Ultrahigh-temperature piezoelectric polycrystalline ceramics: dramatically enhanced ferroelectricity, piezoelectricity and electrical resistivity in Ca$_{1-3x}$Bi$_{2+3x}$Nb$_{2-x}$Mn$_x$O$_9$

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ABSTRACT
Among Aurivillius-phase ferroelectric ceramics, CaBi$_2$Nb$_2$O$_9$ is considered as the best candidate with potential applications in ultrahigh-temperature piezoelectric devices due to the highest $T_c$ ($\sim$ 940 °C). This paper reports that BiMn co-substitution at A and B sites gives rise to dramatic enchantments in ferroelectricity, piezoelectricity, and electrical resistivity of CaBi$_2$Nb$_2$O$_9$ ceramics. The optimum composition (Ca$_{0.97}$Bi$_{2.03}$Nb$_{1.99}$Mn$_{0.01}$O$_9$) with a $T_c$ of 953 ± 3°C shows a high ferroelectric remnant polarization ($P_r$), field-induced strain ($S_{33}$), piezoelectric activity ($d_{33}$ and $d'_{33}$) with values of $\sim$ 11.1 µC/cm$^2$, 4.9 $\times$ $10^{-4}$, 20.8 and 26.1 pC/N, respectively, which are about two to three times those of CaBi$_2$Nb$_2$O$_9$.

IMPACT STATEMENT
Significant ferroelectric remnant polarization ($P_r$ = 11.1 µC/cm$^2$), field-induced strain ($S_{33}$ = 4.9 $\times$ $10^{-4}$), and piezoelectric activity ($d_{33}$ = 20.8 pC/N, $d'_{33}$ = 26.1 pC/N) are simultaneously induced in ultrahigh $T_c$ CaBi$_2$Nb$_2$O$_9$ piezoceramics by BiMn substitution.

1. Introduction
Piezoelectric materials integrated into high-temperature sensors must take into account two essential application requirements: (1) high Curie temperature ($T_c$) and (2) high piezoelectric activity ($d_{33}$), which are desired to meet high operating temperature and high sensitivity, respectively [1–3]. In addition, high electrical resistivity ($\rho$) is required for ferroelectric materials, which will ensure that they are polarized under large electric fields without breakdown or excessive charge leakage. High $\rho$ is also required during device operating at high temperatures, because the piezoelectric material has not only the function of generating electric charge under stress or strain but also the ability to maintain the charge for a time long enough to be detected by the electronic system [3]. The maximum operating temperature for ferroelectric materials is at least $\sim$ 150 °C below $T_c$, because they will be depolarized and most of the piezoelectricity will be lost near this temperature [4]. Single crystals with ultrahigh $T_c$ ( $\sim$ 1000–1400 °C) such as LiNbO$_3$, GaPO$_4$, La$_3$Ga$_5$SiO$_{14}$, YCa$_4$O(BO$_3$)$_3$, GdCa$_4$O(BO$_3$)$_3$ are potential candidates for high-temperature piezoelectric...
applications [3,5–7]. However, the piezoelectric activity of these single crystals is rather low \((d_{33} = \sim 4–7 \text{ pC/N})\) and the cost for them is much high.

The structure of Aurivilius compounds can be described as the intergrowth of \((\text{Bi}_2\text{O}_2)^{2+}\) layers and \((\text{An}_n-1\text{Bi}_n\text{O}_{3n+1})^{2+}\) layers, where \(n (n = 1–6)\) is the number of octahedral layers in the perovskite layers [8]. Some Aurivilius ferroelectric ceramics with high \(T_c\) are CaBi2Nb2O9. Details of the prepared Ca1−xBi2+xMn2−xO9 for x = 0, 0.005, 0.01, 0.015, and 0.02 ceramics and characterizations of their structures and electrical properties are presented in supplemental material. Among all compositions, the optimum composition \((x = 0.01)\) with ultrahigh \(T_c\) \((953 \pm 3^\circ\text{C})\) shows \(d_{33}\) of \(\sim 20.8 \text{ pC/N}\) and \(d_{33}^t\) of \(\sim 26.1 \text{ pC/N}\), which are all higher than those of the above-mentioned piezoelectric single crystals and ceramics with ultrahigh \(T_c\) of \(> 850^\circ\text{C}\).

