



Effect of Nd³⁺ substitution on electric field induced strain behavior in lead zirconate stannate titanate (68/22/10) ceramics



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ABSTRACT

Pb_{1-3x/2}Nd_x(Zr_{0.68}Sn_{0.22}Ti_{0.1})O₃ ceramics with large electrical field induced strain were prepared by Nd³⁺ doping. X-ray diffraction analysis showed that the substitution of Nd³⁺ for Pb²⁺ enhanced the stability of antiferroelectric phase due to the decrease of tolerance factor. Besides, with the increase of Nd³⁺ addition, the strain first improved with a maximum value at $x = 0.02$, and then decreased. Further, with increasing electric field and decreasing measuring frequency, the strain improved obviously. This is because that the reversal of the domains is more sufficient at large electric field and long time. The largest strain of 0.63% is obtained in the specimens with $x = 0.02$ at the frequency 1 Hz.

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1. Introduction

The concept of antiferroelectricity is proposed by Kittel in 1951 [1]. Compared with large polarization in ferroelectric (FE) crystals, the spontaneous of antiferroelectric (AFE) crystal is zero due to the offsetting antiparallel alignment of electric dipoles. However, the AFE phase could be transformed into FE state by applying a sufficiently high electric field. In the switching process, a large macroscopic polarization develops and significant volume expansion occurs [2,3]. Base on the unique phase transition performance, AFE materials are widely used in digital transducers, shape memory, energy storage devices and infrared detectors [2–6]. In contrast to other performances, the most attractive feature of this class of materials is the electric field induced strain properties, because its maximum value of 0.87% is the largest in ceramics based on present reports [7].

So far, PbZrO₃ materials have been the most widely studied AFE systems. In pure PbZrO₃, the free energy difference between the AFE phase and the FE phase is sufficiently large to prevent an electric field-induced phase transition from occurring in bulk ceramic samples at ambient conditions [8]. However, through chemical modification, the gap in free energies can be lowered so that the transition from AFE phase to FE phase is realized at a sustainable electric field. For example, Berlincort found that substitution of Sn⁴⁺ and Ti⁴⁺ for Zr⁴⁺ could decrease the switching field and extend

the tetragonal AFE phase [9]. Thus, in PbZrO₃–PbTiO₃–PbSnO₃ ternary system, it is easier for the occurrence of the phase transformation [9–11]. In this transition process, the variation of the unit cell volume can be expressed by [7]:

$$(\Delta V/V) = (\Delta V/V)_F - (\Delta V/V)_A = Q_h \Omega P_{ind}^2 \quad (1)$$

where P_{ind} is the polarization induced by the electric field, Q_h is the electrostrictive coefficient and Ω is the coupling coefficient between the two sublattices. From Eq. (1), it can be seen that the more stable AFE phase is, the larger the electric field induced strain is. Phase stability of the perovskite structure (ABO₃) can be evaluated in terms of tolerance factor, which is defined as [8]:

$$t = \frac{(R_A + R_O)}{\sqrt{2}(R_B + R_O)} \quad (2)$$

where R_A , R_B , and R_O are respectively the ionic radii of A-site cation, B-site cation, and oxygen anion. Generally, FE phase is stabilized for $t > 1$ and AFE phase is stabilized for $t < 1$. As shown, substitution with smaller ions at the A-site or larger ones at the B-site can stabilize the AFE phase. Similar to La, which is a good AFE phase stabilizer [12], Nd also belongs to rare earth element but its ion radius is smaller. This indicates that the electrical properties of AFE materials may be greatly improved by doping the base composition with Nd. Recently, Yu and Singh studied the effect of Nd³⁺ doping on the electric properties of (Pb, Sr) (Zr, Ti)O₃ ceramics and found that Nd³⁺ addition enhanced substantially the electric field induced strain of the ceramics [13]. This provides a very attractive way for obtaining actuator with high strain energy density, however, the maximum

