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Structural and Electrical properties of La doped Barium Zirconium Titanate

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ABSTRACT

La_2O_3 doped barium zirconium titanate $Ba_{1-x}La_xZr_{0.15}Ti_{0.85}O_3$(BLZT) ceramics have been fabricated by conventional dry route method. Barium carbonate, zirconium oxide, titanium dioxide and lanthanum oxide were the starting material. The dielectric properties of $Ba_{1-x}La_x0Zr_{0.15}Ti_{0.85}O_3$ ceramics have been Investigated. La^{3+} ions substitute for A-site Ba^{2+} ions to enter the unit cell maintaining the perovskite structure of solid solution and induce the occurrence of ferroelectric relaxor behaviour. BLZT ceramics were prepared by mixing, drying and calcining the raw material which were heated in an alumina crucible at 1300˚c for 4hrs and then re-milled and sintered at 1350˚c for 2hrs. The samples were characterized using X-ray diffraction (XRD).It was observed that the Curie temperature (Tc) of $(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ ceramics is remarkably shifted to lower temperature with increase of x.

Keywords: *Barium zirconium titanate, Dry route method, Sintering, Calcination.*

INTRODUCTION

Ferroelectricity is a spontaneous electric polarization of a material that can be reversed by the application of an intense electric field. Barium titanate perovskite, the first ceramic material that exhibits ferroelectric behavior was reported in 1945 (Haertling 1999). Barium zirconate titanate $Ba(Zr_xTi_{1-x})O_3$ solid solution has recently received extensive attention due to its eminent dielectric performance.It became one of the most extensively studied ferroelectric materials due to its ferroelectric properties .Perovskite is a naturally occurring mineral with chemical formula $CaTiO_3$.This is a structrural prototype for many ABO_3 materials which show ferroelectric behavior. The perovskite structure has general stoichiometry ABO_3 where A and B are cations and O is an anion. Barium zirconium titanate $Ba(Zr_xTi_{1-x})$ solid solution has recently received extensive attention due to its eminent dielectric properties. (Moura F.et al. 2008). This system exhibits pinched phase transition and typical ferroelectric behavior with characteristics related to the substitution of Ti^{4+} ions for the Zr^{4+}(.Maiti T. et al, 2006]. BZT is interesting because it is derived from two perovskite lattice i.e. Barium titanate ($BaTiO_3$) and Barium zirconate ($BaZrO_3$) for which it has been reported that the zirconium substitution into the titanium lattice enhances the dielectric properties. Doped BZT ceramics exhibit typical diffuse paraelectric to ferroelectric phase transition behavior in which Tc is shifted to lower temperature by doping La^{3+}ions on the lattice of Barium zirconium titanate. $Ba(Zr_xTi_{1-x})O_3$. An important member of the $BaTiO_3$ based ferroelectric materials family presents high voltage resistance characteristics. As is well known, rare earth oxide doping of ceramics is an effective and common method to maximize dielectric properties (Liang et.al, 2004). Barium lanthanum zirconium titanate (BLZT) is a ferroelectric ceramic formed by

doping La^{3+}ions on the A sites of Barium zirconium titanate. It is reported that the occupation of Barium (Ba) sites by Lanthanum (La) results in a shift of the curie peak towards low temperature. The dielectic loss of BLZT is improved by La-doping (Xiujian et al. 2009).

The main purpose of this research is to analyze the effect of La doping on the dielectric characteristics in $(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ ceramics compared with $BaZr_{0.15}Ti_{0.85}O_3$ (Chunlin et al. 2009). There are several methods for the preparation of ceramics .Each technique has its own advantage and disadvantages. We have used a solid state dry route to synthesize Barium lanthanum zirconium titanate. This method has a number of attractive features like simplicity and low cost of preparation. Barium lanthanum zirconium titanate could be an attractive material for tunable ceramic capacitors and tunable microwave device applications. (Maiti et al. 2011).

