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Dielectric and piezoelectric properties of $(1-x)Ba_{0.7}Sr_{0.3}TiO_3-xBa_{0.7}Ca_{0.3}TiO_3$ perovskites

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ABSTRACT

Dielectric and piezoelectric properties of $(1-x)Ba_{0.7}Sr_{0.3}TiO_3-xBa_{0.7}Ca_{0.3}TiO_3$ (BST−xBCT) ($x=0.2$–0.9) perovskite ceramics have been investigated. BCT has fully incorporated into BST lattice, forming a complete perovskite solid solution, whose lattice constant χ decreases almost linearly with increase in x from 0.2 to 0.4, while showing an anomalous expansion at $0.4<x\leq 0.6$. This, together with the deviation of tetragonal–orthorhombic phase transition temperature (T_{O-T}) from the linear relation T_{O-T} (K)$=-103.7x+239.3$ at $x=0.5$, suggests that a small amount of Ca^{2+} has substituted for Ti^{4+}. Curie temperature T_C increases linearly with increase in x from 0.2 to 0.9, which is mainly contributed to the increase of the Ba/Sr ratio. The calculated degree of relaxation (γ) is in the range of 1.41–1.53, indicating that the BST–xBCT ceramics are ferroelectric materials with diffuse phase transition. Strain and piezoelectric constant (d_{33}) decrease with increasing x, whereas planar electromechanical coefficient (k_p) reaches a maximum (17.0%) at $x=0.6$.

1. Introduction

Barium titanate ($BaTiO_3$) was the first perovskite-type ferroelectric and piezoelectric material developed and studied extensively since its discovery in about the early 1940s [1]. It goes through a paraelectric–ferroelectric phase transition from cubic to tetragonal at 130 °C and two ferroelectric polymorphic transitions: tetragonal to orthorhombic at 0 °C and orthorhombic to rhombohedral at −90 °C [1]. Sr^{2+} and Ca^{2+} ions substitutions for Ba^{2+} ions can form solid solutions, such as $Ba_{1-x}Sr_xTiO_3$ and $Ba_{1-x}Ca_xTiO_3$. These solid solutions have been, and continue to be, of interest for investigation, not only because of their wide applications in the fields of capacitor [2], memory storage [3] and microwave devices [4], but also for their interesting dielectric and ferroelectric behaviors [5–8].

$Ba_{1-x}Sr_xTiO_3$ is a solid solution throughout the substitution concentrations: range from 0 to 1, whose T_C decreases linearly with respect to the substitution concentrations [7,9,10]. According to Lemanov et al. [6], the variation of T_C is usually ascribed to the A-site cation size effect, in which the smaller Sr^{2+} ions cause a decrease in the average radius of the A-cation. There is a different case for $Ba_{1-x}Ca_xTiO_3$. Early reports [5,8] revealed that Ca^{2+} replaced Ba^{2+} ions to form $Ba_{1-x}Ca_xTiO_3$ solid solutions with x up to 0.23, which had a slight effect on T_C. This effect seems to be inconsistent with the A-site cation size effect. For the $Ba_{0.4}Sr_{0.6-x}Ca_xTiO_3$ system [11], it was found that T_C increased linearly with increase in x from 0 to 0.15, while deviating from linear behavior for $x>0.15$. Up to $x=0.25$, T_C increased persistently and thereafter decreased. However, the variation of T_{O-T} with Ca concentration has not been reported till now. In addition, $Ba_{0.7}Ca_{0.3}TiO_3$ is usually added into $Bi_{0.5}Na_{0.5}TiO_3$ [12] and $BaZr_{0.2}Ti_{0.8}O_3$ [13] to modify their piezoelectric properties. Thus, this study was focused on the dielectric and the piezoelectric properties of the BST–xBCT ($x=0.2$–0.9) ceramics. The relationship between property and structure was also discussed.

