

Structural and Dielectric Properties of Cerium-modified BiScO₃-PbTiO₃ Piezoelectric Ceramics

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Abstract. The 0.36(Bi_(1-x)Ce_x)ScO₃-0.64PbTiO₃ ($x = 0.01-0.10$) ceramics were prepared by using conventional mixed oxide ceramic processing, and the effect of Ce addition on the BiScO₃-PbTiO₃ (BSPT) system was investigated. The results of X-ray diffraction show that lower stability of the perovskite phase is produced with the partially substitution of Ce for Bi in the BSPT ceramics, although they all still maintain tetragonal perovskite structure. Moreover, partly substituting Bi with Ce was found to shift the Curie temperature of the BSPT ceramics to lower temperature, and convert the BSPT ceramics from a classical ferroelectric to a relaxor ferroelectric.

Introduction

The (1-x)BiScO₃-xPbTiO₃ (BSPT) system piezoelectric materials were previously reported to possess comparable piezoelectric properties and significantly higher Curie temperature T_c compared to commercial Pb(Zr_xTi_{1-x})O₃ (PZT) systems [1-6]. For instance, the T_c was reported to be 450 °C for the BSPT ceramics at the morphotropic phase boundary (MPB) composition $x = 0.64$ with piezoelectric coefficient d_{33} of 460 pC/N and planar electromechanical coupling factor k_p of 0.56, which indicate that the BSPT system is a kind of promising candidate material for actuation and sensing applications requiring high temperature and temperature stable performance.

However, in order to achieve commercial success, the properties of the BSPT system should be able to be customized for different technical applications by making some appropriate composition modifications, just like the PZT system [7-11]. The commonly used dopants include “soft” donor and “hard” acceptor for the adjustment of formulation in the PZT system [12]. Donor doping were expected to reduce the concentration of oxygen vacancies, thus leading to a reduction in the concentration of domain-stabilizing defect pairs. The resulting enhancement in domain wall mobility will inevitably cause the evident increases in dielectric constant, dielectric loss, elastic compliance and coupling coefficient, and reductions in mechanical quality factor and coercivity. In contrast, a reduction in dielectric constant, dielectric and mechanical loss, and an increase in the coercive field will result from the inhibition of domain wall motion for acceptor doping.

Additionally, there are some additives possessing characteristics of both donor doping and acceptor doping, which are usually metal ions with more than one valence state in the lattice, such as Cr³⁺, Mn⁴⁺, Ce³⁺ and so on [7]. In the current work, the solid solutions with the general formula 0.36(Bi_(1-x)Ce_x)ScO₃-0.64PbTiO₃ were projected and fabricated. The dopant is Ce³⁺ on the A-site, in substitution for Bi³⁺ (following the typical ABO₃ perovskite formula). The structural and electrical properties of this system compared to undoped BSPT ceramics are presented.

Experimental Procedure

The 0.36(Bi_(1-x)Ce_x)ScO₃-0.64PbTiO₃ ($x = 0.01-0.10$) ceramics were prepared by traditional mixed oxide ceramic processing. The raw materials used in the study were Bi₂O₃ (99%), CeO₂ (99.9%), Sc₂O₃ (99%), PbO (99%), and TiO₂ (99.5%) powders. The oxides powders were ball-milled in ethanol with agate media for 24 hours, dried, and then calcined at 800-850 °C for 4 hours in an alumina crucible. These calcined powders were milled and dried again. To improve the

green strength of compacts, an addition of 3-5 wt% of poly (vinyl alcohol) was thoroughly mixed with these powders. These powders were granulated and pressed into pellets of 10 mm diameter and 1 mm thickness under 20 MPa uniaxial pressure. Following a removal of binder at 500 °C for 2 hours, pellets were sintered in sealed crucibles at temperature 1180 °C for 2 hours. The sintering weight loss and volume shrinkage were about ~1% and ~15%, respectively.

Phase determination for sintered pellets was made using X-ray diffraction (XRD) (DX-1000 diffractometer). For electrical characterization, the sintered pellets were polished and electroded using a postfired silver paste, fired on at 700 °C. Temperature dependent dielectric measurements were carried out at temperatures between 25 and 600 °C using a computer controlled precision LCR meter (HP4284A) with a specially designed four-sample furnace.

Results and Discussion

Fig. 1 shows the XRD patterns of $0.36(\text{Bi}_{1-x}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics. It can be seen that all the ceramics exhibit a perovskite structure in the composition range studied in this work. However, some peaks of other phase can also be found at about $2\theta = 28^\circ$ as $x \geq 0.01$, which reveals that the stability of the perovskite phase decreases with the substitution of Ce for Bi, due to the unstable valence state of the cerium ions. As well-known, the Ce^{3+} and Ce^{4+} ions can be coexistent in a crystal lattice. The ionic radius of Ce^{3+} is 0.134nm, which is very close to that of Bi^{3+} of 0.136nm. However, the ionic radius of Ce^{4+} is only 0.114nm, which is far below that of Bi^{3+} . Therefore, according to Goldschmidt's theory [13], a lower tolerance factor t will indispensably be obtained with the replacement of Bi by Ce, which results in the decreasing of the stability of perovskite phase. Furthermore, it can be observed that the [100] and [200] peaks, which located at about $2\theta = 22^\circ$ and 45° , respectively, were split for all cerium-substituted ceramic samples, indicating that they still remain tetragonal structure, just like the pure $0.36\text{BiScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics.

