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Phase transition and piezoelectric, ferromagnetic response of B-site (Co, Nb) modified $BaTiO_3$ ceramics

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Abstract

Structure, phase transformation and electric properties of $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ($0.01 \le x \le 0.10$) ceramics were investigated. Results showed that the compositions with $0.02 < x < 0.07$ contained both orthorhombic and tetragonal phases at room temperature. As the substitution level increased, the evolution of dielectric properties from a sharp ferroelectric peak to a round dielectric peak with pinched phase transitions was observed, accompanying the increased diffuseness. When the substitution level increased up to 0.07, the coexistence of ferroelectric and ferromagnetic behavior was found. Due to the different possible polarization states resulting from the coexistence of orthorhombic and tetragonal phases, the composition with $x=0.05$ exhibited the following optimum piezoelectric properties: $d_{33}^*=272$ pm/V, $d_{33}=195$, and $k_p=32\%$.

Keywords: C. Ferromagnetic properties; C. Piezoelectric properties; Ferroelectrics; Phase transformation

1. Introduction

Perovskite barium titanate ($BaTiO_3$) is one of the most extensively studied ferroelectric materials because of its wide applications in commercial multilayer capacitors [1], ferroelectric memory devices [2], and piezoelectric devices [3]. Its dielectric response shows a paraelectric–ferroelectric phase transition from cubic to tetragonal structure at 406 K, accompanied by a strong and sharp dielectric peak, and two more ferroelectric polymorphic transitions: tetragonal to orthorhombic at 278 K and orthorhombic to rhombohedral at 183 K. Its electrostrain can be in theory as large as ~1% [4]. Unfortunately, it has large hysteresis, which restricts its practical application.

Since $BaTiO_3$ shows an exceptionally tolerant ability to doping, both aliovalent and isovalent ionic substitutions at equivalent sites can tailor the properties to meet various device applications [5–7]. It is well known that donor dopants can induce cationic defects while occupying A or B-site of perovskite lattice. Bi as a donor dopant on Ba site gives rise to a transition from normal ferroelectric to relaxor [8]. Acceptor dopants, e.g., Ca in place of Ti, can improve the stability of $BaTiO_3$-based ceramics since associated charge compensation, involving creation of oxygen vacancies, acts to reduce loss of oxygen during high temperature processing [9]. It was reported that a large nonlinear recoverable electrostrain up to 0.17% at 3 kV/mm was observed for Mn^{3+}+Nb^{5+} hybrid-doped $BaTiO_3$ ceramics, which exceeded that of acceptor-monodoped ceramics [10]. Isovalent substitution by a small A-site ion (e.g., Sr^{2+}) and/or a large B-site ion (e.g., Zr^{4+}, Ce^{4+}) stabilizes the cubic polymorph to lower temperature [11]. The strain level is in the range of 0.14–0.19% at 60 kV/cm with a small hysteresis for the $Ba(Ti_{1-y}Ce_y)O_3$ ceramics with $0.02 \le y \le 0.08$ [12]. Khemakhem et al. [13] ever reported that complex cation $(Zn_{1/3}Nb_{2/3})^{4+}$ substitution for Ti^{4+} exhibited a high d_{31} coefficient of 90 pC/N. However, dielectric and piezoelectric responses of complex cation $(Co_{1/2}Nb_{1/2})^{4+}$ modified $BaTiO_3$ ceramics have not been reported till now.

Recently, Nakayama and Katayama-Yoshida [14] performed *ab initio* total energy calculations for Tm-doped $BaTiO_3$ system (Tm=Sc, V, Cr, Mn, Fe, Co, Ni, Cu), and predicted that Cr, Mn, Co, and Fe-doped $BaTiO_3$ are the most promising ferromagnetism candidates. Subsequently, it was confirmed

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that Co implantation in whether $BaTiO_3$ bulk [15] or $BaTiO_3$ thin film [16] can produce magnetic ordering at room temperature. These theoretical calculations and experimental results imply that it can be desirable to obtain ferromagnetic behavior in complex cation $(Co_{1/2}Nb_{1/2})^{4+}$ modified $BaTiO_3$ ceramics.

