

# High performance Aurivillius type $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$ piezoelectric ceramics with neodymium and cerium modification

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**Abstract:** Bismuth layer-structured ferroelectric ceramics of  $\text{Na}_{0.5}\text{Bi}_{4.5-x}(\text{Nd}_{0.5}\text{Ce}_{0.5})_x\text{Ti}_4\text{O}_{15}$  (NBT- $x$ ,  $0.0 \leq x \leq 0.4$ ) were synthesized by a traditional solid-state reaction. The effect of (Nd,Ce) substitution for A-site on the microstructure and electrical properties of  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT)-based piezoelectric ceramics was investigated. X-ray diffraction (XRD) analysis revealed that the (Nd,Ce)-modified NBT ceramics have a pure four-layer Aurivillius type structure. The piezoelectric properties of NBT ceramics were significantly improved by the modification of neodymium and cerium. The Curie temperature  $T_C$  gradually decreased from 638 °C to 618 °C with increasing the (Nd,Ce) modification. The piezoelectric constant  $d_{33}$ , mechanical quality factor  $Q_m$ , dielectric loss  $\tan\delta$  and Curie temperature  $T_C$  of the  $\text{Na}_{0.5}\text{Bi}_{4.3}(\text{Nd}_{0.5}\text{Ce}_{0.5})_{0.2}\text{Ti}_4\text{O}_{15}$  ceramic were found to be 28 pC/N, 3239, 0.0032 and 630 °C, respectively. Thermal annealing studies indicated that the (Nd,Ce)-modified NBT ceramics possess stable piezoelectric properties, demonstrating that the  $\text{Na}_{0.5}\text{Bi}_{4.3}(\text{Nd}_{0.5}\text{Ce}_{0.5})_{0.2}\text{Ti}_4\text{O}_{15}$  ceramic is a promising candidate for high temperature applications.

**Keywords:** lead-free;  $\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT) ceramics; piezoelectric properties

## 1 Introduction

Aurivillius first reported that the family of bismuth layer-structured ferroelectrics (BLSFs) shows interesting physical properties [1–3]. The BLSFs have a structure expressed by the general formula of  $(\text{Bi}_2\text{O}_2)^{2+}(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$ , which consists of pseudo-perovskite  $(\text{A}_{m-1}\text{B}_m\text{O}_{3m+1})^{2-}$  layers interleaved with bismuth oxide  $(\text{Bi}_2\text{O}_2)^{2+}$  layers along the  $c$ -axis. In the general formula of Aurivillius family, A is a mono-, di- or trivalent ion (or their combination) such as  $\text{Na}^+$ ,  $\text{Ba}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$  or  $\text{Bi}^{3+}$ , B is a transition element suited to octahedral coordination such as  $\text{Ti}^{4+}$ ,

$\text{Ta}^{5+}$ ,  $\text{Nb}^{5+}$  or  $\text{W}^{6+}$ , and  $m$  is the number of  $\text{BO}_6$  octahedral ( $m=1-5$ ) [4–6]. Compounds of this group such as  $\text{Bi}_2\text{WO}_6$  ( $m=1$ ),  $\text{Na}_{0.5}\text{Bi}_{2.5}\text{Nb}_2\text{O}_9$  ( $m=2$ ),  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ( $m=3$ ) and  $\text{SrBi}_4\text{Ti}_4\text{O}_{15}$  ( $m=4$ ) have attracted much attention due to their applications in non-volatile ferroelectric random access memory (NvFRAM).

$\text{Na}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  (NBT) belongs to the Aurivillius family of BLSFs with  $m=4$ , and most part of these solid solutions are oxide ion conductors [1–4,7]. NBT piezoelectric ceramic system chosen herein is due to its high Curie temperature and outstanding piezoelectric and electromechanical properties [8]. At room temperature NBT is orthorhombic with  $a=5.427 \text{ \AA}$ ,  $b/a=1.006$  and  $c=40.650 \text{ \AA}$ , and undergoes a ferro- to para-electric (orthorhombic  $A2_1am$  to tetragonal