### 2. Results and discussion

Phase purity and microstructure of CBNO–1000xBM were monitored using XRD and SEM, respectively (Figures S1 and S2). The results reveal that there is no any impurity phase generated in CBNO–1000xBM, indicating Bi and Mn ions diffusing into the lattices of \(\text{CaBi}_2\text{Nb}_2\text{O}_9\). Notably, CBNO–15BM and CBNO–20BM both show abnormally strong (00l) diffraction peaks, e.g. (008) and (0010), being indicative of an increase in the degree of texture in the c-axis direction. This degree of texture expressed by using the Lotgering orientation factor (LOF) is calculated to be \(\sim 29.9–34.3\%\) for them, much higher than that of other compositions with a lower level of BiMn substitution \((\sim 12.5–16.2\%)\) (inset of Figure S1a). Viewed from cross-section SEM images, the average length of grains increases obviously introducing BiMn substitution. The value of modified CBNO–1000xBM compositions is \(\sim 12.17–16.75 \mu\text{m}\), much higher than that of CBNO–0BM \((\sim 5.36 \mu\text{m})\) (Figure S2a). It is presumable that additives of BiO3 and/or MnO act as effective flux agents functioning as lowering the temperature for ceramics’ sintering. In addition, the average aspect ratio \(t/L\) (thickness/length of grain) first increases and then decreases with increasing \(x\). This ratio of CBNO–0BM, CBNO–10BM, and CBNO–20BM is about 0.23, 0.49, and 0.29, respectively.

Rietveld structural refinement suggests that CBNO–10BM crystallizes in orthorhombic \(A2_1am\) space group with \(a = 5.47992(3) \text{ Å}, b = 5.43959(3) \text{ Å}, c = 24.88649(6) \text{ Å}, \text{ and } V = 741.830(6) \text{ Å}^3\) (Table S1). Figure 1(a) clearly shows that the refined data well fit with the experimental ones and the final factors, \(R_{wp}, R_p\) and \(\chi^2\), are reasonable with values of 8.11%, 5.89%, and 2.015, respectively. Refining the atomic occupancies shows a relatively low degree of cation disordering between the perovskite layer and the \((\text{Bi}_2\text{O}_2)^{2+}\) layer. The occupancy of Ca and Bi at the perovskite A site is 0.8534(8) and 0.1466(8), and the value at the cationic site of the \((\text{Bi}_2\text{O}_2)^{2+}\) layer is 0.0583(5) and 0.9417(5), respectively.

Based on the refined structural parameters (Table S1), the crystal structure of CBNO–10BM is depicted in the inset of Figure 1(a). With \(A2_1am\) orthorhombic symmetry, atomic displacements along the polar axis \((a\text{-axis})\) from the corresponding positions in the parent tetragonal \((I4/mmm)\) structure cause spontaneous polarization \((P_s)\). Figure 1(b) illustrates atomic displacement along the \(a\text{-axis}\) of each constituent ion in CBNO–10BM. Clearly, the perovskite cations and anions show significant displacements. Based on these atomic displacements, the total \(P_s\) of CBNO–10BM can be calculated with the Sivakumar model in the same manner as reported in Ref. [16]. The calculated \(P_s\) of CBNO–10BM is \(\sim 32.8 \mu\text{C/cm}^2\) (Figure 1(c)), much higher than that of CBNO–0BM \((\sim 24.4 \mu\text{C/cm}^2)\) [9]. For Aurivillius-phase ferroelectrics, that \(\text{Bi}^{3+}\) with \(6s^2\)
lone pair electrons occupying the perovskite A site can result in an enhancement in orthorhombic distortion and an increase in ferroelectricity [17]. Therefore, increased $P_S$ in CBNO–10BM is probably attributed to the fact that more highly polarizable Bi$^{3+}$ cations occupy the perovskite A sites. Based on the XRD data (Figure S1a), lattice parameters ($a$, $b$, $c$) of other CBNO–1000BM are also refined. That the unit cell volume ($V$) increases gradually with increasing $x$ should be the result of the integration of Bi$^{3+}$ into the Ca$^{2+}$ site, because Bi$^{3+}$ with 6$s^2$ lone pair electrons relative to Ca$^{2+}$ has a larger polarizability (Bi$^{3+}$: 6.12 Å$^3$ and Ca$^{2+}$: 3.12 Å$^3$) [18].