In this paper, dielectric, piezoelectric and ferromagnetic responses of $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics were reported for $x \leq 0.10$.

2. Experimental procedure

$BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics, where $x=0.01$, 0.02, 0.05, 0.07 and 0.10, were prepared through the conventional solid-state reaction method using starting chemicals of $BaCO_3$ (99.0%), TiO_2 (98.0%), Co_2O_3 (99.0%) and Nb_2O_5 (99.5%). Mixtures based on the compositions of $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ were ball-milled with zirconia media in ethanol for 24 h and dried at 110 °C for 12 h. After drying, the powders were calcined at 1100 °C for 4 h and then re-milled for 24 h. The calcined powders, mixed with 8 wt% polyvinyl alcohol, were pressed into pellets at 100 MPa. The green pellets were kept at 550 °C for 6 h to remove the solvent and the binder. $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics were sintered at 1350 °C for 5 h in air.

Phase compositions of the ceramics were investigated by means of X-ray diffraction (XRD, Bruker D8 Advanced, Germany) with CuK_α radiation. Permittivity (ε) and loss tangent (tan δ) as a function of temperature were measured at frequency from 1 kHz to 1 MHz in temperature range of 175–425 K, using a HP 4284A precision LCR meter (Agilent, Palo Alto, CA). Both polarization–electric field (P–E) and strain–electric field (S–E) curves 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). 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 the piezoelectric coefficient (d_{33}) and planar coupling factor (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 ± 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). The ferromagnetic properties of the pellets were measured by using a vibrating sample magnetometer (VSM, Lakeshone, USA) at room temperature.

3. Results and discussion

XRD patterns of the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics are given in Fig. 1. Only perovskite phase is detected for all compositions, indicating that complex cation $(Co_{1/2}Nb_{1/2})^{4+}$ has completely entered into $BaTiO_3$ lattice and then formed a solid solution. Together with the enlarged XRD patterns, as shown in Fig. 1b, the compositions with $x \leq 0.02$ have an orthorhombic structure, while those with $x \geq 0.07$ possess a

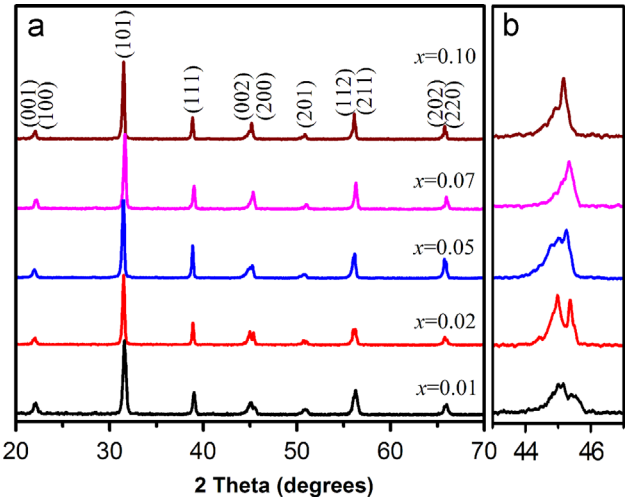

Fig. 1. XRD patterns of the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics and its magnified (200) diffraction peak in the range of 2θ from 43° to 47°.

tetragonal phase. Therefore, it can be suggested that orthorhombic and tetragonal phases coexist in the composition range of $0.02 < x < 0.07$.

Temperature dependence of ε and tan δ for all compositions measured at different frequencies, varying from 1 kHz to 1 MHz, is displayed in Fig. 2. For the composition with $x=0.01$, no obvious frequency dependence of ε is observed, i.e., the three phase transition temperature (T_m, T_1, T_2) are independent of measuring frequency, which is similar to that observed in pure $BaTiO_3$ ceramics. The dielectric peaks of cubic–tetragonal phase transition are broadened with increasing x. Correspondingly, T_m decreases, whereas T_1 and T_2 increase. When x increases up to 0.10, the three phase transitions are pinched into one round dielectric peak. Meanwhile, the distinct frequency dependence is observed. This is similar to that observed in Ba(Ti, Ce)O_3 [17], where frequency dependence occurs at low impurity level.

