

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

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**Abstract:** In porous media, the porosity introduces inhomogeneity in the bulk, which alters the mechanisms of leakage and breakdown exhibited by the dense analog. The presence of pores in solid dielectrics significantly degrades the electrical characteristics and breakdown strength of the material. Lanthanum doped  $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$  composition 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  $\text{La}_2\text{O}_3$  are used to precipitate barium oxalate hydrate, lanthanum oxalate hydrate and zirconium oxy-hydroxide from its water solution onto the surface of suspended  $\text{TiO}_2$  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  $2\theta$  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 ( $\epsilon_r$ ) decreases and loss  $\tan \delta$  decreases with increase in lanthanum percentage. Loss  $\tan \delta$  increases and dielectric permittivity ( $\epsilon_r$ ) decreases with increase in porosity. Resistivity decreases and current density increases with increase in porosity. Neither of the samples shows semiconductivity, which is believed to be because of titanium vacancy compensation.

## INTRODUCTION

The high dielectric permittivity combined with low dissipation factor makes  $\text{BaSrTiO}_3$  (BST) one of the promising candidates for dynamic random access memory, decoupling capacitors, and dielectric field tunable elements for high frequency device applications [1].

However, although the BST composition has been optimized, the dielectric losses are still high and its breakdown field is rather low. 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. Recently,  $\text{Ba}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$  (BZT) has been chosen as an alternative to BST. The solid solution of barium titanate (BT) and barium zirconate  $\text{BaZrO}_3$  (BZ), i.e., BZT, shows great similarity to the BST solid solution. In general  $\text{Zr}^{4+}$  is chemically more stable than  $\text{Ti}^{4+}$ , suitable for BST substitution [2].

Insulating properties increases with Zr content. It is believed that the conduction by electron hopping between  $\text{Ti}^{+4}$  and  $\text{Ti}^{+3}$ , if any would be depressed by substitution of Ti with Zr [3]. Lanthanum doping in barium titanate based perovskites exhibit semi-conducting or highly insulating properties depending on different parameters. [4-6].

Lead-free solid solution BT-BZ shows the highest dielectric susceptibility at room temperature for a 25% Zr substitution in the crystal structure. Moreover, for the compositions between 26% and 40%, bulk ceramics display relaxor behaviour. Lanthanum doping also shows relaxor behavior [6].

The BT-BZ solid solutions are conventionally synthesized through solid oxide route [7-8] and lanthanum doped BT-BZ through solid oxide route [9]. 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 [10].

In many cases, different densities within a ceramic are used to provide a wide continuous range of dielectric constants, mainly for high-frequency applications. Cofiring different ceramic materials together to make a single unified structure to obtain different dielectric constant combinations is quite difficult due to phase stability issues and shrinkage mismatches. However, using various levels of porosity in order to alter the effective dielectric constant in the same material allows patterning different dielectric constants into a single unit. It is well known that the relative permittivity decreases with increasing material porosity. Thus, controlling the porosity can yield a spectrum of dielectric constants from a single material [11].

The incorporation of pores significantly degrades the electrical characteristics and breakdown strength of the material. Enhanced electric field in the pores increases the probability of bond breakage on the pore walls and leads to the lowering of the overall breakdown strength [12].

As far as dielectric technology is concerned, the dielectric losses  $\tan \delta$  is dependent on moisture content. In fact, the dielectric losses are a combined result of electric conduction and orientational polarization of the matter. Some authors tried to treat the effect of moisture on polarization [13]. It is established that the presence of moisture tends to increase the conductivity of

material. Dielectric losses factor  $\tan \delta$  increases with the moisture level.

In the present synthesis  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ ,  $\text{La}_2\text{O}_3$  and  $\text{TiO}_2$  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. This type of powder synthesis has been reported earlier in the literature especially for BT, BTZ and  $\text{SrTiO}_3$  [10, 14-15]. We have prepared Lead-free  $\text{Ba}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$  ceramics through modified chemical route method. The influence of Lanthanum content on the dielectric properties and loss of the insulative  $\text{Ba}(\text{Zr}_y\text{Ti}_{1-y})\text{O}_3$  ceramics with  $y = 0.4$  were examined and discussed. Again we have prepared samples of different densities to investigate the effect of porosity on relative permittivity, dielectric loss and resistivity.