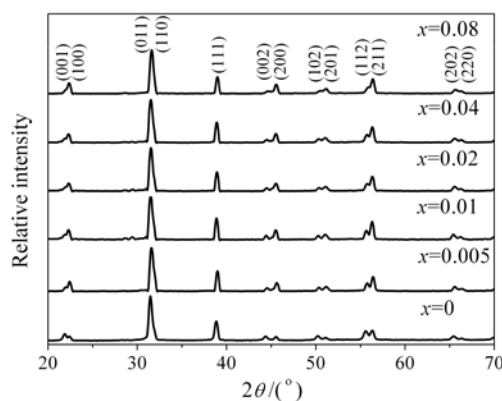


Fig. 1 XRD patterns of $0.36(\text{Bi}_{1-x}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics

The temperature dependence of dielectric constant are shown in Fig. 2 for the $0.36(\text{Bi}_{1-x}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics. It can be found that the dielectric constant peak, which is corresponding to the ferroelectric-paraelectric phase transition, is broadened with the increasing of Ce content, revealing the growing signs of relaxor behavior. The ceramics are normal ferroelectric for $x < 0.02$, as the relationship between the dielectric constant and temperature obeys the Curie-Weiss law well, and the peak temperature of dielectric constant does not vary with the frequency. For $x = 0.02$, there are some deviations from the Curie-Weiss law occurred in the change of the dielectric constant with temperature, and the temperature of the peak dielectric constant becomes higher with increasing the frequency, implying the onset of relaxor behavior. For $x \geq 0.04$, the dielectric curve does not follow the Curie-Weiss law any more, and the frequency dispersion tends to be more pronounced. For $x \geq 0.08$, the ceramics exhibit characteristics of more typical relaxor ferroelectric phase transition, as the shape of the dielectric constant peak has become extremely broad.

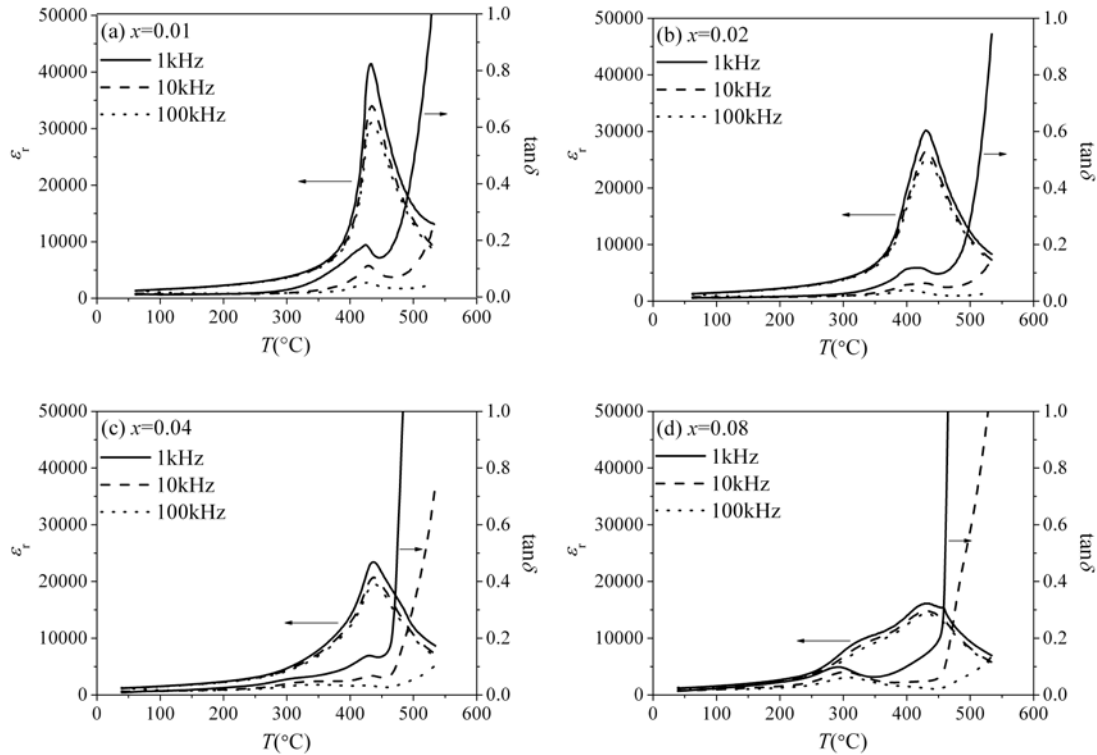


Fig. 2 Temperature dependence of ϵ_r and $\tan\delta$ of $0.36(\text{Bi}_{1-x}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics

