

Thermal Expansion, Ferroelectric and Magnetic Properties in $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$

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Abstract: A zero thermal expansion and multiferroic compound $0.8\text{PbTiO}_3 - 0.2\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ was developed by a chemical modification route. The structure studies showed that the tetragonality of $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ was gradually weakened to cubic by introducing the dopant $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$, and the thermal expansion coefficient changed from $-8.81 \times 10^{-6}/^\circ\text{C}$ to $8.46 \times 10^{-6}/^\circ\text{C}$ in $0.1 \leq x \leq 0.3$ around a wide temperature range (from RT to about 500°C). Weak ferromagnetic behavior was observed in the solid solutions, and the superexchange interaction was incorporated to explain its nonmonotonous evolution. Meanwhile, the good piezoelectricity and ferroelectricity were well retained. Further investigations demonstrated that the $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ceramics possessed good mechanical properties, such as high density and excellent fracture toughness. The improved behaviors make the $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ promising piezoceramics with high thermal stability and mechanical performance. The present work provides a way to design and explore high-performance multiferroic compounds in the synthesis route.

1. Introduction

Piezoelectric ceramics are indispensable to modern industry. But many usual devices may be subject to mechanical degradation and structural instability under thermal shock. PbTiO_3 (PT) exhibits an abnormal negative thermal expansion (NTE),^{1,2} which could be used to tailor the thermal expansion coefficient (TEC) of the perovskite functional ceramics. Since a very good piezoelectric property was found near the morphotropic phase boundary (MPB) of $\text{PbTiO}_3 - \text{BiScO}_3$, the compounds in the $\text{PbTiO}_3 - \text{BiMeO}_3$ system (Me is cations with an average valence of 3+) had received much attention. Moreover, the Curie temperature (T_c) can be maintained and even increased in many cases such as $\text{Me} = \text{Zn}_{1/2}\text{Ti}_{1/2}$, $\text{Mg}_{1/2}\text{Ti}_{1/2}$, $\text{Zn}_{2/3}\text{Nb}_{1/3}$, Fe, Sc, In, and so on.³⁻⁵ However, desirable TECs of these ceramics are needed so as to enhance their structural thermal stability.

In our previous study, some substitute atoms were introduced into A- and/or B-site of PbTiO_3 to investigate the doping effect on the NTE. Most of the modified solid solutions (such as

$\text{Pb}_{1-x}\text{Sr}_x\text{TiO}_3$, $\text{Pb}_{1-x}\text{La}_x\text{TiO}_3$, $\text{Pb}_{1-x}(\text{La}_{0.5}\text{K}_{0.5})_x\text{TiO}_3$, $\text{Pb}_{1-x}\text{Bi}_x\text{TiO}_3$, and so on) showed a weakened NTE with the exception of $\text{Pb}_{1-x}\text{Cd}_x\text{TiO}_3$ and $\text{PbTiO}_3 - \text{BiFeO}_3$, where NTE was enhanced. The thermal expansion coefficients of the ceramics could be tailored by controlling the dopants content.⁶ A zero thermal expansion (ZTE) with high density and good mechanical performance were discovered in the $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Mg}_{1/2}\text{Ti}_{1/2})\text{O}_3$ piezoceramic.⁷ The effective ion radius (r_{EF}) of Ni^{2+} (0.69 \AA) is close to that of Mg^{2+} (0.72 \AA), and $(1 - x)\text{PbTiO}_3 - x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (PT-BNT) has good piezoelectric property;⁴ therefore, this compound might be another ZTE piezoceramic candidate. Moreover, Ni is a magnetic atom, and this dopant would introduce magnetic behavior into the system, so that the ceramics probably become multiferroic at ambient temperature. Such compounds are very few but have attracted extensive attention in recent years due to their potential application in the construction of devices and also for their fascinating physical properties.⁸⁻¹¹

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In this work, we developed a ZTE piezoceramic $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ with high mechanical performance and multifunctional properties by introducing magnetic Ni atoms into the compound. The intrinsic thermal expansion and the apparent thermal expansion of the ceramics were determined by high-temperature X-ray diffraction (HTXRD) and dilatometry measurements. The ferroelectric and magnetic behaviors were measured by polarization–electric-field (P – E) and magnetization–magnetic-field (M – H) loops, respectively. The good piezoelectric property was well retained in our ceramics. Vickers indentation tests and fracture morphology under scanning electron microscope were used to determine the mechanical performances of the ceramics.

