

Structural and impedance spectroscopy study of Samarium modified Barium Zirconium Titanate ceramic prepared by mechanochemical route



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ABSTRACT

Samarium modified Barium Zirconium Titanate (BZT) ceramics with general formula $[\text{Ba}_{1-x}\text{Sm}_{2x/3}](\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3)$ [$x = 0, 0.01, 0.02, 0.03$ and 0.04] have been prepared by high energy ball milling. The Rietveld refinement of $\text{BaZr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ (BZT) shows a single phase tetragonal symmetry with space group $P4mmm$ and TEM micrograph shows that the crystalline size is in the submicron range. X-ray diffraction (XRD) patterns confirm that no phase change occurs with the addition of Samarium in BZT upto $x \leq 0.03$ and a small pyrochlore phase exists at $x = 0.04$. The complex impedance (Nyquist) plots display a single semicircle highlighting the influence of grain resistance on the electrical behavior. Negative temperature coefficient of resistance behavior is observed in all compositions. The activation energy calculated from Z'' and DC conductivity confirms that the oxygen vacancies play an important role in the conduction mechanism.

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1. Introduction

Barium zirconate titanate (BZT) is one of the most important functional materials with various potential applications as piezoelectric transducers, dynamic random access memory (DRAM), tunable microwave devices, and in electrical energy storage unit [1–4]. Due to its high dielectric constant, it is generally adopted in Y5V multilayer ceramic capacitors (MLCC) [5,6]. The intriguing changes in the properties of BaTiO_3 due to doping of rare earth ions prompted the researchers to investigate the doping of rare earth ions into the BZT compounds [7–10]. BZT characteristics have also been improved by inserting a lanthanide ion as dopant because of its low leakage current behavior and low electric field [11–13]. However, extensive studies are still needed on systems where the substitution of a lanthanide ion for barium, requires the generation of A site cationic vacancies to maintain electro neutrality in the perovskite structure. Recently, several researchers have reported that addition of rare earth ions improves the dielectric properties of BZT ceramics and interesting microstructural and dielectric response features have been observed [8,14–17]. In our previous

studies on the investigation of rare earth ions substituted BZT ceramics prepared by the solid state reaction revealed formation of single phase compound and interaction of rare earth ions with BZT lattice exhibited an NTCR behavior for the fabrication of highly sensitive thermistor [18]. In this paper, we report the effect of the replacement of Ba^{2+} by Sm^{3+} ions in BZT ceramic with general formula $[\text{Ba}_{1-x}\text{Sm}_{2x/3}](\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3)$, investigated by means of dielectric relaxation and AC impedance spectroscopy analysis. Moreover, we have also investigated the dielectric/conductivity properties, the relaxation mechanism and defects in lattice of these ceramics.

2. Experimental

Samarium doped Barium Zirconium Titanate (BSZT) ceramics with general formula $\text{Ba}_{1-x}\text{Sm}_{2x/3}\text{Zr}_{0.05}\text{Ti}_{0.95}\text{O}_3$ ($x = 0.0, 0.01, 0.02, 0.03, 0.04$) were prepared by a combination of solid state reaction and high energy ball milling technique. The ball to powder ratio (BPR) was maintained at 20:1 by weight. BaCO_3 (99.9%), Sm_2O_3 (99.9%), ZrO_2 (99.8%) and TiO_2 (99.95%) were used as starting materials and stoichiometry amounts of these materials were weighed. The high energy ball milling of these weighed powders were done in Fritsch planetary ball mill. For proper mixing of the

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weighed powders, the powders were mixed in tungsten carbide balls (10 mm diameter) with toluene as milling media for 5 h at 300 RPM. The milled powders were heat treated at 1100 °C for 4 h by a programmable furnace.

The synthesized BSZT ceramics were structurally characterized by X-ray diffraction (XRD) (PANalytical, Netherlands) with Cu-K α ($\lambda = 1.5418 \text{ \AA}$) radiation in a wide range of 2θ ($20^\circ \leq 2\theta^\circ \leq 70^\circ$) at a scanning rate of 2° min^{-1} . In order to measure the electrical properties of BSZT ceramics, the discs were pressed uniaxially at 200 MPa with 2 wt% polyvinyl alcohol added as a binder. Afterwards, these the discs were sintered at 1200 °C for 4 h. Silver contacts were deposited on the opposite disc faces and heated at 700 °C for 15 min. The frequency (1 Hz–1 MHz) and temperature (30–700 °C) dependent dielectric measurements were carried out using a N4L-NumetriQ (model PSM1735) connected to a computer.