Based on the composition fluctuation theory proposed by Smolenskii [14], the chemical composition and crystal structure are usually inhomogeneous on the nanometer scale for a complex perovskite-type ferroelectric, in which the same lattice position may be occupied by a variety of ions. Consequently, a large number of micro-zones are formed with different polarization behavior, which may lead to the polarization relaxation behavior in a weak field. For the $0.36(\text{Bi}_{(1-x)}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics, the adding of cerium oxide will inevitably increase the composition inhomogeneity. Additionally, the number of ions in each unit cell is not the same any more, because there are some metal cation vacancies existing in a few unit cells, due to the existence of the higher valence state Ce^{4+} ions in the solid solution. Thus, the ceramics transformed from normal ferroelectrics to relaxor ferroelectrics with the addition of Ce.

In addition, a "small shoulders" can be found appearing at the temperature range of 300-350 °C below the dielectric constant peak temperature in the dielectric constant-temperature curve for $x \geq 0.04$, and the "small shoulders" even turns to a small peak in the dielectric loss-temperature curve. The advent of the low temperature peak implies that there must have been a variation in structure or micro-domains occurred near the temperature, which might be related to ferroelectric-ferroelectric phase transition, just as in the $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{-PbTiO}_3$ system near the MPB composition [15].

The temperature corresponding to the dielectric constant peak (1 kHz) were used to determine the Curie temperature T_c of $0.36(\text{Bi}_{(1-x)}\text{Ce}_x)\text{ScO}_3\text{-}0.64\text{PbTiO}_3$ ceramics, as shown in Fig. 3. It can be seen that the T_c decreases gradually with the increasing of Ce content for $x \leq 0.02$. Based on the stability theory of ferroelectric domain proposed by Thomas [16], the stability of ferroelectric domain and the depolarization temperature will be reduced if the coupling effect of A-site cation and BO_6 octahedra is weakened for some reason in perovskite ferroelectrics. For the cerium-modified $\text{BiScO}_3\text{-PbTiO}_3$ piezoelectric ceramics, some of Pb and Bi must have evaporated into the air to maintain electroneutrality in the crystal lattice, because the cerium ions may occupy the A-site in multiple valence states with a higher valence state than that of Pb^{2+} or Bi^{3+} . As a result, some A-vacancies were generated in the lattice, thereby weakening the coupling effect of A-site cation and BO_6 octahedra, and consequently reducing the depolarization temperature, namely the T_c . However, the T_c exhibits a fluctuant trend with $x \geq 0.04$, which could be attributed to the low solubility of Ce^{4+} in the perovskite phase.

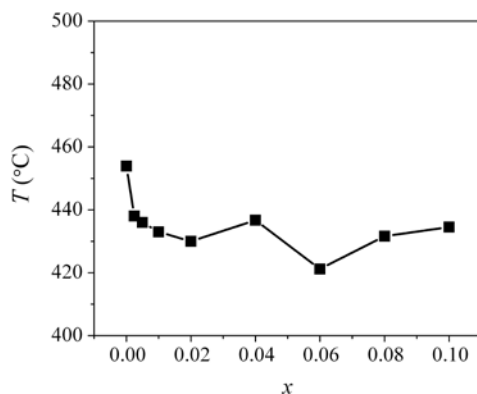


Fig. 3 Curie temperature as a function of x content in $0.36(\text{Bi}_{1-x}\text{Ce}_x)\text{ScO}_3-0.64\text{PbTiO}_3$ ceramics

Summary

The $0.36(\text{Bi}_{(1-x)}\text{Ce}_x)\text{ScO}_3-0.64\text{PbTiO}_3$ ($x = 0.01-0.10$) ceramics were developed by using traditional mixed oxide ceramic processing. The structural and dielectric properties of the ceramics were studied. The results of X-ray diffraction show that all ceramic samples possess a tetragonal perovskite structure, nevertheless, the stability of perovskite phase decreases with the increase of Ce content in the $0.36(\text{Bi}_{(1-x)}\text{Ce}_x)\text{ScO}_3-0.64\text{PbTiO}_3$ system. Moreover, the partially substitution of Ce for Bi moves the Curie temperature of $\text{BiScO}_3\text{-PbTiO}_3$ (BSPT) ceramics towards lower temperature. In addition, the $0.36(\text{Bi}_{(1-x)}\text{Ce}_x)\text{ScO}_3-0.64\text{PbTiO}_3$ ceramics are gradually transformed from normal ferroelectrics to relaxor ferroelectrics with increasing Ce content.

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