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High performance Bi$_{0.5}$Na$_{0.5}$TiO$_3$-BiAlO$_3$-K$_{0.5}$Na$_{0.5}$NbO$_3$ lead-free pyroelectric ceramics for thermal detectors

Zhen Liu,$^{1,2,a}$ Weijun Ren,$^2$ Ping Peng,$^2$ Shaobo Guo,$^2$ Teng Lu,$^1$ Yun Liu,$^{1,a}$ Xianlin Dong,$^2$ and Genshui Wang$^{2,a}$

$^1$Research School of Chemistry, The Australian National University, Canberra, Australian Capital Territory 2601, Australia
$^2$Key Laboratory of Inorganic Functional Materials and Devices, Shanghai Institute of Ceramics, Chinese Academy of Sciences, 1295 Dingxi Road, Shanghai 200050, People’s Republic of China

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Both high pyroelectric properties and good temperature stability of ferroelectric materials are desirable when used for applications in infrared thermal detectors. In this work, we report lead-free ternary 0.97(0.99Bi$_{0.5}$Na$_{0.5}$TiO$_3$-0.01BiAlO$_3$)-0.03K$_{0.5}$Na$_{0.5}$NbO$_3$ (BNT-BA-KNN) ceramics, which not only exhibits a large pyroelectric coefficient ($p \sim 3.7 \times 10^{-8}$ C cm$^{-2}$K$^{-1}$) and figures of merit ($F_r$, $F_v$, and $F_d$) but also shows excellent thermal stable properties. At room temperature, $F_r$, $F_v$, and $F_d$ are determined as high as $1.32 \times 10^{-10}$ mV, $2.89 \times 10^{-2}$ m$^{-2}$C, and $1.15 \times 10^{-5}$ Pa$^{-1/2}$ at 1 kHz and $1.32 \times 10^{-10}$ mV, $2.70 \times 10^{-2}$ m$^{-2}$C, and $1.09 \times 10^{-5}$ Pa$^{-1/2}$ at 20 Hz, respectively. During the temperature range of RT to 85°C, the achieved $p$, $F_r$, $F_v$, and $F_d$ do not vary too much. The high depolarization temperature and the undispersed ferroelectric-ergodic relaxor phase transition with a sharp pyroelectric coefficient peak value of $\sim 400 \times 10^{-8}$ C cm$^{-2}$K$^{-1}$ are suggested to be responsible for this thermal stability, which ensures reliable actual operation. The results reveal the BNT-BA-KNN ceramics as promising lead-free candidates for infrared thermal detector applications. Published by AIP Publishing. https://doi.org/10.1063/1.5020424

Pyroelectric materials have been of strong interest for the development of thermal based sensors, accelerators, and energy harvesters. The utilization of pyroelectric materials for uncooled infrared thermal detectors has recently gained a rapid growth of investigations since they promise a broad range of applications. Pyroelectric materials have good temperature stability of ferroelectric materials and can be responsible for this thermal stability, which ensures reliable actual operation. Recently, Sun et al. reported 0.6(Ba$_{0.9}$Ca$_{0.1}$)TiO$_3$-0.4Ba(Sn$_{0.2}$Ti$_{0.8}$)O$_3$ pyroelectric ceramics with an optimized $p$ value of $2.05 \times 10^{-8}$ C cm$^{-2}$K$^{-1}$ and an $F_d$ value of 0.41 $\times 10^{-5}$ Pa$^{-1/2}$. Despite that many progresses have been reported in lead-free pyroelectric materials, they still exhibit far inferiority to these lead-based materials.

Sodium bismuth titanate (Bi$_{0.5}$Na$_{0.5}$TiO$_3$, BNT) ceramics exhibit large remanent polarization ($P_r = 38 \mu$C/cm$^2$) and high Curie temperature ($T_C = 320^\circ$C), exhibiting favorable characteristics for pyroelectric applications. However, its large leakage current and high coercive electric field (~7.3 kV/mm) make them difficult to be poled. Forming BNT based solid solutions with other perovskites such as BaTiO$_3$, BiAlO$_3$, and (Bi,K)TiO$_3$ not only improves the poling effectiveness but also offers great opportunities for tuning their ferroelectric properties. To fit for real pyroelectric applications, the BNT family must satisfy two aspects of requirements. One is high pyroelectric performance at room temperature, including pyroelectric coefficients and various figures of merit. On the other hand, the good temperature stability of $p$ and FOMs is also inevitable to ensure their reliable operation. Recently, Sun et al. reported that Mn doped 0.946Bi$_{0.5}$Na$_{0.5}$TiO$_3$-0.054BaTiO$_3$ (BNT-BT) single crystals with the (111) orientation possesses high pyroelectric coefficients and large figures of merit.