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$I4/mmm$ ) phase transition at  $T_C=655\text{ }^\circ\text{C}$  [1–3,7]. In addition, NBT is a classical ferroelectric with a sharp maximum of the dielectric permittivity close to  $T_C$ . However, the conductivity in the plane of maximum piezoelectric activity is higher than that in the perpendicular axis, the high coercive fields and the two-dimensional orientation restriction of rotation of the spontaneous polarization, which makes the poling require relatively high electric field and limits the integration in devices at high temperature as the increasing conductivity [9]. In recent years, chemical modifications are intensively investigated to improve the piezoelectric activity in NBT ceramics, and some relatively high piezoelectric properties have been achieved via introducing  $\text{MnCO}_3$ ,  $\text{Ba}^{2+}$  or  $\text{Ca}^{2+}$  modification [4,10,11]. Neodymium (Nd) and cerium (Ce) are the common and widely used additives for perovskite-type  $\text{ABO}_3$  ferroelectric materials or BLSF materials to improve the piezoelectric and ferroelectric properties [12–16]. For example, the density, electrical resistance and piezoelectric coefficient  $d_{33}$  of the intergrowth BLSF compounds  $\text{Bi}_7\text{Ti}_4\text{NbO}_{21}$  ceramics were improved by Nd addition [17]. Wang *et al.* [12] reported that the piezoelectric activities and dielectric properties of  $\text{K}_{0.5}\text{La}_{0.5}\text{Bi}_4\text{Ti}_4\text{O}_{15}$  (KLBT) ceramics are significantly improved by the cerium modification and the piezoelectric coefficient  $d_{33}$  for the 0.50 wt%  $\text{CeO}_2$ -modified KLBT is 28 pC/N. It was reported that the addition of an appropriate amount of (Li,Ce) can also enhance the piezoelectric properties of  $\text{M}_{0.5}\text{Bi}_{4.5}\text{Ti}_4\text{O}_{15}$  ( $\text{M}=\text{Li}, \text{Na}, \text{K}$ ) ceramics [6,18,19]. Some researchers found that (Me,Ce) ( $\text{Me}=\text{Na}, \text{K}$ ) dopants can enhance the piezoelectric activities for even-layer-structured Aurivillius type compounds compared to the pure composition [13,20]. Therefore, we believe that the piezoelectric properties could be improved by (Nd,Ce) co-substitution for the A-site Bi ion of NBT ceramics.

In this work, we aimed to investigate the structure and electrical properties of (Nd,Ce) co-modified NBT ceramics. The (Nd,Ce) co-modified NBT BLSFs were fabricated by a traditional solid-state reaction, and their phase, microstructure and electrical properties were investigated in details.

## 2 Experimental procedure

$\text{Na}_{0.5}\text{Bi}_{4.5-x}(\text{Nd}_{0.5}\text{Ce}_{0.5})_x\text{Ti}_4\text{O}_{15}$  (NBT- $x$ ) ceramics, with  $x=0.0, 0.1, 0.2, 0.3$  and  $0.4$  mol were prepared using a

traditional solid-state reaction. The starting raw materials were high purity oxides and carbonates,  $\text{Na}_2\text{CO}_3$  (99.8%),  $\text{Bi}_2\text{O}_3$  (99%),  $\text{TiO}_2$  (99%),  $\text{Nd}_2\text{O}_3$  (99%) and  $\text{CeO}_2$  (99.95%), which had been treated carefully by a drying process, particularly for  $\text{Na}_2\text{CO}_3$ . The materials were weighed according to the composition, and then wet milled in polyethylene bottles with  $\text{ZrO}_2$  balls for 24 h in alcohol. The milled powders were dried and calcined at  $800\text{ }^\circ\text{C}$  for 2 h. After calcinations, the ball-milled ground powders were pressed into disks under a uniaxial pressure of 16 MPa. Finally, the samples were sintered at  $1060\text{ }^\circ\text{C}$  for 3 h.

The crystalline structure of the crushed samples was analyzed by X-ray diffraction (XRD) methods (D8 Advanced, Bruker AXS GMBH, Karlsruhe, Germany). The microstructure evolution was observed using a scanning electron microscope (SEM, Model JSM-6700F, JEOL, Nippon Tekno Co. Ltd., Akishima, Tokyo, Japan). The temperature dependence of the dielectric constant was performed by an LCR meter in a temperature range from room temperature to  $700\text{ }^\circ\text{C}$  (at 100 Hz–1 MHz). To measure the electrical properties, silver paste was painted on both sides of the samples to form electrodes, subsequently fired at  $830\text{ }^\circ\text{C}$  for 10 min. After this, samples were poled in silicone oil at about  $140\text{--}180\text{ }^\circ\text{C}$  for 20 min under a DC electric field of 8–10 kV/mm.  $d_{33}$  was conducted using a piezo- $d_{33}$  meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, Beijing, China). The mechanical quality factor  $Q_m$  and the planar electromechanical coupling coefficient  $k_p$  of the samples were determined by means of resonant ( $f_r$ ) and anti-resonant ( $f_a$ ) frequencies using an impedance analyzer (Agilent 4294A, Agilent Technology Inc., Santa Clara, CA, USA).