## EXPERIMENTAL PROCEEDURE

Lanthanum doped  $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$  composition  $x = 0.005, 0.01, 0.02, 0.05$  and  $0.1$  at.% 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. 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  $\text{HNO}_3$ , which helps in dissolving colloidal solution of lanthanum dioxide into the solution. Required amount of  $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$  was dissolved in the above solution. Further, appropriate amount of  $\text{TiO}_2$  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  $\text{TiO}_2$  agglomerates. The barium nitrate, lanthanum dioxide and zirconium oxy-chloride mixed solution was added drop-wise into the suspension of  $\text{TiO}_2$  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  $\text{ZrO}(\text{OH})_2$  on the surface of fine  $\text{TiO}_2$  (acting as seed) particles by heterogeneous nucleation [16]. The resulting precipitate was filtered out and then washed repeatedly using deionized water & Isopropyl alcohol, followed by drying at  $50^\circ\text{C}$  for  $24$  h.

The dry powder was then annealed at  $1200^\circ\text{C}$  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  $\Phi$ ) at  $3.5$  tonne pressure with  $0.5$  wt% PVA as binder. The pellets were heated at the rate of  $2^\circ\text{C}/\text{min}$  till  $500^\circ\text{C}$  ( $2$ h) for binder burnout and sintered at  $1200^\circ\text{C}$  - $1400^\circ\text{C}$  depending up on the composition, at the rate of  $2^\circ\text{C}/\text{min}$  and slowly cooled in the furnace. The sintering time was varied to get samples with different porosity. Silver paste was coated,

on both sides of sintered ceramic specimen for dielectric measurement.

X-ray diffraction measurements were done by using Cu ( $K_\alpha$ ) X-ray Diffractometer (PW-1830, Philips, Netherlands). The measurement on the bulk densities of the BLTZ specimens shows the densities of the ceramics are as high as  $75\%$ - $95\%$  of the theoretical density. The capacitance and loss  $\tan \delta$  of the samples were measured using an HP-4192A impedance analyzer. The dielectric permittivity ( $\epsilon_r$ ) was calculated using the formula  $\epsilon_r = c d / \epsilon_0 A$ , where  $\epsilon_0$  is the permittivity of free space,  $c$  the capacitance,  $d$  the thickness and  $A$  the capacitor area. The resistivity was measured using High Resistance Meter (model: 4339 B, Agilent Technologies), USA.

## RESULTS AND DISCUSSIONS

The X-ray diffraction pattern (XRD) of different at.% lanthanum doped  $\text{BaTi}_{0.6}\text{Zr}_{0.4}\text{O}_3$  has already been discussed where perovskite peaks were observed for all the lanthanum percentages without existence of any secondary phases. A gradual shift of  $2\theta$  angles to the higher angle with increasing lanthanum percentage in the BTZ reveals the contraction of perovskite lattice [17]. A rather long sintering time was adopted to ensure a homogeneous dopant distribution.

Small addition of lanthanum ( $<1$  at.%) induces n-type semiconductivity, which has been widely believed to occur via an electronic compensation mechanism. F. D. Morrison *et. al* [5] confirmed that lanthanum doped  $\text{BaTiO}_3$  forms primarily according to an ionic, titanium-vacancy compensation mechanism leading to a general formula  $\text{Ba}_{1-x}\text{La}_x\text{Ti}_{1-x/4}\text{O}_3$ .

The amount of oxygen loss in the lanthanum doped  $\text{BaTiO}_3$  is very small and difficult to control specially heating in air  $>1350^\circ\text{C}$ . 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.

In this study, we have taken minimum lanthanum percentage to  $0.5\%$  and maximum to  $10\%$  and the samples were heated between  $1300^\circ\text{C}$  to  $1400^\circ\text{C}$  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.

Figure 1, shows relative dielectric permittivity ( $\epsilon_r$ ) as a function of lanthanum percentage at room temperature. The density of these samples was more than  $90\%$ . It's value decreases with increasing lanthanum percentage [17].

Figure 2, shows the variation of relative permittivity with different porosity as a function of frequency. Result shows relative permittivity decreases with porosity. Porous specimen contains air and/or moisture inside it's pores. The relative permittivity of air and

moisture is comparatively less than perovskite-based dielectrics.