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strain of 0.45% in this system is a little small for actuator application. Generally, the actuators' performance can be demonstrated by the strain energy density which is a measure of the energy per unit mass an actuator can deliver [14,15]:

$$e_{\max} = 1/\rho \cdot 1/4 \cdot [1/2 \cdot E(s_{\max})^2] \quad (3)$$

where e_{\max} is the strain energy density, E is the actuator's elastic modulus, s_{\max} is the maximum field induced strain, ρ is the actuator's density, and $1/4$ is a factor appropriate for the actuator whose impedance matches to that of its surroundings. From Eq. (3), it can be seen that for designing an actuator with high strain energy density, the strain of the materials should be large as soon as possible. In order to obtain larger strain in Nd doped AFE materials, in this study, Nd^{3+} is incorporated into the $\text{Pb}(\text{Zr}_{0.68}\text{Sn}_{0.22}\text{Ti}_{0.1})\text{O}_3$ system and the effect of Nd^{3+} addition on the crystal structure and electric field induced strain properties were investigated to find out the optimized Nd content, in which the ceramics can obtain the largest strain. Meanwhile, the measuring frequency and electric field dependence of strains were studied in detail.

2. Experimental

$\text{Pb}_{1-3x/2}\text{Nd}_x(\text{Zr}_{0.68}\text{Sn}_{0.22}\text{Ti}_{0.1})\text{O}_3$ (PNZST, $0.01 \leq x \leq 0.04$) ceramics were prepared by conventional solid state synthesis. PbO , Nd_2O_3 , TiO_2 , ZrO_2 , SnO_2 with the purity of over 99% were used as starting materials. The powders were weighed according to the stoichiometric formula and ball milled for 6 h and then calcined in sealed Al_2O_3 crucibles at 900 °C for 6 h. These powders were ball milled again for 6 h, dried and pressed into discs 10 mm in diameter and 0.2 mm in thickness using PVA as a binder. After burning off PVA, the pellets were sintered at 1200–1240 °C for 2 h with a double crucible method, silver paste was fired on both sides of the samples at 550 °C for 10 min.

The crystal structures of sintered samples were determined by using an X-ray diffractometer (XRD, Bruker D8 Advance, Germany). The dielectric properties with variation of temperature and frequency were measured using a HP 4284A precision LCR meter (Agilent). The electric field-induced polarization (P–E) and strain (S–E) were measured using a ferroelectric test system (Precision Premier II) at different frequencies.

3. Results and discussion

The X-ray diffraction (XRD) patterns of PNZST ceramics with various Nd^{3+} additions are shown in Fig. 1. All samples exhibit a pure perovskite structure and no second phases can be detected. Further XRD analysis is performed in the 2θ ranges from 43° to 45° as shown in the inset. As $x = 0.01$, the sample is in the rhombohedral FE phase, because the patterns show single (200) peak. With further increasing x to 0.02, the (200) peak splits into (200)/(002)

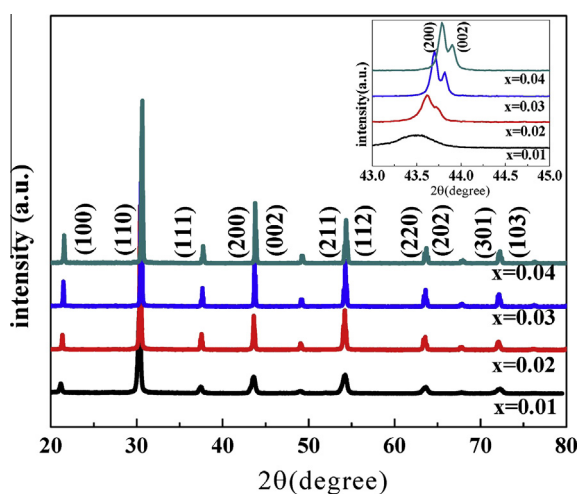


Fig. 1. XRD patterns of PNZST ceramics with various Nd^{3+} content. The inset shows the fine scanning XRD patterns.

reflections, which suggests the occurrence of tetragonal AFE phase. In addition, it is also noted that with the improvement of Nd^{3+} content, the diffraction peaks shift towards higher diffraction angle, which suggests the distortion of the crystal lattice due to Nd^{3+} with smaller ion radius replacing Pb^{2+} .