MATERIALS AND METHOD

$(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ (x=0.00,,0.005,0.01) powder has been prepared by the conventional solid state dry route method. $BaCO_3$(99%), La_2O_3(99.9%) ZrO_2 (99.0%) and TiO_2 (99.0%) were taken in stoichiometric proportions as starting raw materials. These materials were weighed according to the composite formula and mixed using acetone and Zirconium balls in milling media for 72hrs.The samples were placed in an oven for 2-3 days at 50˚c for drying. After drying, the mixtures were calcined in an alumina crucible at 1300˚c for 4 hours, then remilled and dried. Now the samples were ready for XRD which is used to analyze the crystal structure of crystalline materials and find the crystal structure of a material. In order to determine the dielectric properties of the samples the obtained powders were pressed to make disc shaped pellets of 10mm in diameter by applying 7 tons of pressure and the pellets were sintered at 1350^{o}c for 2 hours. The two sides of the pellets were polished with silver paste and fired at 500˚C for 2 hours to form electrodes which were necessary in order to determine the dielectric constant and Curie temperature.

RESULTS AND DISCUSSIONS

The XRD patterns were recorded using diffractometer (Model Rigaku Miniflex 2). Dielectric measurements (Model:Dec-01) were carried out at room temperature. The X-ray diffraction patterns for different $(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ (x= 0.00,0.005,0.01) samples are shown in figure 1.The intensity peaks corresponds to ferroelectric cubic as compared to ICDD file data. As can be seen from the figure, a perovskite structure is observed and no secondary phase is found for La (x=0.00) and La (x=0.005) but in La(x=0.01) a secondary phase is found at 2θ =30.44˚. The diffraction peaks of the samples are shifted to the higher angle side with the increase of La concentration. This shift indicates there is a decrease in lattice constant of $(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ samples with the increase of La content. This can be explained by noting that the doped La^{3+} ions occupy the A sites of $BaZr_{0.15}Ti_{0.85}O_3$ lattice. The ionic radius of La^{3+}(0.136nm) is smaller than that of Ba^{2+}(0.161nm). Therefore the change of lattice constant is determined by cation substitution. It also implies that La^{3+} ions have entered the unit cell maintaining the perovskite structure of solid solution.

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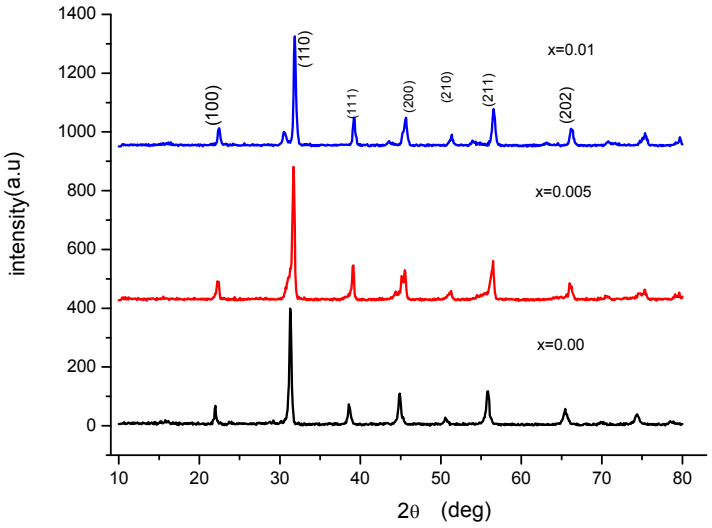

Fig 1
XRD of $(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ (x =0,0.005,0.01)

Data Observed From XRD :

Sample	Crystalline size(A)	Interplaner distance(d) (A)	Bragg's angle (θ)	Lattice constant(a)
$BaZr_{0.15}Ti_{0.85}O_3$	343	4.035	11.00	5.68
$Ba_{0.995}La_{0.005}Zr_{0.15}Ti_{0.85}O_3$	253	3.974	11.17	5.60
$Ba_{0.990}La_{0.01}Zr_{0.15}Ti_{0.85}O_3$	236	3.96	11.19	5.58

The Scherrer equation for FWHM in X-ray diffraction peaks is used in the determination of the size ot Crystallites that are present in the powder. The Scherrer equation can be written as

$$\tau = K \lambda / \beta \cos \theta$$

where τ is the mean size of the crystallite domain which may be smaller or equal to the grain size. K is dimensionless shape factor whose value is close to unity. λ is the X-ray wavelength. β is the peak broadening at half maximum intensity. θ is the Bragg's angle.

The temperature dependence of dielectric constant for $Ba_{1-x}La_xZr_{0.15}Ti_{0.85}O_3$ (x=0.00,0.005) samples are shown in fig. 2 and fig.3 respectively.