In order to further discuss the diffuseness of the phase transition of all compositions, an empirical relation is proposed to describe the high-temperature slope of the dielectric peak [18], i.e.,

$$\frac{1}{\varepsilon} = \frac{1}{\varepsilon_m} + \frac{(T-T_m)^\gamma}{2\varepsilon_m\delta^2} \quad (1)$$

where T_m is the temperature corresponding to ε_m, δ is a measure of the degree of diffuseness of the peak, and $1 \leq \gamma \leq 2$ is a constant which characters the degree of relaxation. The high-temperature slope of dielectric peak was well fitted to Eq. (1), as indicated by the solid line in Fig. 3. The obtained γ value markedly increases from 1.24 for $x=0.01$ to 1.86 for $x=0.10$, which evidently shows the evolution from normal ferroelectric to relaxor. The δ value also considerably increases from 4.7 K for $x=0.01$ to 31.1 K for $x=0.10$, confirming the increased diffuseness of the dielectric peak with increasing substitution level. It is generally believed that the increased diffuseness is ascribed to a random field resulting from the disordered distribution of different ions on B-site, which is commonly

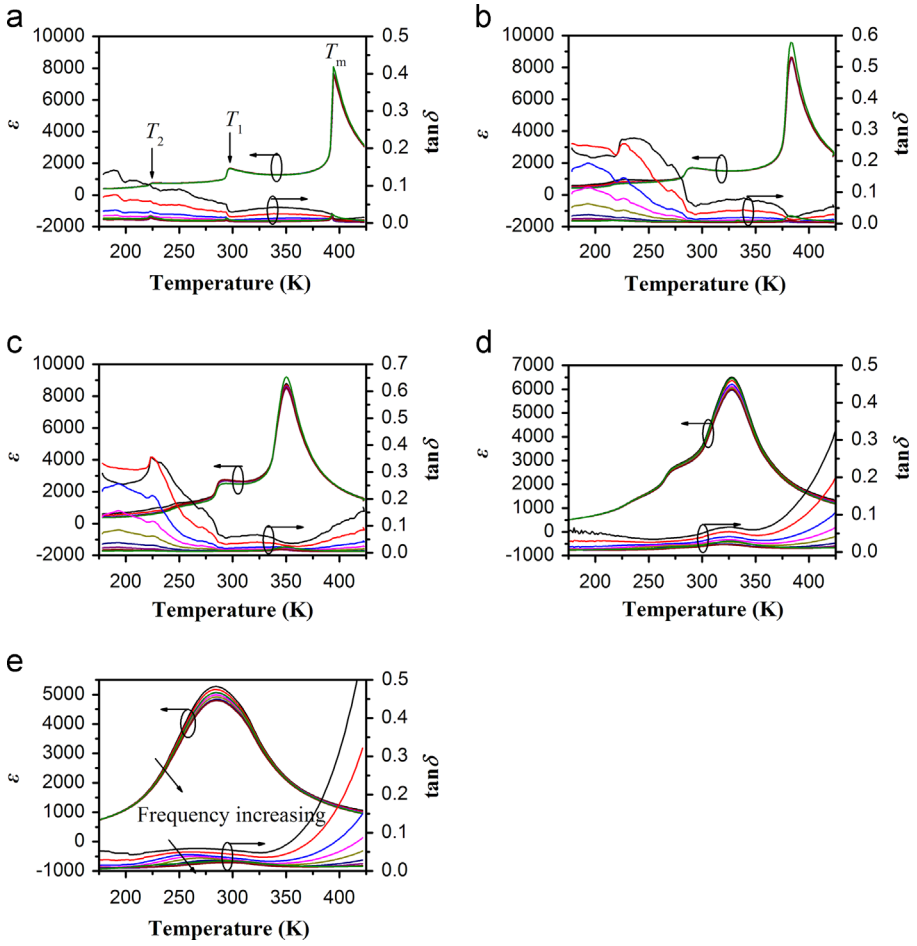

Fig. 2. Temperature dependence of ε and tan δ for the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics: (a) $x=0.01$, (b) $x=0.02$, (c) $x=0.05$, (d) $x=0.07$ and (e) $x=0.10$.