2. Experimental Section

The modified solid-state reaction method was adopted to prepare $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0-0.60$) using analytic reagent grade materials, PbO , Bi_2O_3 , NiO , and TiO_2 (anatase). Stoichiometric starting reagents were ball-milled in ethanol for 24 h. Dried powders were pressed into pellets of 11 mm diameter and 2–3 mm thickness and then calcined at 800 °C for 5 h. Part of the calcined powders were pressed into pellets of the same size and sintered at 1100–1150 °C for 5 h covered with the remaining powders to compensate the evaporation loss of PbO and Bi_2O_3 . After removing the surface layers of the sintered pellets carefully, the pellets were ground into powders and then annealed at 800 °C for 1 h to remove the mechanical strain introduced during the sintering and grinding processes. The chemical analysis and X-ray photoelectron spectroscopic (XPS) analysis on the compounds were carried out to confirm the composition in order to ensure that the properties related to the contents were credible (See results in the Supporting Information).

Phase identification and structural characterization were made by X-ray diffraction (XRD) technique on a 21 kW extra-power powder diffractometer (model M21XVHF22, Mac Science, Yokohama, Japan). For the high-temperature measurements, the scanning speed of the 2θ angle was 5 °C·min⁻¹, and the heating speed was 20 °C·min⁻¹. The lattice parameters were calculated by *PowderX* and *TREOR* software. The macroscopic thermal expansion coefficients of ceramics were determined from dilatometric measurements using a Thermo-mechanical Analyzer (WCP-1) with clubbed samples (diameter 4–6 mm, length 28 mm) at a heating speed of 20 °C·min⁻¹. An advanced analyzer (NETZSCH DIL 402C) was used for accurate dilatometric cycle running measurements with 5 °C·min⁻¹. The ferroelectric loops were measured for specimens with diameters ~10 mm and thicknesses ~0.4 mm by a ferroelectric tester (model aixACCT, TF Analyzer 2000). The ferromagnetic loops were performed using a vibrating sample magnetometer (VSM, HH-15 Instrument Plant of Nanjing University, China), and the M – T curve was measured on a more sensitive instrument (Lake Shore 7410 VSM). Micrographs of the ceramics were obtained with a field-emission scanning electron microscope (FE-SEM, LEO1530). Vickers indentation hardness of the materials was carried on the Digital Microhardness tester (HVS-1000) with different loads and 20 s of dwell time. The piezoelectric property of the poled ceramics with an Ag electrode was measured using a quasi-static d_{33} meter (China Academy of Acoustics, ZJ-3). Poling was performed at 120 °C under a dc field of 7 kV/mm, applied for 5 min.

3. Results and Discussion

From a number of investigations on the PbTiO_3 -based perovskites, we found that the weakened NTE was associated with the reduced tetragonality (c/a) of the compounds.⁶ Figure 1 shows the evolution of the lattice parameters of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0-0.6$) solid solutions as a

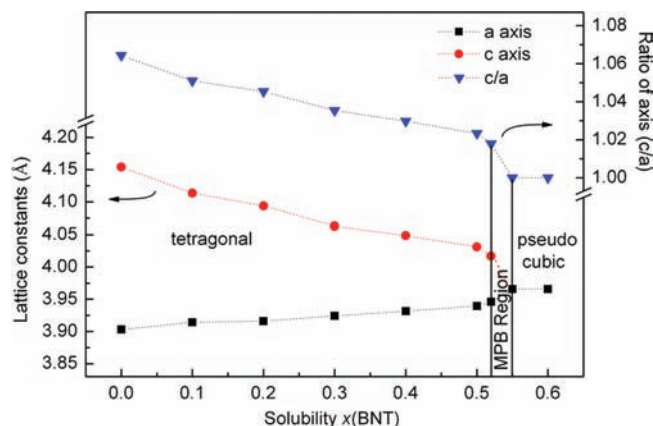


Figure 1. Evolution of the lattice parameters of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0-0.6$) as function of solubility. The increasing a axis and the decreasing c axis corporately make the tetragonality (c/a) to decrease continuously with the solubility of $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$.

