

Studies on the dielectric and relaxor behavior of sol–gel derived barium strontium zirconate titanate thin films

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Abstract

The dielectric behavior of sol–gel derived $\text{Ba}_{0.80}\text{Sr}_{0.20}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($0.0 \leq x \leq 0.50$) thin films is studied. A relaxor behavior is observed for $x \geq 0.35$. The degree of relaxation increases with Zr content. The frequency dependence of the polar regions follows Vogel–Fulcher relation with a characteristic cooperative freezing at freezing temperature (T_f). Below T_f , a long range polarization ordering is likely to take place. The plausible mechanism of the relaxor behavior of BSZT thin films with Zr contents ≥ 0.35 has been proposed based on the measured temperature as well as frequency dependent dielectric data. The solid solution system is visualized as a mixture of Ti^{4+} rich polar regions and Zr^{4+} rich regions; with the increase in Zr content the volume fraction of the polar regions is progressively reduced. At and above 35.0 at.% Zr substitution the polar regions exhibit typical relaxor behavior.

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1. Introduction

Materials based on barium titanate (BaTiO_3 or BT) and lead titanate (PbTiO_3 or PT), have played a dominant role in the field of ferroelectrics. Homovalent or hetero-valent substitutions for barium/lead (A-site) or titanium (B-site) modify the electrical properties and certain dopant(s) beyond a critical concentration produce the relaxor behavior [1–3]. Relaxor ferroelectrics are characterized by diffusivity and frequency as well as temperature dependent dielectric maxima with a relaxation spectrum much broader than the Debye type relaxation [4–9].

Ferroelectric to relaxor behavior has been reported for BaTiO_3 (BTO) substituted with both A-site (Sr, Ca, Ce) and B-site (Zr, Sn, Hf) ions [10–13]. Among barium based materials barium strontium titanate (BST) is well known where it is found that the molar ratio of A-site cations (Ba/Sr ratio) strongly affects the dielectric properties. The composition

$\text{Ba}_{0.80}\text{Sr}_{0.20}\text{TiO}_3$ is widely studied due to its good dielectric and tunable properties [10,14]. Substitution of Zr^{4+} for Ti^{4+} is attractive because Zr^{4+} is chemically more stable than Ti^{4+} and is expected to improve dielectric properties of BST. In this work, we have investigated the effect of Zr content in $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$ thin films.

2. Experimental

$\text{Ba}_{0.80}\text{Sr}_{0.20}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x=0.0, 0.05, 0.20, 0.35$ and 0.50) thin films were deposited on platinum substrates by the sol–gel technique. Details of the precursor sol preparation are reported elsewhere [15]. Films are deposited by spin coating at 4000 rpm for 30 s. Each coating is dried at 400 °C for 5 min followed by firing at 700 °C for 10 min. This process of coating and firing is repeated several times to get the desired film thickness and the final firing is done at 700 °C for 30 min. Crystal structure of the films was investigated by X-ray diffraction. Circular Pt electrodes of 0.2 mm diameter were deposited by dc magnetron sputtering. Electrical measurements were carried out in metal-insulator-metal configuration using an impedance analyzer (HP 4294A.) and a temperature controlled probe station (MMR Technology).

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3. Results & discussion

In the X-ray diffractogram of $\text{Ba}_{0.80}\text{Sr}_{0.20}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ ($x=0.0, 0.05, 0.20, 0.35$ and 0.50) thin films all the reported [14] perovskite peaks of BST (80/20) are observed (Fig. 1a). A clear split of (200) diffraction peak of BST showed that the structure is tetragonal (inset). The tetragonal distortion (c/a ratio) is calculated to be ~ 1.010 . The XRD peaks were found to shift to lower angles with increasing Zr content. Fig. 1b shows the systematic shift in the 110 diffraction peak with various Zr contents indicating solid solubility of Zr in the BST lattice. The calculated a parameters are found to increase linearly with the increase in Zr contents which is justified in view of the larger ionic radii of Zr^{+4} ions (0.86 \AA with C-N ~ 6 for Zr^{+4} , 0.745 \AA with C-N ~ 6 for Ti^{+4}) [16].

In the case of BaTiO_3 the phase transitions occur at 393–408 K (cubic (C) \rightarrow tetragonal (T)), 275–280 K (T \rightarrow orthorhombic (O)) and 180–190 K (O \rightarrow rhombohedral (R)) [17]. Substitution of Ba by isovalent Sr (BST) decreases the C \rightarrow T as well as T \rightarrow O transition temperatures, while the O \rightarrow R transition is relatively unaffected [1,2].

