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Short communication

Relaxor and strain behavior in $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics

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Abstract

A new lead-free perovskite system of $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ($x = 0.02$, 0.05, 0.07 and 0.10) has been synthesized by the mixed-oxide route. Temperature and frequency dependences of permittivity show a crossover from ferroelectric to relaxor behavior. For the samples with $x \geq 0.05$, the frequency-dependent T_m satisfying the Vögel–Fulcher formula indicates a relaxor behavior. The increase with orders of magnitude in E_a with respect to x is possibly ascribed to more Ba-vacancies. Remnant polarization and strain decrease with increasing x due to phase transformation from ferroelectric tetragonal to paraelectric pseudocubic at room temperature.

Keywords: Perovskite structure; Phase transition; Relaxor behavior; Strain behavior

1. Introduction

Growing awareness of the hazardous effect of lead on environment and human health initiated intensive research on lead-free piezoceramics [1]. Among several groups of lead-free candidates, barium titanate ($BaTiO_3$) is quite promising due to high strain at high electric field ~1% [2]. Unfortunately, it has large hysteresis, which blocks practical application [2].

The idea of incorporation ions to matrix is generally adopted to modify its properties. Because $BaTiO_3$ is the most easily compatible host compound for different dopants, both heterovalent [3] and isovalent [4] ionic substitution at equivalent sites can lead to remarkable changes in piezoelectric properties. Since the discovery of very high piezoelectric properties in Zr-doped $BaTiO_3$ single crystals [5], isovalent substitutions for Ba or/and Ti, such as $(Ba_{1-x}Ca_x)TiO_3$ [6], $Ba(Zr,Ti)O_3$ [7], $(Ba,Ca)(Zr,Ti)O_3$ [8] and $(Ba_{1-x}Ca_x)(Ti_{0.96}Sn_{0.04})O_3$ [9], have been studied extensively. In fact, though it has been reported that almost hysteresis-free high strain can be realized by isovalent substitutions, it is logical to explore others modifiers for their piezoelectric behavior. Recently, Khemakhem et al. [10] have 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, piezoelectric properties of complex cation $(Li_{2/3}Nb_{2/3})^{4+}$ modified $BaTiO_3$ ceramics have not been reported.

It has been suggested [11] that heterovalent substitutions could induce a relaxor behavior at moderate substitution levels. Therefore, the aim of the present work is to investigate relaxor and strain behavior of complex cation $(Li_{2/3}Nb_{2/3})^{4+}$ modified $BaTiO_3$ ceramics.

2. Experimental procedure

$BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics, where $x = 0.02$, 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%), Li_2CO_3 (98.0%) and Nb_2O_5 (99.5%). Mixtures based on the compositions of $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ($x = 0.02$, 0.05, 0.07 and 0.10) 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 1150 °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.

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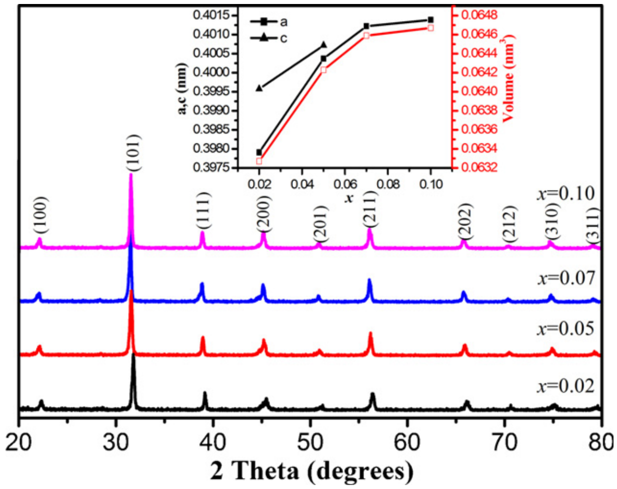


Fig. 1. XRD patterns of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics. The inset presents the variation of the lattice parameters as functions of x.

$BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics were sintered at 1400 °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 and loss tangent as functions of temperature were measured at frequencies from 1 kHz to 1 MHz in temperature range of 125–450 K, using a HP 4284A precision LCR meter (Agilent, Palo Alto, CA). 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.

3. Results and discussion

XRD patterns of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics are shown in Fig. 1. Analysis of the diffraction spectra reveals the tetragonal perovskite structure for the samples with $x \leq 0.05$ and the pseudocubic one for those with $x \geq 0.07$ at room temperature. Lattice parameters calculated from the diffraction spectra fitted by space groups *P4mm* ($x \leq 0.05$) or *Pm3m* ($x \geq 0.07$) are plotted in the inset of Fig. 1. The lattice parameters increase with increasing x. It can be explained that the ionic radius of Li^+ (0.760 Å) and Nb^{5+} (0.640 Å) in 6-fold coordination is larger than that of Ti^{4+} (0.605 Å)[12]. Therefore, ionic radius of complex cation $(Li_{2/3}Nb_{2/3})^{4+}$ is larger than that of Ti^{4+}, which led to lattice expansion.

Temperature dependence of permittivity and loss tangent of all samples measured at different frequencies, varying from 1 kHz to 1 MHz, is displayed in Fig. 2. As x increases, the dielectric anomalous peaks of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics, corresponding to the cubic-tetragonal phase transition (paraelectric–ferroelectric transition), are suppressed and broadened. The obvious reduction in the temperature at permittivity maxima (T_m), as shown in Fig. 2, is attributed to the deterioration of ferroelectric long-range order [13]. It should be noted that the merger of all polymorph transformations occurs at $x = 0.05$, due to pinched phase transition [11].