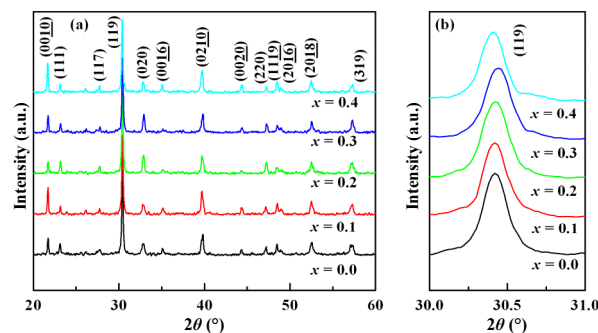
## 3 Results and discussion

Figure 1(a) presents the XRD patterns of the pure and (Nd,Ce)-modified NBT piezoelectric ceramic powders. According to the XRD analysis, the values of  $2\theta$  and relative intensities of the peaks in XRD patterns are all essentially consistent with those given in Joint Committee on Powder Diffraction Standards Data Card for the BLSF compounds with  $m=4$  [10,12,21,22]. It can be seen that all the ceramics are only a bismuth oxide layer-type structure with  $m=4$ , and no secondary

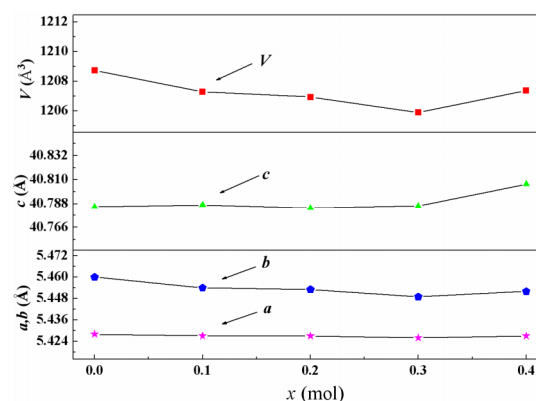
phases are observed in the range detected [10,12]. The strongest diffraction peak for the pure and (Nd,Ce)-modified NBT piezoelectric ceramics is (119), which is consistent with the fact that the highest diffraction peak of BLSFs is  $(112m+1)$  [10,12,14], indicating that neodymium and cerium ions have diffused into crystal lattice of the NBT ceramics and formed a solid solution. Compared with the pure NBT ceramics, the intensities and peak positions of these (Nd,Ce)-modified NBT in XRD patterns shift slightly, as shown in Figs. 1(a) and 1(b). This can be attributed to the variations in lattice distortions of the samples by the co-introduction of  $\text{Nd}^{3+}$  and  $\text{Ce}^{3+}$  into A-site  $\text{Bi}^{3+}$  of NBT ceramics. The theoretical density of (Nd,Ce)-modified NBT ceramics does not change significantly as the peak positions shift slightly [12]. The lattice parameters ( $a$ ,  $b$  and  $c$ ), including unit cell volume ( $V$ ), were calculated from the obtained XRD data by using the MAUD program for the pure and (Nd,Ce)-modified NBT ceramics, as shown in Fig. 2 and Table 1. As the content of (Nd,Ce) modification increases, the cell volume ( $V$ ) firstly decreases but then increases ( $x > 0.3$ ). This change corresponds to the peak positions shifting slightly as shown in Fig. 1(b) [12]. Compared with the pure NBT ceramic sample, the value of the lattice constant  $a$  almost retains the same, but  $b$  decreases with the (Nd,Ce) modification. The value of  $c$  has no significant change when  $x \leq 0.3$ , but increases with the (Nd,Ce) content further increasing. Such a lattice distortion can be attributed to the replacement of the A-site  $\text{Bi}^{3+}$  by  $\text{Nd}^{3+}$  and  $\text{Ce}^{3+}$ . Table 1 also shows that the value of the orthorhombic distortion ( $b/a$ ) decreases, but the tetragonal strain ( $c/a$ ) increases because of the neodymium and cerium introduced. But the data of the crystal lattice  $b/a$  and  $c/a$  indicate that the NBT system retains the orthorhombic symmetry [21]. Moreover, the (Nd,Ce) modification induces the lattice distortion, the complex structure, which is supposed to lead to the enhanced polarizability [12,19,23]. It is anticipated to be beneficial to the piezoelectric properties of the ceramics [12,23].