The value of $p$ can reach as high as $5.88 \times 10^{-8}$ C cm$^{-2}$K$^{-1}$ and does not increase too much with temperature varying from 20°C to 85°C. However, for their ceramics counterparts, although a large $p$ value of $5.7 \times 10^{-8}$ C cm$^{-2}$K$^{-1}$ was realized by Guo et al. on 0.07Ba(Zr$_{0.655}$Ti$_{0.345}$)O$_{3}$ (BNT-BZT) pyroelectric ceramics near the morphotropic phase boundary (MPB), the value of $p$...
soared to 20.6 × 10⁻⁸ C cm⁻² K⁻¹ with temperature increasing to 50 °C. Quite recently, Balakt et al. obtained even higher \( p > 7.42 \times 10^{-8} \) C cm⁻² K⁻¹ at room temperature on La doped 0.94Bi₀.₅Na₀.₅TiO₃-0.06BaTiO₃ ceramics. However, the great enhancement of \( p \) was realized at the expense of bringing the depolarization temperature \( (T_d) \) down to near room temperature, which will also result in the temperature instability. Moreover, the ceramics will experience polarization loss during the heat-involved manufacture procedures, thus affecting their reusability, which limits their applicability as well. Therefore, BNT based ceramics possessing both high pyroelectric properties and favorable thermal stability necessarily deserve further research.

In present work, a potential lead-free pyroelectric ceramics was presented for thermal detectors. A large pyroelectric coefficient of 3.9 × 10⁻⁸ C cm⁻² K⁻¹ and enhanced FOMs were achieved at room temperature in 0.97(0.99Bi₀.₅Na₀.₅TiO₃-0.01BiAlO₃)-0.03K₀.₅Na₀.₅NbO₃ (BNT-BA-KNN) ceramics. Moreover, the obtained \( p \) and FOMs demonstrate good temperature stability over a wide temperature range of RT to 85 °C. The high depolarization temperature and undispersed ferroelectric-relaxor phase transition of BNT-BA-KNN are suggested to be responsible for the improvement. Our results reveal the great potential of BNT-BA-KNN ceramics for infrared thermal detector applications.

The BNT-BA-KNN ceramics were prepared through a conventional solid-state reaction method. BiAlO₃ (BA) was chosen due to its ability to improve the polarization of BNT. K₀.₅Na₀.₅NbO₃ (KNN) was added since it was widely used to tune the depolarization temperature of BNT-based materials. Bi₂O₃ (99.9%), TiO₂ (99.8%), Na₂CO₃ (99.8%), Al₂O₃ (99%), K₂CO₃ (99%), and Nb₂O₅ (99.9%) were used as the starting raw materials. The mixed oxides were calcined at 850 °C for 2 h and sintered at 1180 °C for 2 h in a covered alumina crucible. To minimize the evaporation of the volatile elements Bi, Na, and K, the disks were embedded in atmospheric powder of the same composition. The samples were ground to disks with a thickness of 0.5 mm and a diameter of 8 mm. Both sides of the disks were coated with a thin layer of silver paste with a diameter of 7.8 mm through screen printing and were fired at 700 °C for 30 min.