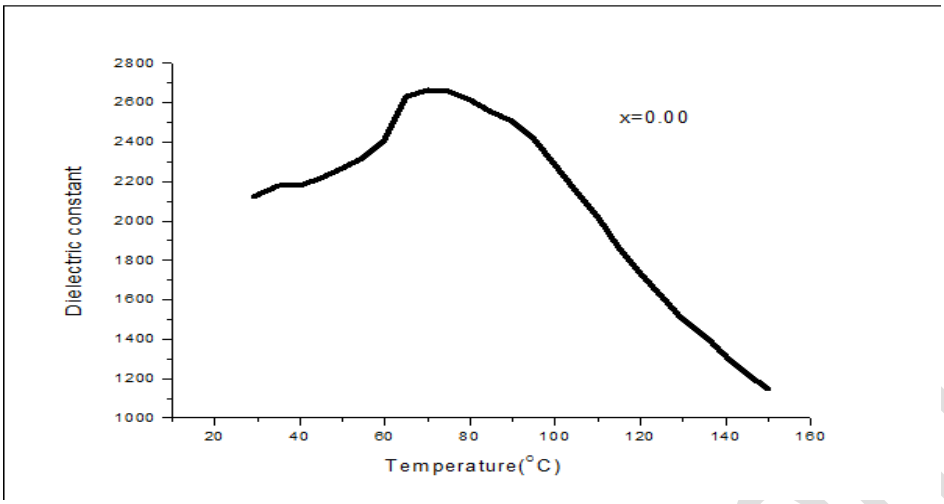

Fig 2

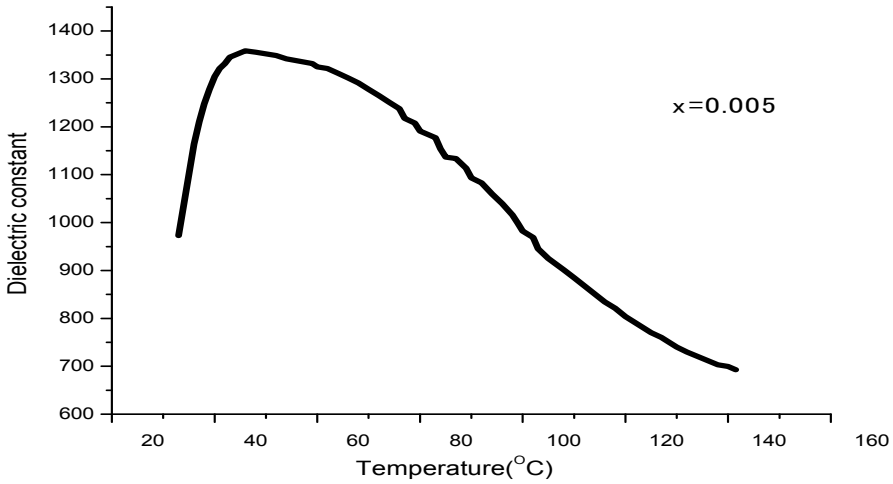

Fig 3

From the graphs, we get the observed value of Curie temperature of $Ba_{1-x}La_xZr0_{.15}Ti_{0.85}O_3$(x=0.00) as 70^OC -75 ^OC and of $Ba_{1-x}La_xZr_{0.15}Ti_{0.85}O_3$(x=0.005) as 46^OC.
It is known that the dielectric constant of a normal ferroelectric material in paraelectric region generally follows the Curie – Weiss law described by

$$1/\varepsilon= (T-T^0)/C \quad (T>Tc)$$

Where T^0 is the Curie-Weiss temperature and C is Curie – Weiss constant.
For a cubic lattice d the distance between successive planes is

$$d=a/\sqrt{h^2+k^2+ l^2}$$

where d is the interplaner spacing, a is the lattice constant, (hkl) is the crystal plane index (Dekker A.J.).

CONCLUSION

$(Ba_{1-x}La_x)Zr_{0.15}Ti_{0.85}O_3$ ceramics have been fabricated by conventional dry route method. La^{3+} ions enter the unit cell and substitute for A site Ba^{2+} ions maintaining the perovskite structure of solid solution. The ionic size of La^{3+} is compatible with Ba^{2+}. Therefore Lanthanum is exclusively substituted at the Ba site. Lanthanum doped BZT was found to have reduced cubic lattice parameter for higher fraction of lanthanum. A gradual shift of peak angle to higher substitution 2θ values with increasing La percentage reveals a contraction of perovskite lattice because of the smaller size of La^{3+}ion compared to $Ba^{2+.}$ On increasing the Lanthanum content Curie temperature (Tc) goes on decreasing.

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