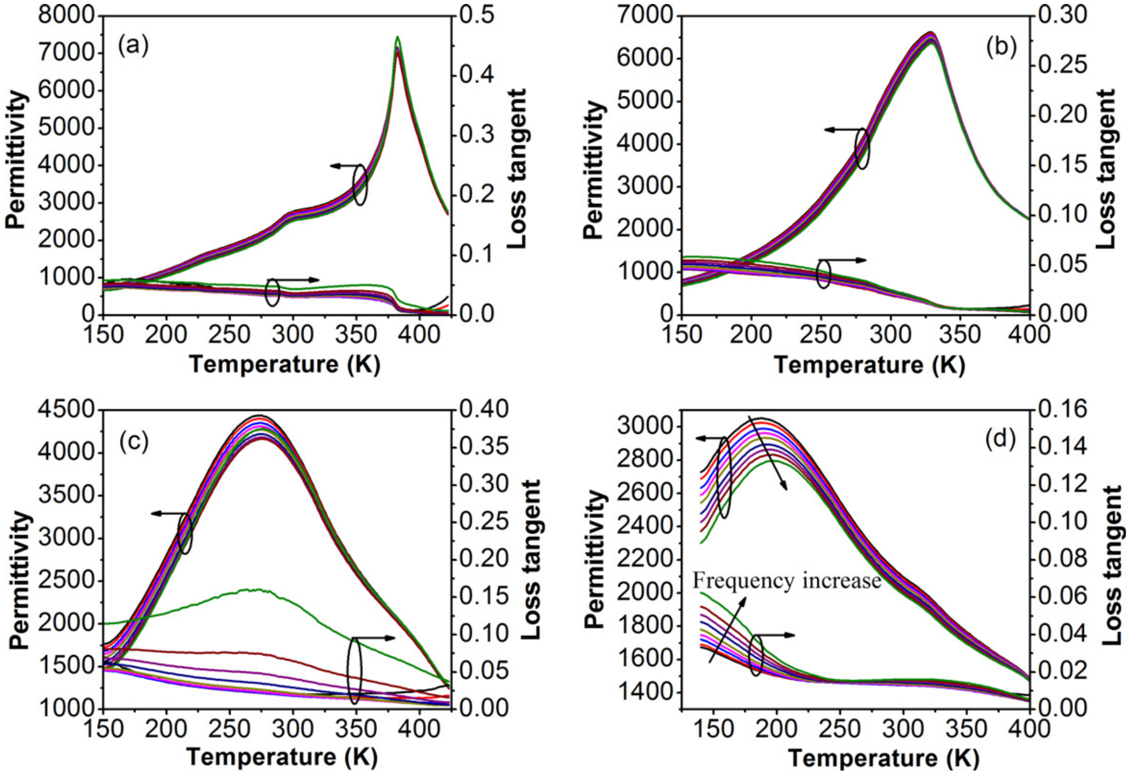


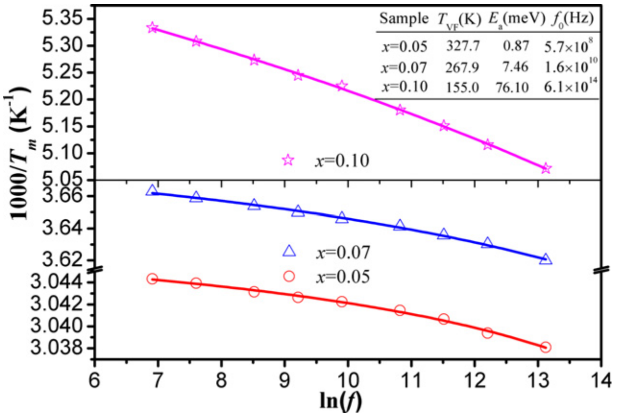
Fig. 2. Temperature dependence of permittivity and loss tangent for the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics: (a) $x = 0.02$, (b) $x = 0.05$, (c) $x = 0.07$ and (d) $x = 0.10$.

An evident dielectric diffuseness represented by extremely high dielectric peak, reflecting a strong frequency dispersion feature, is also shown in Fig. 2. The spectral features are strong dependent on composition. For the sample with $x = 0.02$, there is a strong and sharp dielectric peak at 381 K with no frequency dispersion, similar to that observed in pure $BaTiO_3$. As x increases, the strong and sharp dielectric peak gradually becomes a diffuse peak with frequency dispersion. A small shift in T_m toward high temperature with increasing frequency is observed in the compositions with $x \geq 0.05$, which is typical of the relaxor behavior. The relaxor state can be induced by a relatively low substitution levels, which is similar to others heterovalent substituted $BaTiO_3$, *e.g.* $x = 0.075$ for $Ba_{1-x}Na_x[Ti_{1-x}Nb_x]O_3$ [14], $x = 0.055$ for $Ba_{1-x}La_x[Ti_{1-x}(Mg_{0.5}Ti_{0.5})_x]O_3$ [15] and $x = 0.06$ for $Ba_{1-x/2}\square_{x/2}[Ti_{1-x}Nb_x]O_3$ [16].

In many relaxors, the relationship between the probe frequency f and the temperature T_m can be described by the Vögel–Fulcher (VF) formula [17]:

$$f = f_0 \exp\left[\frac{-E_a}{k_B(T_m - T_{VF})}\right], \tag{1}$$

where f_0 is the Debye frequency, E_a the activation energy, and T_{VF} the freezing temperature of the polarization fluctuation. Frequency dependence of T_m of the compositions with $x \geq 0.05$ well fits to the VF formula (as shown in Fig. 3), whose fitting parameters are presented in the inset of Fig. 3. It is found that T_{VF} together with T_m markedly decrease as x increases, while E_a and f_0 increase with the order of magnitude, which is consistent with the trend observed in $Ba(Zr_yTi_{1-y})O_3$ system [11]. According to Shvartsma and lupascu [11], the relaxor behavior of $BaTiO_3$-based compositions originates from quenched random electric fields and randomly interacting polar nanoregions at temperatures much higher than T_m [18,19]. For $Ba(Zr_yTi_{1-y})O_3$ relaxor, the role of random fields is not obvious. Thus we can conclude that the relaxor behavior of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ system is mainly dominated by randomly interacting polar nanoregions. There is a nominal excess of cations in B-site, therefore A-site vacancies are required and the exact stoichiometry becomes $Ba\square_{x/3}Ti_{1-x}(Li_{2/3}Nb_{2/3})_xO_{3+\delta}$, where $\square$ corresponds to Ba-vacancies. The compositions with high substitution levels have a high E_a, which may be ascribed to more Ba-vacancies. The more Ba-vacancies cause a weak interaction between polar nanoregions [20], which contributes to an additional relaxation process.