**Table 1** Lattice parameters of NBT- $x$  ceramics

$x$	$a$ (Å)	$b$ (Å)	$c$ (Å)	$V$ (Å <sup>3</sup> )	$b/a$	$c/a$
0.0	5.428±0.0007	5.460±0.0007	40.785±0.0059	1208.725	1.006	7.514
0.1	5.427±0.0010	5.454±0.0007	40.787±0.0053	1207.249	1.005	7.516
0.2	5.427±0.0007	5.453±0.0008	40.784±0.0051	1206.938	1.005	7.515
0.3	5.426±0.0007	5.449±0.0010	40.786±0.0057	1205.890	1.004	7.517
0.4	5.427±0.0008	5.452±0.0008	40.806±0.0052	1207.368	1.005	7.519

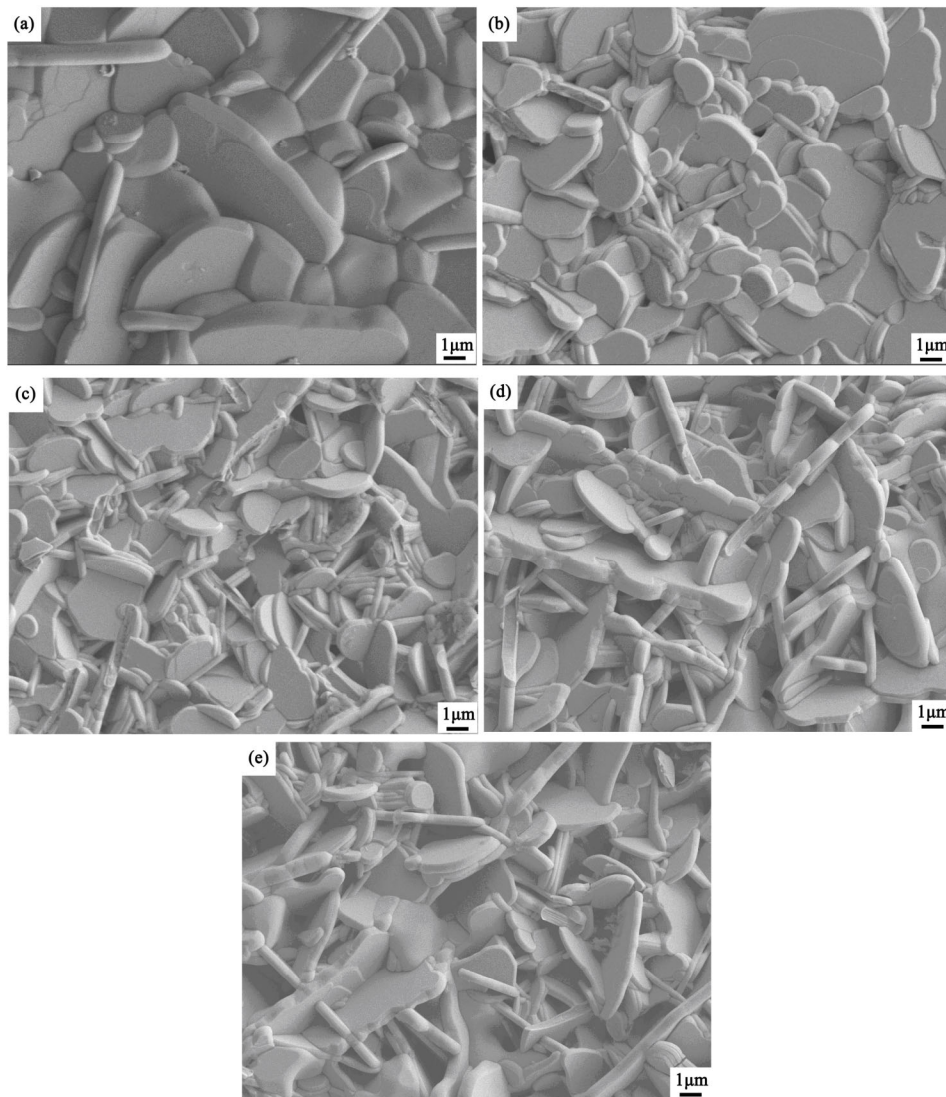


**Fig. 1** (a) XRD patterns of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics; (b) enlarged XRD patterns of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics in the range of  $2\theta$  from  $30^\circ$  to  $31^\circ$ .



