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Phase formation and dielectric study of Bi doped $(Ba_{0.8}Sr_{0.2})Ti_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$ ceramic

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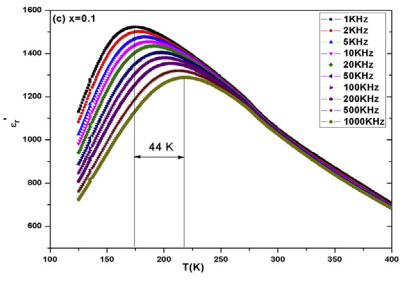
HIGHLIGHTS

- The Bi-doped BSTZN ceramics were synthesized using the solid-state reaction method.
- The Bi-doped BSTZN ceramics leads to diffuse ferroelectric behavior.
- The ac conductivity spectrum is found to obey Jonscher's universal power law.

GRAPHICAL ABSTRACT



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ABSTRACT

The solid solutions of $(Ba_{0.8}Sr_{0.2})_{1-1.5x}Bi_xTi_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$ (Bi_x-BSTZN) (with x = 0, 0.05 and 0.1) ceramics were prepared by the solid-state reaction route and their structural, dielectric and electric properties were investigated. The room temperature XRD study suggests that all the compositions have a single phase pseudocubic symmetry with space group Pm-3m. Temperature dependent dielectric studies of the ceramics have been investigated in the frequency range of 1 KHz–1 MHz. The dielectric constant and transition temperature decrease with the increase in Bi concentration due to the decrease in grain size. The substitution of Bi ion induces diffuse ferroelectric behavior and the degree of diffuseness increases with the increase in doping concentration. The electrical behavior for x = 0.05 ceramic has been studied by non-destructive complex impedance spectroscopy as a function of frequency at different temperatures. Variation of ac conductivity as a function of frequency shows that the compound exhibits Arrhenius-type of electrical conductivity.

1. Introduction

The ferroelectric materials with perovskite structure can be split into two different classes: classical ferroelectrics or relaxor ferroelectrics [1]. The latter have found great interest both in device applications and in the understanding of the fundamentals of ferroelectric systems [2–4]. These days much research interests are directed towards lead free relaxor materials with perovskite structure which have been recently prepared and investigated in terms of their dielectric relaxation, ferroelectric phase transition and electrical properties [5,6]. Lately, the barium strontium titanate

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$Ba_{1-x}Sr_xTiO_3$ (BST) have been widely employed in several industrial applications, such as: dynamic random access memory, microwave filters, voltage controlled oscillators and telecommunication technologies [7–9]. Complex perovskites, having general formula $(AA')(BB')O_3$ containing both order/disorder structure, are basically relaxor ferroelectric materials that show interesting properties.

Most studies are focused on the temperature dependence of the dielectric constant, the nature of phase transition, and the relaxor behavior of these materials [10,11]. However, recent research interest is in both homovalent substitution at the 6 coordination number crystallographic site (B-site) and heterovalent substitutions at the 12 coordination number crystallographic site (A-site) [12,13]. The relaxor state is characterized by a strong dispersion of the dielectric constant for temperatures below the maximum permittivity temperature T_m, by a shift of T_m towards higher values when the frequency is increased and by a deviation from the Curie-Weiss law in the paraelectric phase around T_m [14,15]. Not long ago, we have investigated the effect of heterovalent atoms substitution of the B site BST and reported a relaxor behavior in the $Ba_{0.8}Sr_{0.2}Ti_{1-y}(Zn_{1/3}Nb_{2/3})_yO_3$ system [16]. Depending on the (Zn^{2+},Nb^{5+}) content, this material can exhibit either a normal ferroelectric or relaxor behavior [16]. Many studies have concluded this relaxor character by the substitution of the cationic sites in the A ions by ABO_3 system Bi^{3+} ions [17–20]. Accordingly, to trigger the coexistence between order (ferroelectric) and disorder (relaxor), we decided to add another degree of freedom by introducing a disorder on the A site (Ba^{2+}, Sr^{2+}) in $Ba_{0.8}Sr_{0.2}Ti_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$ ceramic. This can be achieved by the heterovalent substitution of (Ba^{2+}, Sr^{2+}) cation with Bi^{3+}. The choice of Bi^{3+} cation is due to its $6sp^2$ lone pair (like Pb^{2+}) and such an electronic environment is favorable for the relaxor effect without the disadvantage of lead pollution [21].

Previous reports on Bi-doped $Ba_{1-x}Ca_xTiO_3$ [22] and Bi doped strontium titanate [23], show relaxor behavior by heterovalent substitution at the A-site. A widely accepted viewpoint is that a random-field-induced domain state is suggested to be responsible for the relaxor behavior when Bi^{3+} incorporates into the ABO_3 type structure like $BaTiO_3$, Bi^{3+} believed to replace Ba^{2+} (A-site) and charge imbalance is created which must be compensated by either cation vacancies on the A-site (ionic compansation), or by electrons (electronic compensation). Therefore, the substitution of Bi^{3+} for Ba^{2+} will take place, according to the Kroger-Vink notation, as follows:

$$Bi_2O_3 \rightarrow 2Bi^{*}_{Ba} + V''_{Ba} + 3O^{x}_{O}$$

where Bi and Ba stand for a bismuth atom on barium site with one positive charge, V''_{Ba} for a barium vacancy with two negative charges and O^x_O for a neutral oxygen atom on an oxygen site.