3. Results and discussion

3.1. X-ray diffraction

The Rietveld refinement plot of BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$ (BZT) powder calcined at 1100 °C for 4 h is shown in Fig. 1(a). The plot shows that BZT ceramic exhibits a single phase tetragonal structure with space group P4mm which is in agreement with the respective Joint Committee on Powder Diffraction Standards (JCPDS) card No. 44-0093 [19]. Fig. 1(b) shows the TEM micrograph of the BaZr $_{0.05}$ -Ti $_{0.95}$ O $_3$ powder and the crystallite size of the BZT powder is found to be around 100 nm. XRD patterns of Ba $_{1-x}$ Sm $_{2x/3}$ Zr $_{0.05}$ Ti $_{0.95}$ O $_3$ ($x = 0.0, 0.01, 0.02, 0.03, 0.04$) powders are shown in Fig. 1(c). The XRD patterns indicate that no secondary peak is observed in samarium doped BZT upto $x \leq 0.03$ and an additional peak appeared at $x = 0.04$, which has been identified as pyrochlore. Similar kind of pyrochlore phase is also observed in Sm doped PZT [20]. Carim et al [21] have suggested that pyrochlore phase is an essential step in the formation of perovskites which occurs due to oxygen deficient, and so, it is a metastable transient phase [22]. Also diffraction peaks of the samples shift to higher angle side with increase in Sm concentration. This shift indicates a decrease of lattice constant of (Ba $_{1-x}$ Sm $_{2x/3}$)Zr $_{0.05}$ Ti $_{0.95}$ O $_3$ samples with increase of Sm-doped content which explained that doped Sm $^{3+}$ ions occupy the A site of the BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$ lattice structure. The effective ionic radius of Sm $^{3+}$ (0.110 nm) is smaller than that of Ba $^{2+}$ (0.149 nm) [23]. Therefore, the changes of lattice constant are determined by the cation substitution. It also implies that Sm $^{3+}$ ions have entered the unit cell maintaining the perovskite structure of solid solutions. According to Shan et al. [7], substitution of Ba $^{2+}$ ion by Sm $^{3+}$ ions into the A sites lead to distortions in the BZT structure due to different atomic radii. Lattice parameters and crystallite size are calculated by using Check cell software and presented in Table 1. It is also observed that the tetragonality decreases with Sm doping and structure changes from tetragonal to pseudo-cubic.

3.2. Microstructural study

Scanning electron micrographs of sintered BSZT pellets are shown in Fig. 2. Nature of the microstructures of BSZT samples, indicate that the grains are almost uniform and densely packed. Incorporation of samarium cations in the perovskite lattice of BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$ modifies the microstructural properties of BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$. The smaller ionic size samarium ions predominantly dissolve in A-sites, act as donors and it slows down the overall diffusion rate during the sintering process. The dissolution of samarium dopant into perovskite lattice may increase the oxygen vacancies and contribute to increase of overall cationic

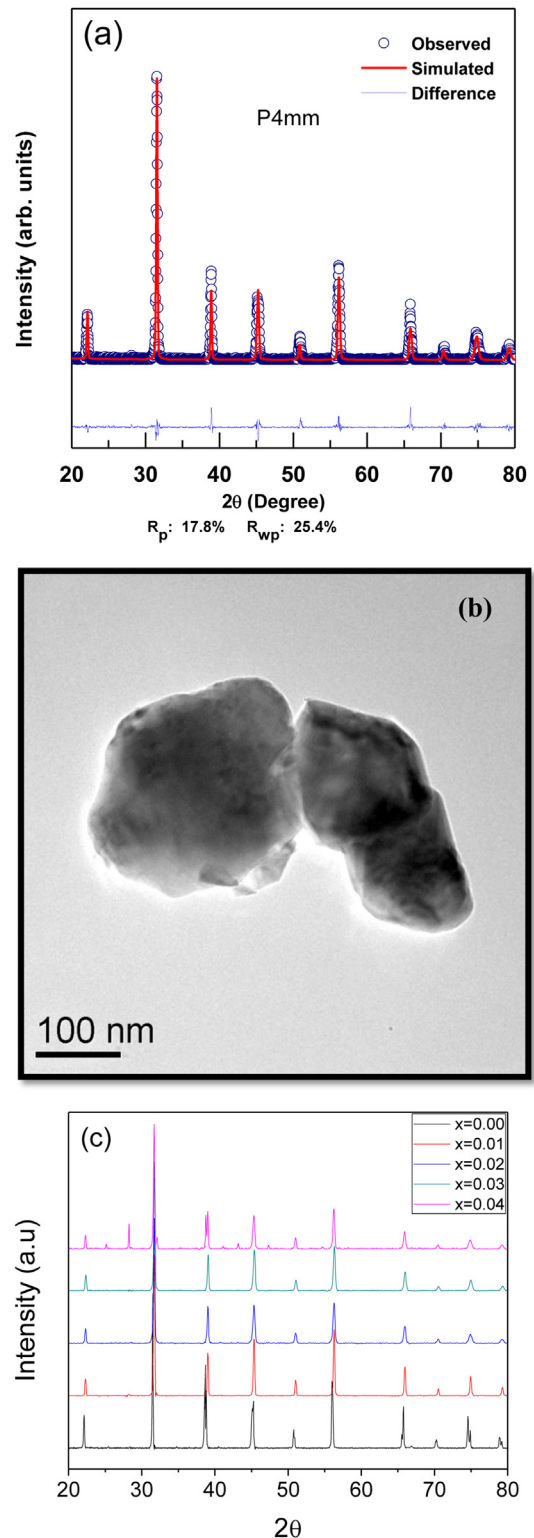


Fig. 1. (a) XRD patterns of Ba $_{1-x}$ Sm $_{2x/3}$ Zr $_{0.05}$ Ti $_{0.95}$ O $_3$ ceramics sintered at 12,000 °C for 4 h [$x = 0.0, 0.01, 0.02, 0.03$ and 0.04] (b) Rietveld Refinement of BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$ ceramic sintered at 12,000 °C for 4 h (c) TEM micrograph of BaZr $_{0.05}$ Ti $_{0.95}$ O $_3$ ceramic calcined at 11,000 °C for 4 h.

transport. All compositions show non-uniformly distributed grains due to the characteristic of matter transport mechanism between grains during sintering process. At initial stages of solid state reaction, the carbonates and oxides were ball milled in order to

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