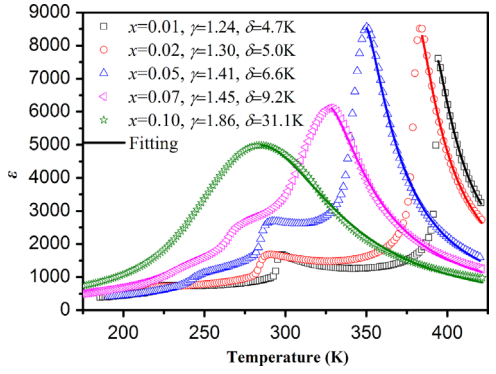

Fig. 3. Temperature dependence of ε for the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics at 10 kHz. The symbols indicate the experimental data and the solid lines represent fitting to the relation (1).

observed in many perovskite solid solutions, such as Ba(Ti, Ce)O_3 [17] and $Pb(Ba_{1/3}Nb_{2/3})O_3$ [19].

Fig. 4a shows the polarization hysteresis loops of all compositions measured at room temperature and a field of 30 kV/cm. Compositional dependence of maximum polarization (P_m), remanent polarization (P_r) and coercive field (E_c) are depicted in the inset of Fig. 4a. The compositions with $x\leq0.02$ exhibit a well-saturated typical ferroelectric behavior. Noticeably, the *P–E* loop of the composition with $x=0.05$ becomes slightly constricted, deformed and different from the typical ferroelectric *P–E* loop, and the observed P_r decreases significantly. The result is evident not a double-loop of antiferroelectric ceramics [20]. Similar results of the deformed *P–E* loops have been reported for $Bi_{0.5}Na_{0.5}TiO_3$-based ceramics in recent researches [21,22]. It is suggested that the anomaly in the *P–E* loop may result from the electro-mechanical interaction between polar and nonpolar regions that coexist in the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics near/above depolarization temperature [21]. A slight increase in the substitution level apparently quickens the transformation from nonpolar to polar state, which is evident from the increase in P_m from 13.3 to 14.0 μC/cm^2 and P_r from 3.1 to 7.6 μC/cm^2, respectively. As the substitution level further increases, the loop starts to tilt.

Unipolar *S–E* curves of all compositions are also measured at room temperature and shown in Fig. 4b. No obvious compositional dependence of hysteresis strain is observed for the samples with low substitution levels ($x\leq0.07$), which reaches ~0.08%. The hysteresis strain is possibly associated with domain switching [23]. Those with high substitution level (x–0.10) have a low hysteresis strain ~0.03%, due to the measuring temperature near to T_m.

Fig. 5 presents compositional dependence of normalized strain d_{33}* ($=S_{max}/E_{max}$) at a field of 30 kV/cm. The corresponding piezoelectric properties d_{33} and k_p are also provided in

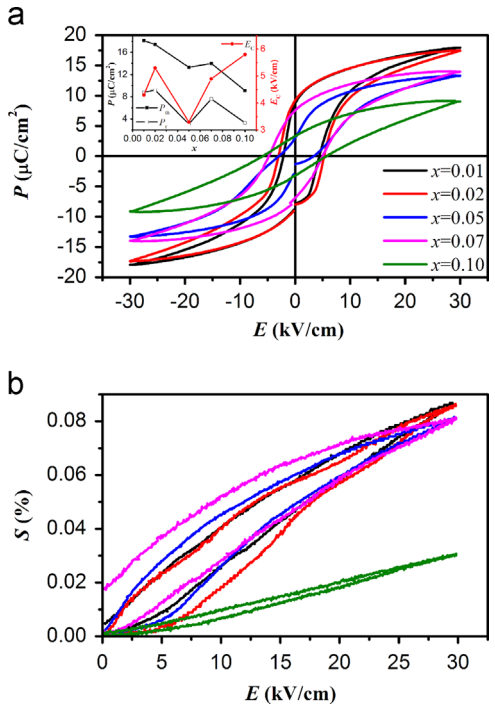

Fig. 4. (a) *P–E* hysteresis loops and (b) *S–E* curves of the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics measured at room temperature and 30 kV/cm. The inset presents P_m, P_r and E_c as a function of *x*.

