Society*, Vol. 87, Issue 11, pp. 2132-2134 November 2004.
- [10] F. D. Morrison, Derek C. Sinclair and Anthony R. West, "Characterisation of lanthanum doped barium titanate ceramics using impedance spectroscopy," *J. American Ceramic Society*, Vol. 84, Issue 3, pp. 531-538, 2001.
- [11] F. D. Morrison, Derek C. Sinclair and Anthony R. West, "Doping mechanisms and electrical properties of La-doped BaTiO_3 ceramics," *International Journal of Inorganic Materials*, Vol. 3, pp. 1205-1210, 2001.
- [12] J. Bera and S.K. Rout, "On the formation mechanism of BaTiO_3 - BaZrO_3 solid solution through solid-oxide reaction," *Materials Letters*, Vol. 59, pp. 135-138, 2005.
- [13] D. F. K. Hennings, B. Schreinemacher and H. Schreinemacher, "High-permittivity dielectric ceramics with high endurance," *J. European Ceramic Society*, Vol. 13, Issue 1, pp. 81- 88, 1994.
- [14] K. Aliouane, A. Guehria-Laidoudi, A. Simon and J. Ravez, "Study of new relaxor materials in BaTiO_3 - BaZrO_3 - $\text{La}_{2/3}\text{TiO}_3$ system," *Solid State Sciences*, Vol. 7, Issue 11, pp 1324-1332, November 2005.
- [15] M.S. Dash, J. Bera and S. Ghosh "Study on phase formation and sintering kinetics of $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$ powder synthesized through modified chemical route," *Journal of Alloys and Compounds*, in press, 2006.
- [16] P. K. Roy and J. Bera, "Formation of SrTiO_3 from Sr-oxalate and TiO_2 ," *Materials Research Bulletin*, Vol. 40, pp. 599-604, 2005.
- [17] J. Bera and D. Sarkar, "Formation of BaTiO_3 from barium oxalate and TiO_2 ," *J. Electroceramics*, Vol.11, pp. 131-137, 2003.
- [18] Terry A Ring, *Fundamentals of Ceramic Powder Processing and Synthesis*, Academic Press, Inc., California, 1996, pp. 191.