



Synthesis and Structure Analysis of Samarium Doped Barium Zirconium Titanate

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Abstract : Barium samarium zirconium (BSZT) was prepared by a cost effective dry route method using barium carbonate, zirconium oxide, titanium dioxide and samarium oxide as the starting material by mixing, drying, calcining the raw material and sintering it. The Curie temperature T_c remarkably shifted to lower value by increasing x in $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ and consisted with recent reports.

Key words: Barium samarium zirconium titanate (BSZT), Curie temperature, Dry route method, sintering, calcination.

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Introduction :

Ferroelectric ceramics was born in the early 1940s with the discovery of phenomenon of ferroelectricity as the source of unusually high dielectric constant of ceramic barium titanate (BT) capacitor (Haertling 1999). Barium titanate was the first material exhibiting ferroelectric properties such as high dielectric constant and used, in piezoelectric transducers, in medical ultrasounds, SONARS and in ferroelectric thin film memories.

It exhibits perovskite structure which is a class of naturally occurring minerals with general stoichiometry ABO_3 , where A and B are cations and O is an anion. BSZT sample shows phase transition and ferroelectric behaviour with characteristics related to the substitution of Sm^{+3} ions for the Ba^{+2} (Maiti et al. 2006). With the increase of frequency, T_c shifts to higher temperature which makes the sample more ferroelectric and enhances the dielectric properties. (Chunlin et al. 2009)

In barium samarium zirconium titanate (BSZT), formed by doping Sm^{+3} ions on the A site of BZT, Sm^{+3} is a rare earth element and it is seen that doping of ceramics with rare earth oxides enhances

dielectric properties (Chou et al. 2009) and shifts the curie point to lower temperature (Moura et al. 2008).

We report the synthesis and structural analysis of BSZT sample and the effect of doping of Sm^{+3} ion in different amount in the samples in this paper. We find the dry route method for the preparation of ceramics as a low cost effective method (Nierman,1988).

Materials and Methods:

Raw materials for the preparation of sample $(\text{Ba}_{1-x}\text{Sm}_x)\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$ ($x=(0.00,0.005,0.01)$) powder were BaCO_3 (99%), Sm_2O_3 (99.9%) ZrO_2 (99.0%) and TiO_2 (99.0%) taken in stoichiometric proportions. These materials were weighed and mixed with acetone, zirconium balls and kept in ball mill for 72 hours. The properly mixed sample was placed in oven at 50°C for 2-3 days for drying and then calcined in an alumina crucible at 1300°C for 4 hours. After calcination, in which process oxygen was removed, samples were remilled and dried. Now the sample was ready for XRD characterizations in powder form.

A major portion of powder obtained was used to make pellets of 10mm in diameter by using Die Punch at a pressure of 7 ton and was sintered at 1350°C for 2 hours. The pellet was then polished with silver paint for electroding and measuring the dielectric constant and Curie temperature.

The XRD patterns were recorded using diffractometer (Model Miniflex 2). The dielectric measurements (Model:Dec-01) were carried out at room temperature.

Results and Discussion:

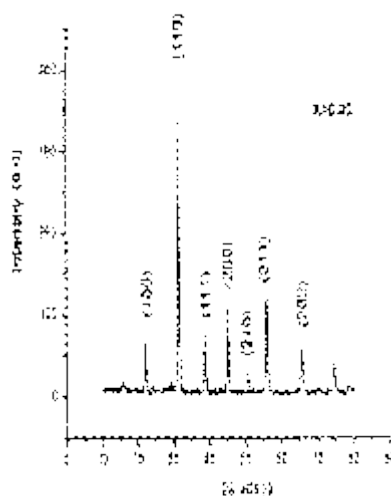


Fig 1. (XRD pattern for $(\text{Ba}_{1.00}\text{Sm}_{0.00})\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$)