Figure 2(a) shows the temperature dependence of dielectric permittivity ($\varepsilon'$) of CBNO–1000xBM. The maximum $\varepsilon'$ ($\varepsilon'_{\text{max}}$) corresponds to the ferroelectric-to-paraelectric phase transition, and the error for extracted $T_c$ is within ±2–3°C. In the inset of Figure 2(a), $T_c$ of CBNO–1000xBM ranges from ~ 901 ± 2°C to ~ 953 ± 3°C. $T_c$ first increases and then decreases as $x$ increases from zero to 0.02, which is the same as the change in orthorhombicity defined as $2(a-b)/(a+b)$. This implies that ferroelectricity in CBNO–1000xBM is associated with their structural distortion. It is noted that BiMn substitution gives rise to an obvious decrease in the dielectric loss ($\tan\delta$) in the high-temperature segment (~ 400–940°C) (Figure 2(b)). The loss of CBNO–10BM is lower than 0.1 below 700°C (inset of Figure 2(b)), which will be important
for its high-temperature piezoelectric applications. This decrease in dielectric loss is attributed to an increase in electrical resistivity. Inspection from the impedance spectra of CBNO–1000xBM reveals that the size of high-frequency semicircle associated with bulk resistivity ($\rho_b$) increases with the BiMn substitution (Figure S3). $\rho_b$ of CBNO-10BM relative to CBNO-0BM increases by about two orders of magnitude at 450–600°C.

CBNO–0BM is a typically mixed $p$-type ($h^*$) and ionic conductor where holes are created due to the oxidation of oxygen vacancies ($V_{O}^{**}$) (Figure S3):

$$0.5O_2 + V_{O}^{**} \rightarrow O^{X}_O + 2h^*$$ (1)

Here, the oxygen vacancies are primarily generated during processing due to the loss of Bi$_2$O$_3$. In particular, BiMn co-substitution at the A/B sites results in no additional $V_{O}^{**}$ in CBNO–1000xBM. In the starting compositions of them, the charge compensation for Mn$^{2+}$ acceptor substitution for Nb$^{5+}$ at the B site involves in Bi$^{3+}$ donor substitution for Ca$^{2+}$ at the A site:

$$1.5Bi_2O_3 + MnO \rightarrow 3Bi_{Ca}^* + Mn_{Nb}'' + 5.5O^{X}_O$$ (2)

The EPR results indicate that parts of Mn$^{2+}$ ions have been oxidized to Mn$^{3+}$ and Mn$^{4+}$ due to the absorption of $h^*$ (Figure S4):

$$Mn''_{Nb} + h^* \rightarrow Mn''_{Nb}$$ (3)

$$Mn''_{Nb} + 2h^* \rightarrow Mn'_{Nb}$$ (4)

**Figure 2.** Temperature dependences of dielectric properties at 1MHz for CBNO–1000xBM: (a) dielectric permittivity ($\varepsilon'$) with an inset showing extracted $T_c$ and structural orthorhombicity $[2(\alpha - \beta)/(\alpha + \beta)]$; (b) dielectric loss (tan$\delta$) with an inset showing regionally enlarged drawing.
This oxidization of Mn$^{2+}$ promotes the completion of reaction (1). Therefore, the amount of both V$^\bullet_{CB}$ and h$^\bullet$ in modified CBNO–1000xBM decreases. This can be confirmed by the fact that CBNO–10BM shows the intrinsic electronic conduction with a high activity energy of 1.75 eV (Figure S3).

CBNO–1000xBM shows saturated P–E loops and butterfly-typed strain curves, which are plotted in Figure 3(a–e). Extracted ferroelectric remnant polarization ($P_r$) and field-induced strain ($S_{33}$) of CBNO–1000xBM are $\sim$ 3.8–11.1 μC/cm$^2$ and $\sim$ 2.6–4.9 × 10$^{-4}$, respectively (Figure 3(f)). The change trends in $P_r$ and $S_{33}$ are similar to those in $T_c$, i.e. they first increase and then decrease with increasing x. In addition, inverse piezoelectric coefficient $d_{33}^*$ of the samples can be calculated directly from the slope of the strain versus electric field curves. $d_{33}^*$ of CBNO–1000xBM is $\sim$ 11.2–26.1 pm/V (pC/N) (Figure 4(a)). Also, piezoelectric coefficients $d_{33}$ and $d_{31}$ of the samples can be measured after DC field poling. $d_{33}$ and $d_{31}$ of CBNO-0BM are $\sim$ 9.7 and $\sim$ 13.5 pC/N,

**Figure 3.** (a–e) P–E loops and (f) extracted $P_r$ and $S_{33}$ of CBNO–1000xBM measured at 140°C and 10 Hz.
and the values of modified composition increases to \(\sim 16.7-20.8\) and \(\sim -20.3-26.5\) pC/N, respectively. For each composition, the \(d_{33}\) value is lower than that of, and the difference in them could be attributed to difficulties accurately determining the slope from the S–E loop.