2. Experimental procedure

All the reagents were of analytical grade (Sinopharm Chemical Reagent Co., Ltd., China) and were used as received without further purification. $(1-x)Ba_{0.7}Sr_{0.3}TiO_3-xBa_{0.7}Ca_{0.3}TiO_3$ ($x=0.2$–0.9) ceramics were prepared by using a solid-state reaction method. $BaCO_3$ (99.0%), $SrCO_3$ (99.0%), $CaCO_3$ (99.0%) and TiO_2 (98.0%) powders were used as starting materials for the synthesis of $Ba_{0.7}Sr_{0.3}TiO_3$ and $Ba_{0.7}Ca_{0.3}TiO_3$ powders at 1100 °C. Thereafter, the powders were mixed according to the stoichiometric ratio of BST–xBCT (where $x=0.2$, 0.3, 0.4, 0.5, 0.6, 0.7, and 0.9) and milled in polypropylene bottles with zirconia grinding media for 24 h. The dried powders were granulated using 8 wt% polyvinyl alcohol as a binder and then pressed to yield the diameter and thickness of 10 mm and 1mm, respectively. The green pellets

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were kept at 550 °C for 6 h to remove the solvent and the binder. The pellets were sintered at 1350 °C for 4 h in air.

All samples had densities higher than 90% of theoretical limits. Phase compositions of the ceramics were investigated by means of X-ray diffraction (XRD, Bruker D8 Advanced, Germany) using CuK_α radiation. Temperature dependences of permittivity (ε) and loss tangent were measured using an HP 4284A precision LCR meter (Agilent, Palo Alto, CA) at 10 kHz in the temperature range of 125–450 K. Polarization versus electric field (P–E) hysteresis loops were measured in a silicon oil bath by applying an electric field of triangular waveform at 10 Hz by means of a ferroelectric testing system (Radiant Precision Premier II Technology). MTI 2100 photonic sensor was used for strain measurement. Samples were poled in a silicon oil bath at room temperature with a DC electric field of 20 kV/cm for about 30 min, which was used for d_{33} and k_p measurements. d_{33} was measured using a quasistatic d_{33} meter (ZJ-6A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The accuracy of d_{33} measurement is $\pm$0.1 pC/N. k_p was determined by means of a resonance–antiresonance method using a precision impedance analyzer (HP4294A, Agilent, Palo Alto, CA).

3. Results and discussion

XRD patterns of the BST–xBCT (x=0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.9) ceramics are given in Fig. 1. It can be seen that all samples have a perovskite tetragonal structure without impurity phases, which indicates that BCT has been fully incorporated into BST lattice forming a complete perovskite solid solution.

Lattice constants a, c and χ (for tetragonal symmetry, the average lattice constant $\chi=\sqrt[3]{a^2c}$ is taken, where a and c are the lattice parameters of tetragonal cell) as functions of x are shown in Fig. 2. It is found that χ decreases almost linearly with increase in x from 0.2 to 0.4 and then increases with a further increase up to x=0.6 and thereafter decreases, which is similar to the results of the $Ba_{0.4}Sr_{0.6-x}Ca_xTiO_3$ system reported by Zheng et al. [11]. The ionic radius of Ca^{2+} (1.340 Å) in 12-fold coordination is smaller than that of Ba^{2+} (1.610 Å) and Sr^{2+} (1.440 Å) [14], which led to the lattice shrinkage in the range of $0.2 \le x \le 0.4$. The anomalous expansion at $0.4 < x \le 0.6$ is due to a small amount of Ca^{2+} substitution for Ti^{4+} (0.605 Å), which is confirmed by Zheng et al. [11]. When $x > 0.6$, besides those that have been substituted for Ti^{4+}, the remaining Ca^{2+} substitute for Sr^{2+}. The variation of c/a with x shows a "V" shaped curve in the range of $0.2 \le x \le 0.6$, indicating that the tetragonality initially becomes weak with increasing x and then becomes strong. Thereafter, the tetragonality remains almost unchanged.

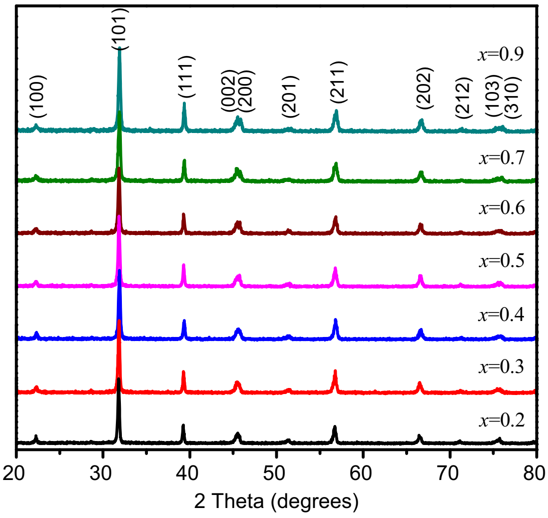

Fig. 1. XRD patterns of the BST–xBCT (x=0.2, 0.3, 0.4, 0.5, 0.6, 0.7 and 0.9) ceramics.