The aim of the present paper is to study the influence of heterovalent substitutions (in the A-site) by Bi^{3+} on the structural, dielectric properties of $(Ba_{0.8}Sr_{0.2})Ti_{1-y}(Zn_{1/3}Nb_{2/3})_yO_3$ compound, with special focus on the degree of diffuseness and the relaxation of the ferroelectric-paraelectric phase transition and to investigate the relaxor behavior of the $(Ba_{0.8}Sr_{0.2})_{1-1.5x}Bi_xTi_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$ system. In order to pinpoint the effect of Bi^{3+} substitution on the dielectric properties, an impedance spectroscopy technique is used to separate out the contribution of grain and grain boundary.

The value of y = 0.05 was chosen to be below the threshold value for the onset of relaxor behavior in $(Ba_{0.8}Sr_{0.2})Ti_{1-y}(Zn_{1/3}Nb_{2/3})_yO_3$ [16].

2. Experimental procedure

Ceramic samples with the chemical formula $(Ba_{0.8}Sr_{0.2})_{1-1.5x}Bi_xTi_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$ with x = 0, 0.05 and 0.1 (referred to as Bi_x-BSTZN) were prepared by the conventional solid-state reaction method [24], using stoichiometric proportions of high purity powders of ($BaCO_3$), ($SrCO_3$), (Bi_2O_3), (ZnO), (Nb_2O_5) and (TiO_2) powders, with 99.99% purity used. Appropriate quantities of these precursors were weighed, thoroughly mixed in an agate mortar and pestle, and subsequently calcined at 1100 °C in alumina crucibles under an air atmosphere for 12 h. After cooling, the obtained powder was pressed into pellets (of about 1 mm thickness and 8 mm diameter), and sintered to 1400 °C, 1270 °C and 1290 °C for x = 0, 0.05, 0.1,respectively, for 3 h, then cooled in a furnace to produce relatively dense ceramics. The experimental density (ρ_{exp}) was determined from the weight and geometrical dimensions of the cylindrical pellets and then compared to the theoretical density (ρ_{the}) determined from X-ray measurements. The densities of the specimens, ranging between 93% and 96% of the theoretical density and the porosity (($\rho_{the} - \rho_{exp})/\rho_{the}$), are presented in Table 1.

The X-ray diffraction (XRD) analysis was performed at room temperature using CuKα_1 (λ = 1.5406 Å) and CuKα_2 (λ = 1.5444 Å) radiation in the 2θ range 10–110° with a step size of 0.02°. For the dielectric measurements, the sample electrodes were obtained by painting both sides of the pellets with a low firing temperature silver paint. The dielectric properties of the samples were then measured as a function of temperature from 125 to 400 K and at different frequencies (1 KHz to 1 MHz) using a liquid nitrogen cryostat and an HP4284 impedance analyzer interfaced with a PC.

The general morphologies of this synthesized structure were examined by field emission scanning electron microscopy (FESEM; JEOL-JSM-7600F). Frequency and temperature dependence of the electrical properties were measured using an Agilent 4284 A analyzer with the rising temperature of 1.2 °C/min from 480 °C to 530 °C.

3. Results and discussion

3.1. Microstructure and X-ray diffraction analysis

The phase formation of the prepared sample was confirmed by the X-ray diffraction technique at room temperature. The X-ray diffraction pattern shown in Fig. 1 reveals that the compositions x = 0, 0.05 and x = 0.1 displayed a pseudocubic phase. The close observation of the X-ray diffraction data indicate shifts in diffraction peaks towards higher 2θ values as shown in the inset of Fig. 1. This indicates the reduction of the lattice parameter with an increase in the Bi content. This decrease can be explained by the low ionic radius Bi^{3+} ion (1.17 Å) substituting the higher ionic radius Ba^{2+} (1.61 Å) and Sr^{2+} (1.44 Å) ions. The lattice parameters for these compositions were summarized in Table 1 which decrease with the Bi content. These results are in good agreement with those reported [25] ceramics. In addition, the XRD peaks are intense and very narrow suggesting a good crystallinity of the samples.

Fig. 2 shows the microstructures of $(Ba_{0.8}Sr_{0.2})_{1-1.5x}Bi_xTi_{0.95}(Zn_{1/}$

Table 1
Structure, lattice parameters, Relative density and Porosity of different compositions in the system $(Ba_{0.8}Sr_{0.2})_{1-1.5x}Bi_xTi_{0.95}(Zn_{1/3}Nb_{2/3})_{0.05}O_3$.

Composition(x)	0 [16]	0.05	0.1
Structure	Pseudocubic	Pseudocubic	Pseudocubic
Lattice parameters (Å)	3.9890	3.9753	3.9618
Relative density = ρ_{exp}/ρ_{the}	96.6%	94.60%	92.95%
Porosity (($\rho_x - \rho_{exp})/\rho_x$)	3.39%	5.39%	7.04%