Figure 4(b) shows the effects of thermal depoling on \(d_{33}\) of CBNO–1000xBM. These \(d_{33}\) values were measured at room temperature after annealing for 2h at each \(x\)-axis temperature. All the compositions demonstrate good piezoelectric stability against temperature,

Figure 4. (a) \(d_{33}^*, d_{33}\) and \(d_{31}\) and (b) effect of thermal temperature (for 2 h) on \(d_{33}\) of CBNO–1000xBM. (c) Cross-section topographic and vertical PFM (V-PFM) images of CBNO–10BM. (d) Microscopic piezoelectric response of CBNO–10BM at various voltage. (e) Schematic illustration of the 3D domain structure in CBNO–10BM. (f) Locally microscopic displacement–voltage curve \((D–V)\) and piezoelectric hysteresis loop \((d_{33}^*–V)\) of CBNO–10BM.
and CBNO–10BM and CBNO–15BM still have high $d_{33}$ of $\sim 20.6$ and 18.5 pC/N after 800°C thermal depoling. A possible reason for this stable $d_{33}$ is a small contribution from the piezoelectrically active non-180° domain walls. The fraction of the total $d_{33}$ that is due to the irreversible displacement of domain walls is estimated to be $\sim 8.85$% and $\sim 18.6$% for CBNO–10BM and CBNO–20BM, respectively, in terms of the Rayleigh law (Figure S6). For each composition, $d_{33}$ decreases rapidly when the annealing temperature is near $T_c$ and then becomes almost zero above $T_c$.

Furthermore, the domain structure of CBNO–1000xBM was characterized by PFM measurements. Figure 4(c) shows cross-section topography and vertical PFM images of CBNO–10BM. Clearly, CBNO–10BM shows a complicated domain configuration with high-density domain walls. Through the PFM image, bright and dark stripes correspond to antiparallel 180° domains and most of domain walls are parallel to the $a$–$b$ plane and perpendicular to the $c$-axis. This domain pattern is much less regular than that of Bi$_4$Ti$_3$O$_{12}$ but similar to law (Figure S6). For each composition, $d_{33}$ of decreases rapidly when the annealing temperature is near $T_c$ and then becomes almost zero above $T_c$.

Among all compositions, CBNO–10BM shows the highest $P_r$, $S_{33}$, $d_{33}$, $d_{31}$, and $d_{33}$ with values of $\sim 11.1 \mu$C/cm$^2$, $4.9 \times 10^{-4}$, 20.8, 26.1 and $-26.5$ pC/N, respectively. Comparisons in $T_c$ and $d_{33}$ reveal that the obtained $T_c$ ($\sim 953 \pm 3 ^\circ C$) and $d_{33}$ of CBNO–10BM are both higher than the reported values ($T_c = \sim 868–939 ^\circ C$, $d_{33} = \sim 12.6–17.5$ pC/N) of other modified CaBi$_2$Nb$_2$O$_{9}$ ceramics reported in the literature (see Figure S7). Dramatically enhanced ferroelectric properties and electro-mechanical characteristics of CBNO–10BM can be attributed to three effects induced by BiMn substitution. First, $P_S$ of CBNO–10BM increases significantly from 24.4 (CBNO–0BM) to 32.8 $\mu$C/cm$^2$. Commonly, piezoelectricity of the ferroelectrics is dominated by both intrinsic lattice contribution and extrinsic contribution from movements of non-180° domain walls [21,22]. For modified CBNO–1000xBM, enhanced piezoelectricity seems to be primarily attributed to the increases in $P_S$ and $P_r$. Second, BiMn substitution can decrease effectively the V$^{\bullet\bullet}_O$ concentration ([V$^{\bullet\bullet}_O$]) at the perovskite lattices due to the oxidation of Mn$^{2+}$ to Mn$^{3+}$ and/or Mn$^{4+}$. This is consistent with the results of Mn-substituted 0.62Bi$_{0.5}$Na$_{0.5}$TiO$_3$–0.06BaTiO$_3$–0.32 (Sr$_{0.7}$Bi$_{0.2}[\square]_{0.1}$) TiO$_3$ ceramics [23]. For CBNO–0BM, ferroelectric polarization is slightly pinched at around $E = 0$ kV/cm (Figures 3(a) and S5(a)) and the measured $P$–$E$ loop after dc poling (150 kV/cm) is strongly asymmetric with the establishment of a large internal bias field ($E_{ib} = 35.1$ kV/cm) (Figure S5(b)). It is suggested that one degradation mechanism of its $P_r$ is the pinning of domain walls due to the oxygen vacancies. With decreasing [V$^{\bullet\bullet}_O$], this pinning effect disappears and the number of available switching domain wall increases; thus, CBNO–10BM shows significant $P_r$ and $S_{33}$. Simultaneously, relatively high leakage current and electrical conductivity in CBNO–0BM decrease significantly with BiMn substitution (Figure S3). This ensures that CBNO–10BM is sufficient to be poled under higher applied field and thus improves its ferroelectricity and piezoelectricity. Third, CBNO–10BM ceramic shows a sound grain growth with much large size and high $t/L$ ratio, because the additive of BiMn controls the growth of plate-like grains. As a result, there may be more crystallographic directions suitable for polarization [24]. In ferroelectric ceramics, the neighboring grain boundaries have a significant influence on the switching of domains within one grain under electrical poling [7,25]. Lowering the volume of grain boundaries and relieving internal stresses are also beneficial to that the domains switching in the coarse grains of CBNO–10BM. The results also lead to increased $P_r$, $S_{33}$, and $d_{33}$ for CBNO–10BM.