function of solubility (see the XRD patterns in Figure S1 in the Supporting Information). The decreased tetragonality is due to the character of the divalent Ni^{2+} , which is d -state partial occupied, and disfavors hybridization.¹² This fact makes it possible to design a ZTE material in the PT-BNT solid solution.

3.1. Thermal Expansion. Figure 2a shows the unit cell volume as a function of temperature of the solid solutions $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0-0.3$), determined by HTXRD. The figure shows that all compounds have a positive thermal expansion with similar variability above the T_c , which was also observed in other PbTiO_3 -based solid solutions (the TEC $\bar{\alpha}_V = 3.6 \times 10^{-5}/^\circ\text{C}$).⁶ Below the T_c , however, the compound 0.9PT–0.1BNT exhibited a very small negative thermal expansion and its T_c (~520 °C) was slightly raised, the unit cell volume of 0.8PT–0.2BNT changed little over the range from room temperature (RT) to its T_c (~500 °C), while 0.7PT–0.3BNT showed an obvious positive thermal expansion below its T_c (~450 °C). The average TECs of the solid solutions were calculated and are listed in Table 1. The magnitude of 0.8PT–0.2BNT compound ($\bar{\alpha}_V = 1.21 \times 10^{-6}/^\circ\text{C}$) was very small, which could be regarded as a ZTE ceramic. Moreover, a linear correlation between the volumetric TEC and the solubility was derived (the inset of Figure 2a), which could probably predict the TEC of other compounds.

Dilatometric measurements on clubbed PT-BNT ceramics were taken to characterize the materials' apparent thermal expansion (see Figure 2b). The linear expansion of the ceramics changed from contraction to expansion in the range from RT to T_c with increasing dopant concentration. Dilatometric heating and cooling cycles for the compound ($x = 0.2$) (see the inset of Figure 2b) demonstrate the reproducibility of its thermal expansion behavior, which reveals the ceramics perform good thermal stability. The intrinsic and the apparent thermal expansion data (Table 1) were in good agreement according to the relationship: $\alpha_V \approx 3\alpha_l$ (see the derivation in the Supporting Information). Although derived by different methods, both sets of TECs ($\bar{\alpha}_V = 1.21 \times 10^{-6}/^\circ\text{C}$ and $\bar{\alpha}_l = 0.38 \times 10^{-6}/^\circ\text{C}$) revealed the nature of a zero thermal expansion in the ceramic at $x = 0.2$.

3.2. Ferroelectrics and Ferromagnetics. Figure 3 compares the ferroelectric P – E loops as function of solubility ($x = 0.1, 0.2, 0.3$) in $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$. The residual

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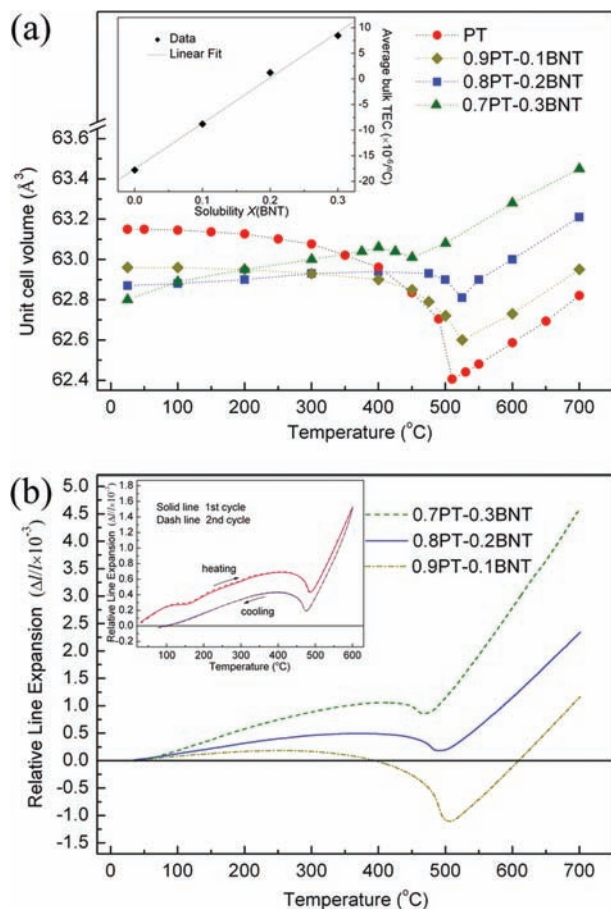