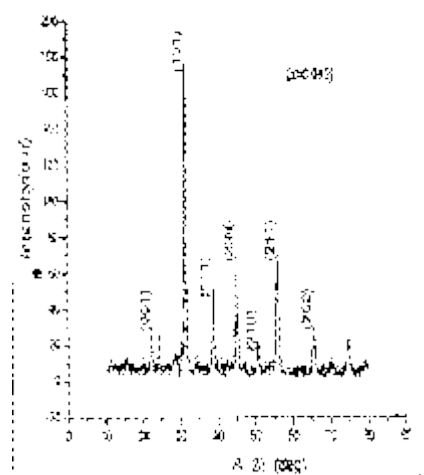


Fig 2. (XRD pattern for $(\text{Ba}_{0.995}\text{Sm}_{0.005})\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$)

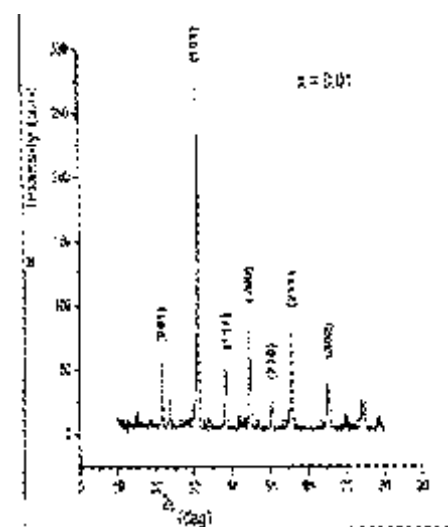


Fig 3. (XRD pattern for $(\text{Ba}_{0.99}\text{Sm}_{0.01})\text{Zr}_{0.15}\text{Ti}_{0.85}\text{O}_3$)

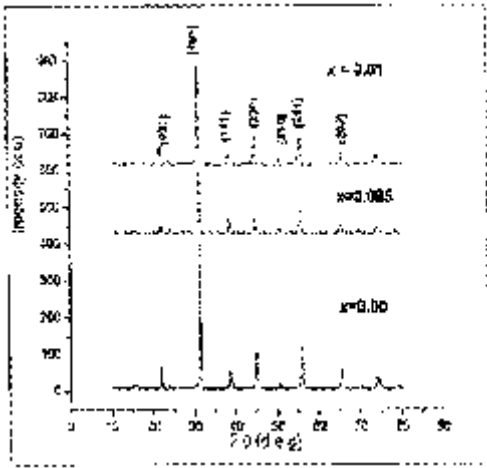


Fig 4. XRD pattern for superimposed graphs of $Ba_{(1-x)}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x = 0.00, 0.005, 0.01$)

Table 1. Data Observed From XRD of $(Ba_{1-x}Sm_x)Zr_{0.15}Ti_{0.85}O_3$

Sample	Particle size (nm)	Interplanar distance (d)(Å)	Bragg's angle (q) (deg)	Lattice constant (a)(Å)
$BaZr_{0.15}Ti_{0.85}O_3$	343	4.035	11.00	5.68
$Ba_{0.995}Sm_{0.005}Zr_{0.15}Ti_{0.85}O_3$	218	2.8477	15.6935	4.0272
$Ba_{0.990}Sm_{0.01}Zr_{0.15}Ti_{0.85}O_3$	222	2.8583	15.634	4.0424

The x-ray diffraction pattern of different amount of $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x=0,0.005,0.01$) samples are shown in Fig.1-3. These plots show the perovskite structure. By analysing the superimposed graph (Fig 4) it was observed that diffraction peaks of samples are shifted to the higher angle side with the increase of Sm doped concentration. It can be explained by noting that doped Sm^{3+} ions occupy the A sites of $BaZr_{0.15}Ti_{0.85}O_3$ lattice structure carried out at room temperature. The phase transition peaks seem to be sharper in case of undoped BZT than those of Sm doped BZT. It can also be observed from XRD plots that sharpness of peaks increase as we increase the amount of doping element Sm. The substitution of Sm^{3+} ion at A sites Ba^{2+} ions is for maintaining the perovskite structure of solid solution and resulting in the disorder distribution of A-sites ions. Therefore,

the chemical in homogeneity of $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ceramics and the distortion of the lattice of perovskite structure ABO_3 are formed. The particle size decreased after doping of Sm^{3+} in BZT as founded by Sagar et al (2011).