In order to study the effect of Zr contents on dielectric properties and phase transition characteristics, we measured the temperature and frequency dependence of dielectric constant as well as loss tangents of BSZT thin films. Fig. 2 shows the variation of dielectric constant

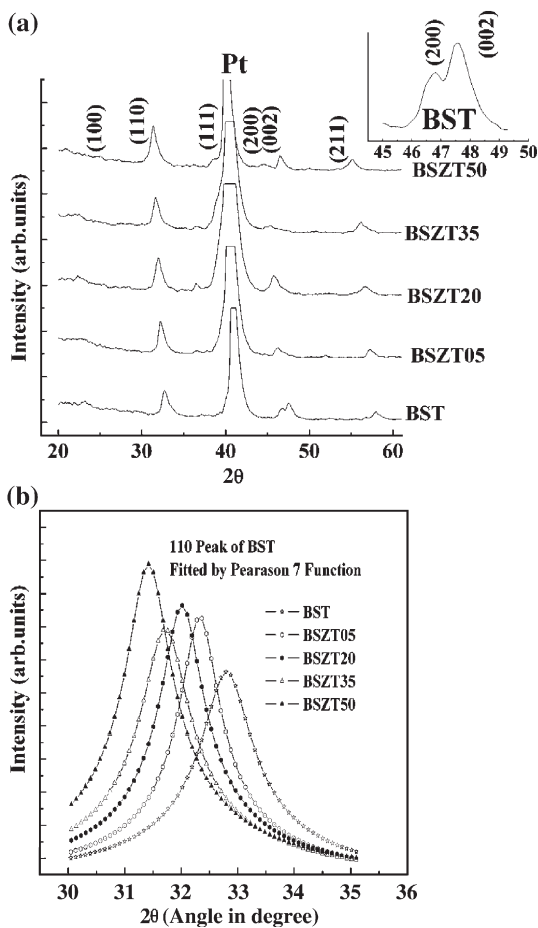


Fig. 1. (a) X-ray patterns of all BSZT thin films: inset shows splitting of (200) peak. (b) Variation of peak position of (110) peak of BSZT; the symbols represent the experimental data points and the solid line is fitted according to Pearson-VII function.

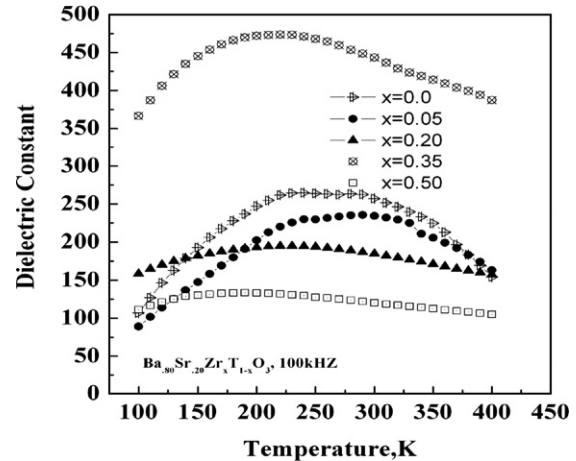


Fig. 2. The temperature dependence of dielectric constant of BSZT thin films measured at 100 kHz.

(measured at 100 kHz) as a function of temperature for all the $\text{Ba}_{0.80}\text{Sr}_{0.20}\text{Zr}_x\text{Ti}_{1-x}\text{O}_3$ thin films.

In the case of BST ($x=0.0$) (Fig. 2), we observed two peaks at around 230 K and 270 K, corresponding to lower transitions in BST i.e. R \rightarrow O at 230 K, O \rightarrow T at 270 K; these transitions were found to shift to 240 K and 300 K respectively for the films with 5 at.% Zr (Fig. 2). For the films with higher Zr contents a broad dielectric anomaly is seen and the transition temperatures are not easily discernible. From Fig. 2 it is however clear that the room temperature dielectric constant is decreased, except for $x=0.35$, whereas the diffuseness of the dielectric anomaly is increased with the increase in Zr contents. The broad nature of dielectric anomaly is common to thin films [17], which renders it difficult to identify the phase transition temperatures unlike in their bulk counterpart. Moreover in multicomponent thin films based on BST, it is difficult to maintain homogeneity in the cation distribution. As a result, the inhomogeneity can result in broadened phase transition, as well as suppression in the peak permittivity or dielectric constant.

The temperature dependent capacitance and loss tangent of thin films were measured in a frequency range of 100 kHz–1 MHz. For the composition $x=0.35$ and 0.50 , a relaxor like behavior was observed as evidenced by an increase in the peak temperature with frequency. This is shown for $x=0.50$ in Fig. 3. A broad dielectric anomaly is apparent both in dielectric constant and loss tangent plots; however, the temperatures corresponding to the dielectric constant maxima (T_m) do not coincide with the corresponding loss tangent maxima (T_m'). For the BSZT35 thin film, similar features were observed in the temperature dependent dielectric constant and loss tangent behaviors as a function of frequencies. A slight decrease of peak temperature T_m was observed with the increase in Zr contents from $x=0.0$ to 0.5 at.% as mentioned in Table 1 (although the relaxor behavior is observed only for $x=0.35$ and 0.50).

In the vicinity of the broadening of dielectric maxima in relaxor ferroelectrics the temperature variation of dielectric constant (K) is known to follow a power relation [18]:

$$1/\varepsilon(f, T) = 1/\varepsilon_m(f) \{1 + [T - T_m(f)]^2 / 2\Delta^2\} \quad (1)$$

where ε is the dielectric constant, ε_m is the peak dielectric constant, T is the temperature, T_m is the peak temperature corresponding to the dielectric constant maxima, γ is the degree of relaxation, and Δ is the broadening parameter.

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