Figure 2. (a) Unit cell volumes of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3$) as function of temperature in the range of 25–700 °C. The inset shows the linear correlation between the TECs and solubility x . (b) Dilatometric curves of ceramic bars of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ for $x = 0.1, 0.2, 0.3$. The inset shows two heating and cooling cycles of the 0.8PbTiO₃–0.2 Bi(Ni, Ti)_{1/2}O₃ ceramic bar.

Table 1. Average TECs of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$

x	TEC ^a ($\times 10^{-6}/^\circ\text{C}$)			temperature range (°C)
	$\bar{\alpha}_v$	$\bar{\alpha}_l$	$3\bar{\alpha}_l$	
0.1	−8.81	−2.30	−6.90	25–525
0.2	1.21	0.38	1.14	25–525
0.3	8.46	2.31	6.93	25–450

^a $\bar{\alpha}_v$, average bulk TEC, measured by HTXRD; $\bar{\alpha}_l$, average linear TEC, measured using a dilatometer.

polarization P_r was increased with solubility for the tetragonality (c/a) of the compounds descended to facilitate the domain switching. The point of intersection between the curve and the horizontal axis electric field E_i of $x = 0.3$ compound reached up to ~ 70 kV/cm, proved that the P – E loop was inclined to saturation with the composition approaching the MPB of the compound. Compared to the electric hysteresis loop of the ceramic in ref 4, our compounds exhibited less leakage current and higher ferroelectric stability. In our investigations the d_{33} of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0.1, 0.2, 0.3$) were 32, 62, 89 pC/N, respectively, and the highest d_{33} (~ 250 pC/N) composition was near the MPB ($x = 0.52$, Figure 1 and Figure S1 of Supporting Information), in agreement with the literature.⁴ Dopant BNT improved the ferroelectric and piezoelectric properties in PbTiO₃ by stabilizing the ceramic structure and reducing the internal stress.

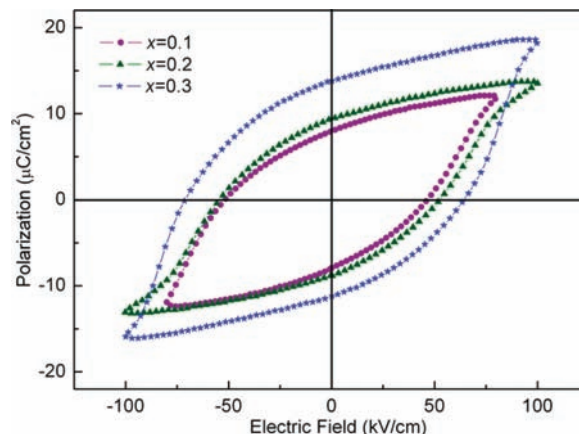


Figure 3. Electrical hysteresis loops of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0.1, 0.2, 0.3$) measured at room temperature and 10 Hz.

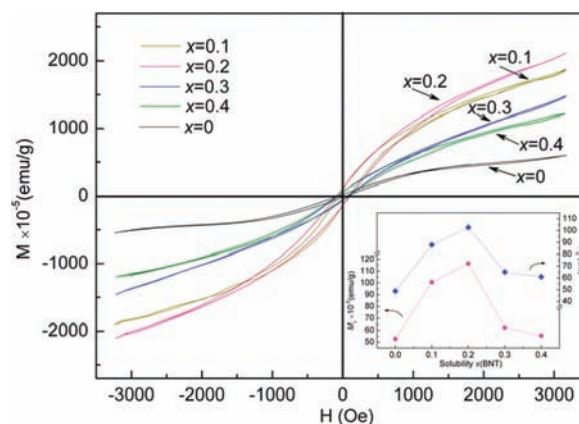


Figure 4. Magnetic hysteresis loops of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($x = 0, 0.1, 0.2, 0.3, 0.4$) at room temperature, with inset the evolutions of M_r and H_c with the solubility.