It was also observed that size of the particle increased with increase in doping amount. The lattice constant also decreased after doping of Sm^{3+} in BZT and increased with increase in doping concentration.

The temperature dependence of dielectric constant for $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x=0.00, 0.005, 0.01$) samples are shown in Fig. 5-7.

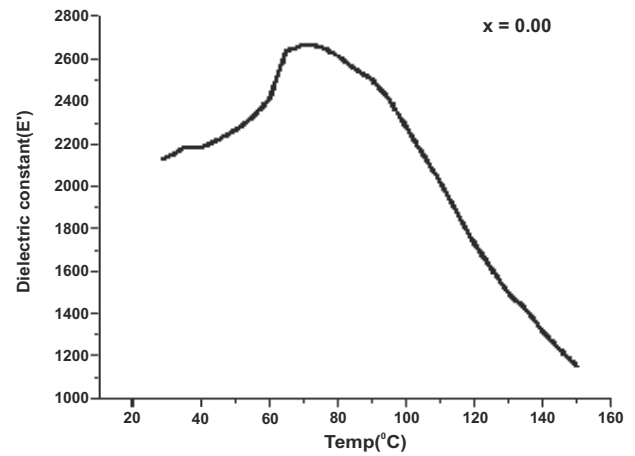


Fig 5. Curie temperature T_c of $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x=0.00$) at 71-75°C

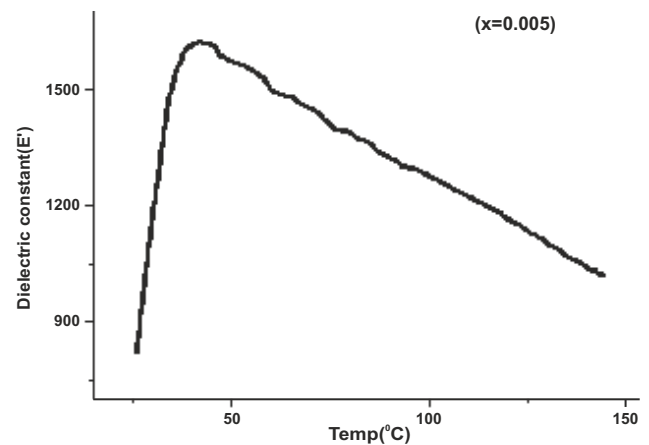


Fig 6. Curie temperature T_c of $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x=0.005$) at 42°C

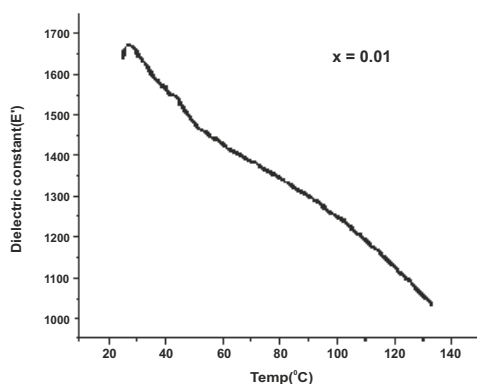


Fig 7. Curie temperature T_c of $Ba_{1-x}Sm_xZr_{0.15}Ti_{0.85}O_3$ ($x=0.01$) at $28^\circ C$

The maximum value of the dielectric constant is decreased with increasing frequency (Maiti et al. 2011). It is known that the dielectric constant of a normal ferroelectric in paraelectric region generally follows the Curie – Weiss law described by

$$1/\epsilon = (T - T^0)/C$$

In the non-polar (paraelectric) phase which appears above a characteristic temperature is called Curie point (T_c). C and T^0 in the equation are called Curie constant and Curie temperature, respectively.

It was observed from the Fig 5-7 that T_c shifted to lower temperature after substitution of Sm in BZT. It was also observed that T_c shifted to still lower temperature after increasing the amount of Sm.

Conclusion:

Reduced lattice parameter was obtained after substitution of Sm in BZT. There is gradual shift of X-ray peaks of samples to the higher angle side with the increase of Sm dopant concentration. Curie temperature T_c shifted to lower temperature after substitution of Sm^{+3} in BZT, with increasing the amount of Sm^{+3} shifting T_c to a still lower temperature.

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