The degradations in ferroelectricity and piezoelectricity of CBNO–15BM and CBNO–20BM could be resulted
from a dimensional mismatch between perovskite and bismuth oxide layers [24], due to higher level of BiMn substitutions. It is well known that the electrical properties of layer-structured Aurivillius ferroelectrics are dominant in the a–b plane (normal to c-axis). Therefore, higher c-oriented texture is not in favor of the improvements in ferroelectric and piezoelectric properties for them.

3. Conclusions
Dielectric, ferroelectric, and piezoelectric properties of CBNO–10BM ceramics are characterized. BiMn co-substitution at A and B sites results in an increase in P<sub>d</sub> and a decrease in [V<sub>O</sub>]<sup>−</sup> as well as a sound grain growth. Therefore, modified CBNO–1000 compositions relative to CBNO–0BM show dramatically enhanced ferroelectricity, piezoelectricity, and electrical resistivity. CBNO–10BM with T<sub>c</sub> of 953 ± 3°C has P<sub>d</sub>, d<sub>33</sub>, and e<sub>d33</sub><sup>−</sup> with values of 11.1 μC/cm<sup>2</sup>, 20.8 and 26.1 pC/N, respectively, which are all higher than those of the reported piezoelectric single crystals and ceramics with ultrahigh T<sub>c</sub> of > 850°C. This combined stable d<sub>33</sub> and high resistivity suggests that it is a very promising material with potential applications in ultrahigh piezoelectric devices.

Disclosure statement
No potential conflict of interest was reported by the authors.