Sample	T_{VF}(K)	E_a(meV)	f_0(Hz)
x=0.05	327.7	0.87	5.7×10^8
x=0.07	267.9	7.46	1.6×10^{10}
x=0.10	155.0	76.10	6.1×10^{14}

Fig. 3. Frequency dependent $1/T_m$ of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics. The symbols indicate the experimental data and the solid lines are the fitting curves using VF relation. The inset shows the fitting results according to the VF formula.

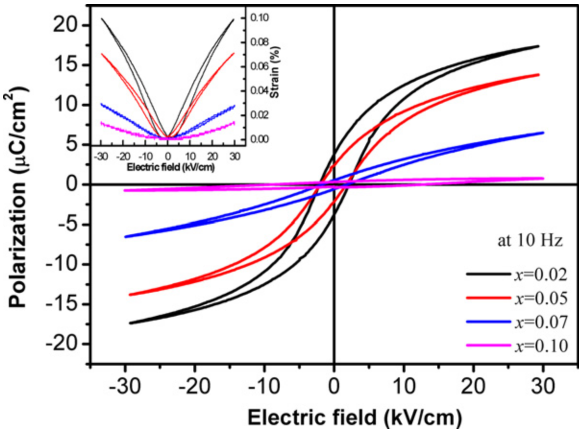


Fig. 4. P–E hysteresis loops of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics measured at room temperature. The inset presents S–E curves of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics.

P–E ferroelectric hysteresis loops of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics measured at room temperature and a field of 30 kV/cm are exhibited in Fig. 4. It is clear that S-shaped loops with high remnant polarization (P_r) are observed for the samples with $x \leq 0.05$. As x increases, the loops start to tilt and become slim. The profiles of P–E curve are closely related to crystalline structure of the samples. The compositions with $x \leq 0.05$ have ferroelectric tetragonal phase at room temperature, as shown in Figs. 1 and 2, thus saturated polarization loops with high P_r are obtained. For those with $x \geq 0.07$, there exists paraelectric pseudocubic phase and T_m is below room temperature. A nonlinear P–E curve implies a ferroelectric relaxor behavior due to the existence of polar nanoregions above T_m [21].

The unipolar strain–electric field (S–E) curves of the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics are shown in the inset of Fig. 4. The unipolar strain level is ~0.10% at 30 kV/cm for the sample with $x = 0.02$. The hysteretic strain is possibly associated with domain switching [22]. As x increases, the strain is decreased, accompanied by decreasing hysteresis. The compositions with high substitution levels ($x \geq 0.07$) do not show any strain–field hysteresis, but exhibit just electrostriction typical for paraelectric state.

4. Conclusions

Only single perovskite structure was observed in the $BaTi_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics with $0.02 \leq x \leq 0.10$, which transformed from tetragonal to pseudocubic structure at room temperature with increasing x. Meanwhile, the $Bai_{1-x}(Li_{2/3}Nb_{2/3})_xO_3$ ceramics experienced a transformation from ferroelectric to paraelectric phase. For the samples with $x \geq 0.05$, the permittivity exhibited relaxor behavior with the frequency dependence of T_m obeying the VF formula. The compositions with high substitution levels had a high E_a, which may be ascribed to more Ba-vacancies. Such high E_a implied a weak interaction between polar nanoregions. Remnant polarization and strain decrease with increasing x due to the change in crystalline structure.

Acknowledgements

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