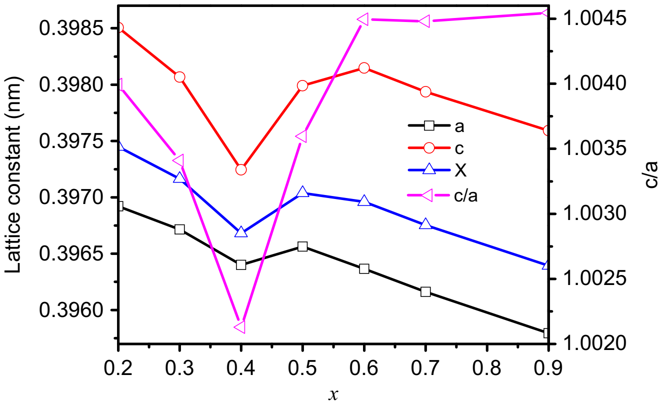

Fig. 2. Lattice constants a, c and χ of the BST–xBCT ceramics as functions of x.

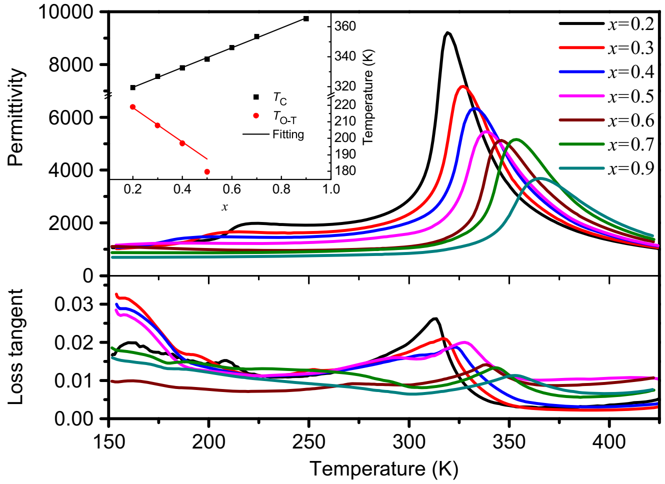

Fig. 3. Temperature dependences of permittivity and loss tangent of the BST–xBCT ceramics measured at 10 kHz. Inset shows T_C and T_{O-T} of the BST–xBCT ceramics as functions of x.

Temperature dependences of permittivity and loss tangent for all samples measured at 10 kHz are displayed in Fig. 3. The dielectric peaks of both cubic–tetragonal phase transition and tetragonal–orthorhombic phase transition for the BST–xBCT ceramics are suppressed and broadened with increasing x. $CaTiO_3$ is known as the typical depressor in $BaTiO_3$ ceramics, which led to significant suppression of dielectric permittivity and loss [15]. Li et al. [16] reported that addition of Ca did not strongly affect the T_C of the $(Ba_{1-x}Ca_x)(Ti_{0.96}Sn_{0.04})O_3$ system, but pushed T_{O-T} toward a lower temperature. Interestingly, in present system, T_C increases with increasing x, whereas T_{O-T} decreases. T_C and T_{O-T} of the BST–xBCT ceramics as functions of x are shown in the inset of Fig. 3. The relationship between T_C and x for $0.2 \le x \le 0.9$ is linear, which can be described by T_C (K)=66.0x+306.4. Amazedly, the deviation of T_C from the linear behavior observed in the $Ba_{0.4}Sr_{0.6-x}Ca_xTiO_3$ system [11] is not found in the present system. The increase of T_C with the increase of Ca concentration in the $Ba_{0.4}Sr_{0.6-x}Ca_xTiO_3$ system is in distinct contrast to the decrease of T_C with respect to Sr concentration in the $Ba_{1-x}Sr_xTiO_3$ system, which cannot be understood within the framework of the A-site cation size effect [11]. According to a slight variation of T_C in $Ba_{1-x}Ca_xTiO_3$ series [5,8] and a linear decrease of T_C in