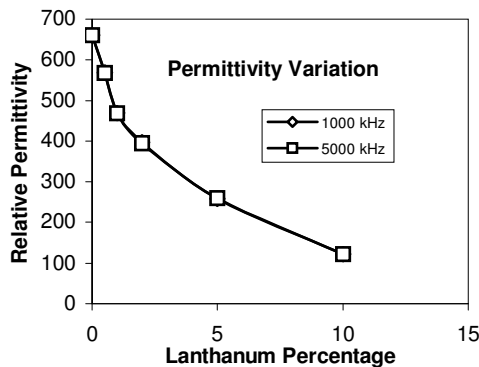


Figure 1: Relative permittivity of different lanthanum doped  $\text{Ba}(\text{Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3$  at room temperature.

As our specimen contains open pores and we did capacitance measurements in relatively humid atmosphere, it is quite obvious that relative permittivity will decrease with porosity. Polar molecules play an important role in relative permittivity [18]. It can be explained by the bonding strengths of water molecules between them and/or with the other molecules. These connections come to limit the freedom of movement of these molecules inducing a reduced effect on the permittivity. In low-density samples the material content is less than the dense analog, which again reduces the total charge carried by the samples, which reduces the capacitance.

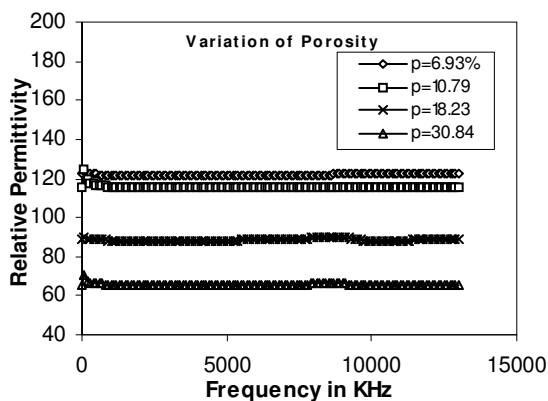


Figure 2: Relative permittivities of 10 at.% lanthanum doped  $\text{Ba}(\text{Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3$  with different porosity at room temperature.

Figure 3, shows the variation of  $\text{Tan } \delta$  as a function of lanthanum percentage. Here the density of these samples was more than 90%. Loss tangent obeys a decreasing tendency with increasing lanthanum percentage [17].

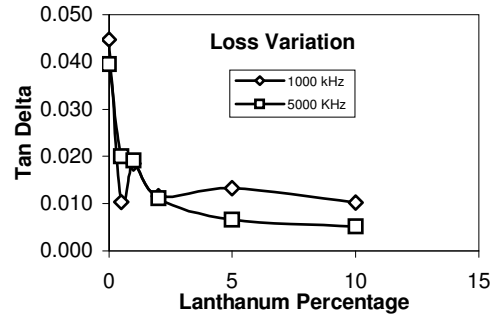


Figure 3: Loss tan delta of different lanthanum doped  $\text{Ba}(\text{Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3$  at room temperature.

Figure 4, shows loss tan delta variation with porosity as a function of frequency. Loss increases with increase in porosity. The large number of holes means a large surface area with dangling bonds of the ceramic particles that tend to absorb species and water. These bonds absorb electrical energy, particularly at high frequencies, which leads to a high loss tangent [19]. However, loss tangent has been controlled by Xun Gong *et. al.*[11].

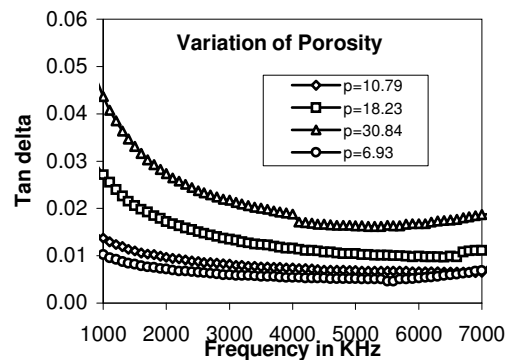


Figure 4: Loss tan delta of 10 at.% lanthanum doped  $\text{Ba}(\text{Ti}_{0.6}\text{Zr}_{0.4})\text{O}_3$  with different porosity at room temperature.

## CONCLUSIONS

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. Perovskite peaks were observed for all the lanthanum percentages without existence of any secondary phases. A gradual shift of  $2\theta$  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  $\text{Tan } \delta$  of the ceramics has been investigated. It is found that dielectric permittivity ( $\epsilon_r$ ) decreases and loss  $\text{Tan } \delta$  decreases with increase in lanthanum percentage. Loss  $\text{Tan } \delta$  increases and dielectric permittivity ( $\epsilon_r$ ) decreases

with increase in porosity. Resistivity decreases and current density increases with increase in porosity.

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