**Fig. 2** Lattice parameters as a function of  $x$ .

The SEM images of surface for the pure and (Nd,Ce)-modified NBT piezoelectric ceramics are shown in Fig. 3. As shown, the grain growth is structurally highly anisotropic. It is also found that all the ceramics have the plate-like morphology. This plate-like morphology of the grain is a characteristic feature of bismuth layer compounds. Due to the high grain growth rate in the direction perpendicular to the  $c$ -axis of the BLSFs crystal, the length  $l$  of the plate-like grain is much bigger than the thickness  $t$  [6,24]. Moreover, with the increasing (Nd,Ce) content, the (Nd,Ce)-modified NBT ceramics display a smaller grain size compared with that of the pure NBT ceramics, indicating that the (Nd,Ce) modification can inhibit the grain growth of the ceramics. According to the reports, both sintering and grain growth are closely associated with ion migration as observed in (Nb,Ta), Nd or La-modified  $\text{Bi}_4\text{Ti}_3\text{O}_{12}$  ceramics [25–27]. Thus if the incorporation of  $\text{Nd}^{3+}$  and  $\text{Ce}^{3+}$  into NBT leads to an increase in the activating energy for ion migration and a reduction in the surface or grain boundary energy, a reduction in the grain growth speed would be expected with increase of (Nd,Ce) content.

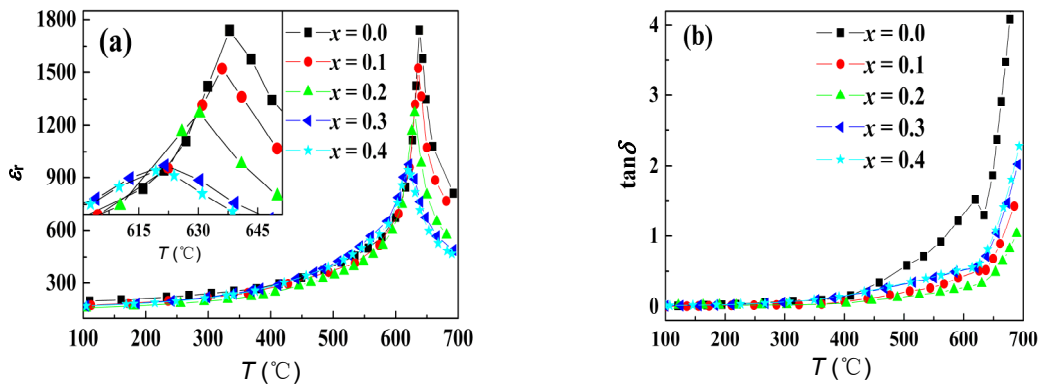


**Fig. 3** SEM images for polished and thermally etched surfaces of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics: (a)  $x=0.0$ , (b)  $x=0.1$ , (c)  $x=0.2$ , (d)  $x=0.3$  and (e)  $x=0.4$ .

Figure 4 shows the temperature dependence of the dielectric constant  $\epsilon_r$  and dielectric loss  $\tan\delta$  for the (Nd,Ce)-modified NBT piezoelectric ceramics at 100 kHz. The inset of Fig. 4 and Table 2 clearly show that the Curie temperatures  $T_C$  of the ceramics in this work gradually decreases from 638 °C to 618 °C with the increasing (Nd,Ce) modification. Shimakawa *et al.* [28,29] suggested that  $T_C$  of the Aurivillius phase materials depends strongly on the crystal structure distortion. The decrease of  $T_C$  is due to the lattice distortion [1–3,28,29], the electronic configuration [30], the decrease of electronegativity [31] (Nd 1.14, Ce 1.12, Bi 2.02) and the Bi amounts [1–3,31] in NBT piezoelectric ceramics by the A-site  $\text{Nd}^{3+}$  and  $\text{Ce}^{3+}$  co-substitution for  $\text{Bi}^{3+}$ . With the increasing of (Nd,Ce)

content, the dielectric peak values decrease and the dielectric maximal peak becomes broad, as shown in Fig. 4(a). The broadened peak can be attributed to the compositional fluctuation and/or substitution disordering in the arrangement of cations at one or more crystallographic sites in the lattice structure [32]. The dielectric loss  $\tan\delta$  is also presented in Fig. 4(b). As shown, the dielectric loss slightly increases, and the values of  $\tan\delta$  in the (Nd,Ce)-modified NBT piezoelectric ceramics are very low, only about 15% of the pure NBT ceramic at 500 °C, which suggests that the (Nd,Ce)-modified NBT ceramics may be an appropriate candidate for high temperature applications.