Generally, ferromagnetic behavior is present in materials containing free atoms and ions of the first transition series which have incomplete d shells to provide net magnetic moment.¹³ PbTiO₃ has a weak ferromagnet due to states hybridizations (see detailed explanation in the Supporting Information). The Ni²⁺ ion has two unpaired electrons in the $3d$ shell, is introduced into PbTiO₃, and probably increases the compound's ferromagnetic behavior. The M – H loops of PT–BNT with different compositions at room temperature are shown in Figure 4. The ferromagnetic behavior of the compounds were obviously increased, compared to that of pure PbTiO₃, but were not monotonously raised with the Ni solubility (see the inset of Figure 4). Both the residual magnetization M_r and the coercive field H_c reached maximum values ($M_r = 116.46 \times 10^{-5}$ emu/g, $H_c = 102.61$ Oe) in the $x = 0.2$ compound and then decreased with increasing dopant concentration. The ferromagnetic mechanism in PT–BNT could be explained by the Dzyaloshinskii–Moriya superexchange interaction.^{14–16} A Ni atom interacts indirectly with its neighboring Ni atoms through electron state overlapping with the mediation of O atoms, then producing ferromagnetic properties. Figure 5a is a schematic diagram to interpret the superexchange interaction in the structure. In this

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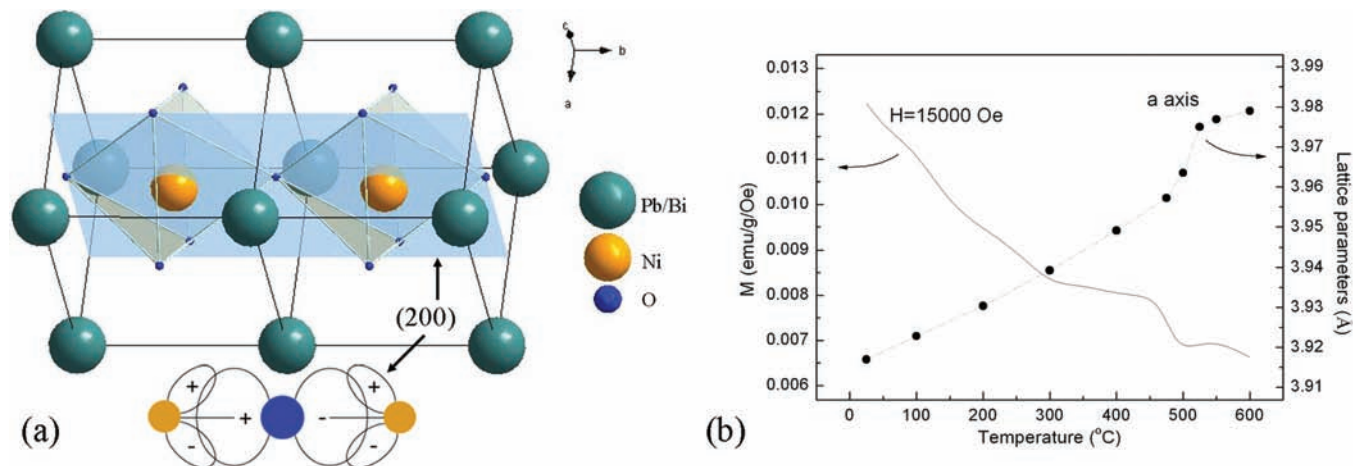


Figure 5. (a) Schematic diagrams of lattice and electronic shell structure of ions in PT-BNT to reveal the mechanism of ferromagnetics. The bottom graph is the sectional drawing along [100] orientation. (b) The comparison of the temperature dependence of the magnetic moment and the evolution of the *a* axis of $0.8\text{PbTiO}_3-0.2\text{Bi}(\text{Ni},\text{Ti})_{1/2}\text{O}_3$.