Fig. 2 shows the variation in the permittivity of PNZST specimens as a function of temperature and Nd^{3+} content. As can be seen from the figure, with increasing x from 0.01 to 0.04, the dielectric constant, the Curie temperature (T_c) and the dielectric loss gradually decrease. It is known that the dielectric constant of ceramics relies on mostly the contribution of spontaneous polarization (P_s). For conventional lead titanate (PbTiO_3) ceramics, the P_s is very large because Pb^{2+} has outer electron cloud structure with non-inert gas type for which the polarization between Ti^{4+} , O^{2-} and Pb^{2+} is large. However, when Pb^{2+} is partially replaced by Nd^{3+} with the outer electron cloud structure of inert gas-type, the spontaneous polarization decreases. This reduces the dielectric peak. In ferroelectric ceramics, the Curie temperature can be written as [16]:

$$T_c = \gamma C (C = Np^2/3\epsilon_0\kappa) \quad (4)$$

where γ is Lorentz coefficient, ϵ_0 is the permittivity of free space, p is the spontaneous of single dipole, N is the number of dipoles within the unit volume, κ is Boltzmann constant. As shown, microscopic dipole and macro Curie–Weiss temperature is contacted by Eq. (4) and it can be also seen that the Curie temperature is determined by the number of dipoles and the spontaneous polarization of single dipole. When Nd^{3+} replaces Pb^{2+} , because of the reduction of polarization, the Curie temperature decreases, as illustrated by the fact that the T_c of PbTiO_3 (490 °C) is much higher than those of BaTiO_3 (120 °C) and SrTiO_3 (–220 °C) [17]. As for the decrease of the dielectric loss, this is because that the stability of AFE phase improves with increasing Nd^{3+} content. Besides, with the increase of Nd^{3+} addition, the dielectric peak gradually become wide, indicating the increase of dielectric diffuse properties. This is because Nd^{3+} with high valence replacing Pb^{2+} with low valence produces lead vacancies, which will make crystal structure distorted and brings a normal antiferroelectrics to a relaxed antiferroelectrics. The inset shows the dielectric constant and dielectric loss of the specimen with $x = 0.03$ in a wide frequency range (from 1 kHz to 1000 kHz) as a function of temperature. As can be seen from the figure, the maximum dielectric constant and dielectric loss decrease with the increase of measuring frequency.

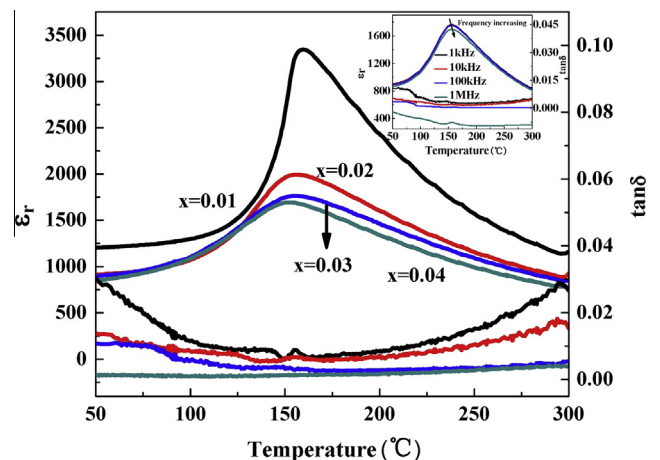


Fig. 2. Temperature dependence of dielectric constant and loss of PNZST ceramics with different Nd^{3+} addition. The inset shows the dielectric constant and dielectric loss of the specimen with $x = 0.03$ in a wide frequency range (from 1 kHz to 1000 kHz) as a function of temperature.

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