**Fig. 4** Temperature dependence of (a) dielectric constant  $\epsilon_r$  and (b) dielectric loss  $\tan\delta$  for the (Nd,Ce)-modified NBT piezoelectric ceramics at 100 kHz.

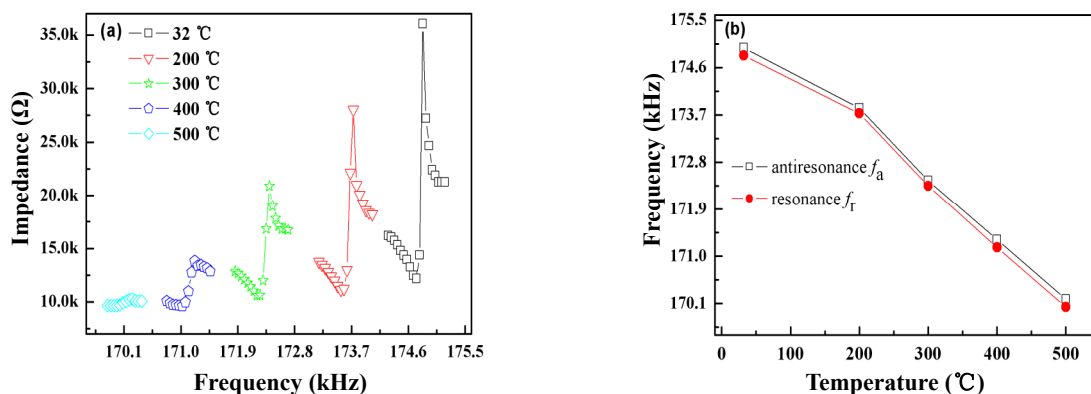
**Table 2** Room temperature electrical properties of (Nd,Ce)-modified NBT piezoelectric ceramics

$x$	$T_C$ (°C)	$\rho$ (%)	$\epsilon_r$	$\tan\delta$	$d_{33}$ (pC/N)	$Q_m$	$k_p$ (%)	$k_t$ (%)
0.0	638	96.6	178	0.0043	16	1090	3.9	10.6
0.1	636	97.5	157	0.0036	20	1966	5.2	12.4
0.2	630	98.2	147	0.0032	28	3239	6.6	14.8
0.3	621	96.3	139	0.0057	19	1792	5.5	9.1
0.4	618	94.9	133	0.0069	17	1256	4.7	8.3

The detailed electrical properties of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics are characterized at room temperature and listed in Table 2. It can be seen that  $T_C$  is found to be 636 °C for NBT-0.1 ceramic and gradually decreases with (Nd,Ce) modification. The dielectric loss  $\tan\delta$  of NBT-based ceramics reduces with the moderate amount of (Nd,Ce) modification, where  $\tan\delta$  of NBT-0.2 is found to be only 0.32%. This may be attributed to the reduction of bismuth and oxygen vacancies formed by the volatilization of bismuth when the moderate amount of (Nd,Ce) co-substituted A-site  $\text{Bi}^{3+}$  of the NBT piezoelectric ceramics [26]. But  $\tan\delta$  increases with the further increasing amount of (Nd,Ce) modification due to the enlarged lattice distortion and the increased oxygen vacancies in the perovskite layer. The piezoelectric coefficient  $d_{33}$  of NBT-0.2 is found to be 28 pC/N, the highest value among the NBT-based ceramics, which is also higher than those of other reported BLSF systems [1–3,13,24]. The enhancement of the piezoelectric activities can be attributed to induced lattice distortion, increased density and decreased dielectric loss  $\tan\delta$ . Neodymium and cerium probably play the variant roles in the NBT-0.2 ceramic [33,34]. One is that a reduction in the volatilization of bismuth, densifying the NBT ceramics for Nd–O and Ce–O bonds are much stronger than Bi–O bond, thus the higher electric field can be conducive to make