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References
[1] Turner RC, Fuierer PA, Newhamand RE, et al. Materials of high temperature acoustic and vibration sensor: a review. Appl Acoust. 1994;41:299–324.
[2] Damjanovic D. Materials for high temperature piezoelectric transducers. Curr Opin Solid State Mater Sci. 1998;3:469–473.
[3] Zhang SJ, Yu FP. Piezoelectric materials for high temperature sensors. J Am Ceram Soc. 2011;94(10):3153–3170.
[4] Yan HX, Zhang HT, Reece MJ, et al. Thermal depoling of high Curie point Aurivillius phase ferroelectric ceramics. Appl Phys Lett. 2005;8:082911.
[5] Zhang SJ, Frantz E, Xia R, et al. Gadolinium calcium oxyborate piezoelectric single crystals for ultra-high temperature ((1000°C) applications. J Appl Phys. 2008;104:084103.
[6] Zhang SJ, Fei Y, Chai B, et al. Characterization of piezoelectric single crystal YCa<sub>2</sub>O(BO<sub>3</sub>)<sub>3</sub> for high temperature applications. Appl Phys Lett. 2008;92:202905.
[7] Yan HX, Ning H, Kan Y, et al. Piezoelectric ceramics with super-high Curie points. J Am Ceram Soc. 2009;92(10):2270–2275.
[8] Aurivillius B. Mixed bismuth oxides with Lauer lattices: I. Ark Kemi. 1949:1:463–471.
[9] Yan HX, Zhang HT, Ubic R, et al. A lead-free high-Curie-point ferroelectric ceramic Ba<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>. Adv Mater. 2005;17:1261–1265.
[10] Swartz S, Schulze WA, Biggers JV. Fabrication and electrical properties of grain oriented Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> ceramics. Ferroelectrics. 1981;38:765–758.
[11] Peng ZH, Chen Q, Wang Y, et al. Enhancement of piezoelectric properties of (LiCePr)-multidoped CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> high temperature ceramics. Mater Lett. 2013;107:14–16.
[12] Zhang XD, Yan HX, Reece MJ. Effect of A site substitution on the properties of CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> ferroelectric ceramics. J Am Ceram Soc. 2008;91:2928–2932.
[13] Xing X, Cao F, Peng Z, et al. The effects of oxygen vacancies on the electrical properties of W-doped CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> piezoceramics. Curr Appl Phys. 2018;18:1149–1157.
[14] Xie J, Zhong J, Wu C, et al. Enhanced electrical properties related to structural distortion of CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub>-based piezoelectric ceramics. J Am Ceram Soc. 2019;102:1287–1295.
[15] Liu G, Ren S, Wu C, et al. Enhanced thermal stability of (NaCe)-multidoped CaBi<sub>2</sub>Nb<sub>2</sub>O<sub>9</sub> by A-site vacancies-induced pseudo-tetragonal distortion. J Am Ceram Soc. 2018;101:4615–4626.
[16] Shimakawa Y, Kubo Y, Nakagawa Y, et al. Crystal structures and ferroelectric properties of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> and Sr<sub>0.91</sub>Bi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. Appl Phys Lett. 1999;74(13):1904–1906.
[17] Withers RL, Thompson JG, Rae AD. The crystal chemistry underlying ferroelectricity in Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub>, Bi<sub>3</sub>TiNbO<sub>9</sub>, and Bi<sub>2</sub>WO<sub>6</sub>. J Solid State Chem. 1991;94:404–417.
[18] Yang F, Wu P, Sinclair DC. Enhanced bulk conductivity of A-site divalent acceptor-doped non-stoichiometric sodium bismuth titanate. Solid State Ionics. 2017;299:38–45.
[19] Katayama S, Noguchi Y, Miyayama M. 3D domain structure in Bi<sub>4</sub>Ti<sub>3</sub>O<sub>12</sub> crystals observed by using piezoresponse force microscopy. Adv Mater. 2007;19:2552–2555.
[20] Ding Y, Liu JS, MacLaren I, et al. Ferroelectric switching mechanism in SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub>. Appl Phys Lett. 2001;79:1015–1017.
[21] Zhang QM, Pan WY, Jiang SJ, et al. Domain wall excitations and their contributions to the weak-signal response of doped lead zirconate titanate ceramics. J Appl Phys. 1988;64:6445.
[22] Wang CM, Wang JF, Zhang SJ, et al. Electromechanical properties of A-site (LiCe)-modified sodium bismuth titanate (Na<sub>0.5</sub>Bi<sub>4</sub>Ti<sub>3</sub>O<sub>15</sub>) piezoelectric ceramics at elevated temperature. J Appl Phys. 2009;105:094110.
[23] Li F, Zhai J, Shen B, et al. Simultaneously high-energy storage density and responsivity in quasi-hysteresis-free Mn-doped Bi<sub>0.5</sub>Na<sub>0.5</sub>TiO<sub>3</sub>-BaTiO<sub>3</sub>-Sr<sub>0.8</sub>Bi<sub>2</sub>Ta<sub>2</sub>O<sub>6</sub> (SRT) piezoelectric relaxor ceramics. Mater Res Lett. 2018;6:345–352.
[24] Hou JG, Kumar RV, Qu YF, et al. B-site doping effect on electrical properties of Bi<sub>4</sub>Ti<sub>3</sub>−<sub>2</sub>Nb<sub>2</sub>Ta<sub>2</sub>O<sub>12</sub> ceramics. Scr Mater. 2009;61:664–667.
[25] Zhang HT, Yan HX, Ning HP, et al. The grain size effect on the properties of Aurivillius phase Bi<sub>13</sub>Nd<sub>0.85</sub>Ti<sub>12</sub>O<sub>3</sub> ferroelectric ceramics. Nanotechnology. 2009;20:385708.