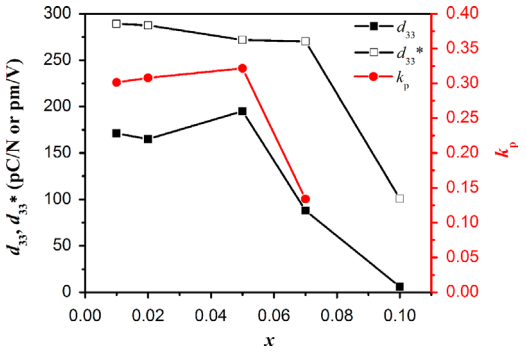

Fig. 5. d_{33}, d_{33}*, and k_p of the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics as a function of *x*.

Fig. 5. Similar to the unipolar strain, d_{33}✻ initially decreases tardily and then decreases markedly with increasing substitution levels. d_{33}✻ is higher than d_{33}, because d_{33}✻ includes the domain contribution due to high applied voltage and low measuring frequency [24]. The highest values of d_{33} and k_p are obtained at $x=0.05$, due to the coexistence of orthorhombic and tetragonal phases. As *x* further increases, d_{33} decreases markedly, whereas d_{33}✻ still keeps at the same level. Similar results have been reported in $(Bi_{1/2}Na_{1/2})TiO_3$–$(Bi_{1/2}A_{1/2})TiO_3$ (A=Li and K) ceramics [25].

Fig. 6 exhibits the *M–H* curve of the ceramics with $x=0.05$ and 0.07 measured at room temperature, after subtracting the background contribution. The linear *M–H* behavior is visible for the ceramics with $x=0.05$, whereas the slim hysteresis loop is observed for those with $x=0.07$ (the inset in Fig. 6), indicating the weak ferromagnetic behavior for those with

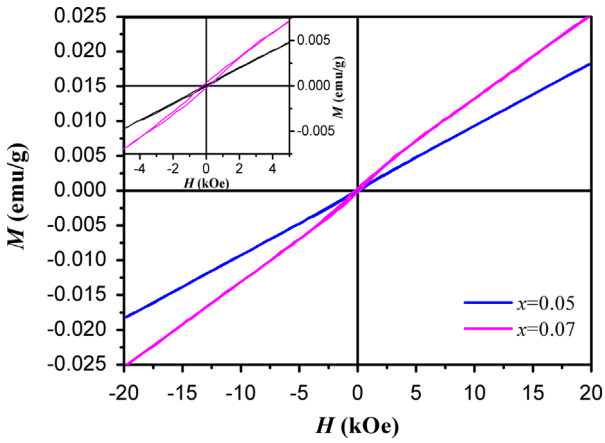

Fig. 6. *M–H* hysteresis loops of the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics with $x=0.05$ and 0.07.

$x=0.07$. This is similar to the observed results in other Co-doped materials, such as Co-doped SnO_2 thin film [26], and Co-doped $BaTiO_3$ thin film [27] and $Ba_{0.4}Sr_{0.6}Ti_{1-y}Co_yO_3$ ceramics [28].

4. Conclusion

The electric properties of single phase $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ($x=0.01$–0.10) ceramics were investigated in detail. $(Co_{1/2}Nb_{1/2})^{4+}$ substitution for Ti^{4+} broadened the phase transition temperature region and increased the diffuseness of cubic–tetragonal phase transition, which resulted in the pinched phase transitions. The deformed *P–E* loop was observed for the ceramics with $x=0.05$, possibly resulting from the electro-mechanical interaction between polar and nonpolar regions that coexisted in the $BaTi_{1-x}(Co_{1/2}Nb_{1/2})_xO_3$ ceramics. XRD analysis indicated that the orthorhombic and tetragonal phases coexisted in the range of $0.02<x<0.07$ at room temperature. Accordingly, the optimum piezoelectric properties of d_{33}*=272 pm/V, $d_{33}=195$, and $k_p=32\%$ were obtained for the ceramics with $x=0.05$. *M–H* curves indicated that the ceramics with $x=0.07$ showed ferromagnetic behavior at room temperature.

Acknowledgments

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