poling more sufficient. Another role is the cerium donor, which is suggested being the contributed substitution based on the fact that the value of  $d_{33}$  can be significantly enhanced [33]. The contributed substitution leads to the constraint of maintaining the overall charge neutrality of the structure, and cations' vacancies are formed possibly at A-site. According to the reports, the cations' vacancies generated in the structure efficiently reduce the amount of oxygen vacancies and easy movement of walls [35,36]. The mechanical quality factor  $Q_m$  and the planar coupling factor  $k_p$  of NBT-0.2 ceramic are found to be 3239 and 6.6%, respectively. The thickness coupling factor  $k_t$  is about 14.8% at room temperature, much higher than the value of the planar coupling factor  $k_p$  (~6.6%), exhibiting so much stronger anisotropic behavior. Thereby, the piezoelectric and electromechanical properties of NBT ceramics have been effectively enhanced by the right amount of (Nd,Ce) modification.

The anti-resonance  $f_a$  and resonance  $f_r$  method is applied to describe the real-time behavior of electromechanical coupling properties of the piezoelectric ceramics, and the impedance and resonant frequency are strongly dependent on temperature and sample size [37]. Figure 5(a) depicts the electrical impedance modulus of the (Nd,Ce)-modified NBT piezoelectric ceramic ( $x=0.2$ ) as a function of frequency at various temperatures, which clearly shows resonance in the vicinity of 170 kHz with a steadily decreasing amplitude of impedance modulus with increasing temperature up to 500 °C. However, the amplitude of impedance modulus becomes very weak as the temperature approaches to the Curie temperature ( $T_C=630$  °C), indicating that the material becomes softer. Figure 5(b) shows that the anti-resonance  $f_a$  and resonance  $f_r$  as a function of



**Fig. 5** (a) Electrical impedance modulus as a function of frequency at various temperatures; (b)  $f_a$  and  $f_r$  as a function of temperature for the (Nd,Ce)-modified NBT piezoelectric ceramic ( $x=0.2$ ).

temperature for the (Nd,Ce)-modified NBT piezoelectric ceramic ( $x=0.2$ ). With the increasing temperature up to 500 °C,  $f_a$  and  $f_r$  shift to lower frequency, showing the negative temperature coefficient behavior.

The thermal annealing behavior of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics is shown in Fig. 6. It can be seen that the four-layer NBT orthorhombic-structured ceramics are stable to thermal annealing and the piezoelectric constants  $d_{33}$  of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics show a slight decrease when the annealing temperature is below 500 °C. When the annealing temperature is near the Curie temperature  $T_C$ ,  $d_{33}$  of NBT-based ceramics depresses sharply. Moreover,  $d_{33}$  of NBT-0.2 piezoelectric ceramic maintains over 86% of its initial values (~28 pC/N) even if the annealing temperature reaches up to 500 °C, indicating that the NBT-0.2 piezoelectric ceramic has a good thermal

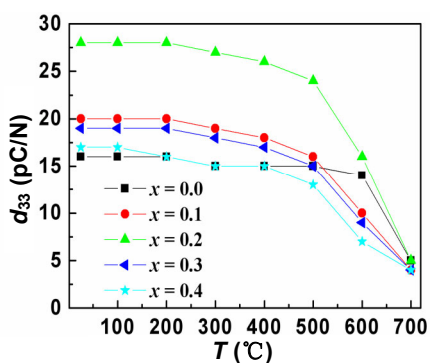
stability and it may be an appropriate candidate for high temperature applications.

### 4 Conclusions

In summary, NBT-based ceramics with A-site vacancy were investigated by using the traditional solid-state processing. The (Nd,Ce) modification of NBT-based ceramics resulted in the obvious enhancement of the piezoelectric activity. A combination of high  $d_{33}$  (~28 pC/N), high  $Q_m$  (~3239), high  $T_C$  (~630 °C) and stable electrical properties demonstrates that  $\text{Na}_{0.5}\text{Bi}_{4.3}(\text{Nd}_{0.5}\text{Ce}_{0.5})_{0.2}\text{Ti}_4\text{O}_{15}$  ceramic is a promising candidate for high temperature piezoelectric applications.

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**Fig. 6** Effect of annealing temperature for 2 h on the piezoelectric constant  $d_{33}$  (measured at room temperature) of the pure and (Nd,Ce)-modified NBT piezoelectric ceramics.

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