Table 2. Mechanical Performances of $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$

<i>x</i>	sintering temperature (°C)	theoretical density ($\text{g}\cdot\text{cm}^{-3}$)	relative density (%)	hardness H_v (GPa)	fracture toughness K_{IC} ($\text{MPa}\cdot\text{m}^{1/2}$)
0.1	1150	8.02	94.9	2.57	9.44
0.2	1130	8.09	96.8	2.74	11.45
0.3	1120	8.15	97.4	2.88	12.22

model, two factors determine the magnitude of ferromagnetism, the content of the Ni atoms, and the distance between them. From $x = 0-0.2$, the effect of increasing Ni content was dominant, and the introduction of more magnetic atoms enhanced the total ferromagnetic behavior. With solubility increasing, meanwhile, the $a (= b)$ axis of the lattice as well as the distance between the Ni atoms was increasing (see Figures 1 and 5), and then gradually weakened the overlapping state (see more details in the Supporting Information). When $x \geq 0.3$, the latter effect played a dominant contribution, leading to the reduction of the total magnetic moment of the solid solution (see the inset of Figure 4). In Figure 5b, the temperature dependence of the magnetic moment curve ($M-T$) proves that the mechanism of the atoms distance determined the evolution of magnetism in the compound. With the temperature rising, the growth of the a axis results in the distance of magnetic Ni atoms increasing, which weakens the superexchange interaction and reduces the apparent magnetic moment of the compound.

3.3. Mechanical Properties. The mechanical properties of this type of compound are very important to practical applications, because they are often fragile and brittle. The density and the mechanical performances of the ceramics PT-BNT were measured and are listed in Table 2. The actual measured density was close to the theoretical density of the solid solutions, revealing that the ceramics were well sintered and much compact (Figure S5 in Supporting Information). Both the hardness and the fracture toughness (K_{IC}) of the PT-BNT ceramics were raised with the end member of $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ (see Table 2 and Supporting Information, Figure S6), for $0.7\text{PT}-0.3\text{BNT}$ the K_{IC} was up to more than $12\text{MPa}\cdot\text{m}^{1/2}$. It is found that the fracture toughness of PT-BNT ceramics are better than many of the other PbTiO_3 -based solid solutions¹⁷⁻¹⁹ and even better than that of $\text{PbTiO}_3-\text{Bi}(\text{Mg},\text{Ti})\text{O}_3$,⁷ which also had excellent mechanical

properties. This enhancement was attributed to the BNT dopants, because they reduced the lattice distortion in PbTiO_3 and decreased the defects inside the ceramic by weakening the thermal expansion or contraction during sintering.

4. Conclusions

We prepared a zero thermal expansion material in the $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ($\bar{\alpha}_l = 0.38 \times 10^{-7}/^\circ\text{C}$ for $x = 0.2$), and realized the multifunctionalization in the compounds by introducing magnetic Ni into the solid solution. The ferroelectric and piezoelectric properties of PT-BNT ceramic were improved, for the P_r was increased with dopant $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ and the maximum d_{33} was up to 250pC/N at $x = 0.52$. The ferromagnetic behavior changed nonmonotonously with dopant $\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$. This abnormal behavior was attributed to the superexchange interaction among the doping Ni atoms. The $(1-x)\text{PbTiO}_3-x\text{Bi}(\text{Ni}_{1/2}\text{Ti}_{1/2})\text{O}_3$ ceramics were dense and their fracture toughness were excellent, for $x = 0.3$ the K_{IC} was up to more than $12\text{MPa}\cdot\text{m}^{1/2}$. The present material is promising due to its better thermal stability, improved piezoelectricity, higher mechanical performances, and multiferroic properties.

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Supporting Information Available: XRD patterns, chemical analysis, and XPS analysis of the compounds; explanation for the mechanism of ferromagnetics in PT-BNT; and detailed calculation of the toughness. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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