The crystal structure of the as-sintered ceramics was characterized using an X-ray diffractometer (XRD, D8 Advance, Bruker, Karlsruhe, Germany), operated with Cu Ka radiation at room temperature (≈30 °C). The microstructure of the ceramics was taken using a field emission scanning electron microscope (FE-SEM, S-4800, Hitachi, Japan). For dielectric and pyroelectric measurements, the samples were poled in silicone oil under an electric field of 7 kV/mm at 100 °C for 30 min and then cooled to room temperature without electric field removal to make sure that the samples were fully poled. The dielectric constant \( (\varepsilon_r) \) and dielectric loss (tan \( \delta \) ) were measured using an aix ACCT TF 2000 analyzer measuring system (aix ACCT Co., Aachen, Germany). The pyroelectric coefficient was measured by the Byer-Roundy method as a function of temperature. The pyroelectric current was recorded with a Keithley 6517A electrometer/high resistance meter for poled samples both on heating and cooling with a rate of 2 °C/min. Figure 1 shows the XRD pattern of BNT-BA-KNN ceramics, and the inset illustrates the surface microstructure of the as-sintered samples. The XRD result confirms that the ceramics are crystallized into a perovskite structure. A small trace of the bismuth-deficient Bi₂Al₄O₉ secondary phase was detected at around 20 = 29°, which was also observed previously in BNT-BA ceramics. The amount of the impurity phase is calculated to be around 0.32 mol. % through integrating the related peaks. The samples exhibit a dense and void-free microstructure, and the grain sizes vary from 1 to 6 μm. This is consistent with the high relative density (>97%) determined by the Archimedes method.

Figure 2(a) presents the temperature dependent dielectric constant \( (\varepsilon_r) \) and dielectric loss (tan \( \delta \) ) of pre-poled BNT-BA-KNN ceramics measured at different frequencies from room temperature to 400 °C. A general frequency-dispersion is clearly visible for both \( \varepsilon_r \) and tan \( \delta \), which indicates their relaxor characteristic. As temperature increases, three anomalies can be detected, similar to previous reports. The first characteristic temperature \( T_{F,R} \) can be determined by the frequency-independent dielectric loss peak and dielectric constant inflection point at 118 °C, which denotes the transition from ferroelectric to the ergodic relaxor (FE-ER) phase with increasing temperature, as supported by the temperature dependent polarization hysteresis measurements in Fig. 2(b) and the TEM study. The FE-ER phase transition will result in reoriented dipoles and a significant reduction in remanent polarization. Thus, \( T_{F,R} \) had also been regarded as the depolarization temperature \( T_{de} \). The second transition temperature is characterized by the frequency dispersion vanishing point at 225 °C. The third transition temperature \( T_m \) happens at the maximum dielectric constant, which provides the evolution to the paraelectric phase. Although many works have been performed with regard to the temperature dependent evolutions of the BNT family, the structural variations during these phase transitions still remain controversy.
For pyroelectric applications, it is important to evaluate the dielectric properties at lower frequencies of \(< 100 \text{ Hz}\). However, previous studies performed on the BNT-based ceramics usually report the dielectric properties at higher frequencies. Figure 3 shows the \(f\) dependent dielectric constant and loss of poled BNT-BA-KNN ceramics at room temperature during the \(f\) range of 20–10 kHz. It can be seen that as \(f\) decreases from 10 kHz to 20 Hz, \(\varepsilon_r\) slightly increases and \(\tan \delta\) decreases slightly first and then increases slightly. To be specific, \(\varepsilon_r\) is 514, 536, and 551 and \(\tan \delta\) is 0.029, 0.028, and 0.030 at 1 kHz, 100 Hz, 20 Hz, respectively. The relatively stable dielectric parameters at lower frequencies are favorable for their potential pyroelectric applications.

Figure 4 shows the temperature dependent pyroelectric coefficient on heating calculated according to the following definition:22

\[
P = \frac{dP_r}{dT} = \frac{I(T)}{A \cdot (dT/dt)},
\]

where \(I(T)\) represents the pyroelectric current, \(A\) is the electrode area of the sample, and \(dT/dt\) is the heating rate. At room temperature, a large \(P\) value of \(3.9 \times 10^{-8} \text{ C cm}^{-2}\text{K}^{-1}\) upon heating is achieved, which is comparable to the commercially used PZT pyroelectric ceramics.23 The room temperature \(P\) upon cooling is also measured to be as large as \(3.5 \times 10^{-8} \text{ C cm}^{-2}\text{K}^{-1}\). It should also be noted that due to the higher \(T_d\), the \(P\) value obtained here is slightly lower than that of BNT-BZT22 and La-doped BNT-BT.23 However, a high \(T_d\) is necessary because it defines the upper limit temperature of real pyroelectric-based applications. From the peak of the pyroelectric curve, \(T_d\) is determined as 118 °C, which equals the value of \(T_{F-R}\) recorded from the \(\varepsilon_r-T\) and \(\tan \delta-T\) curves. This is different from the situation of BNT-BT, for which \(T_d\) measured from the pyroelectric current curve locates 10 °C lower than \(T_{F-R}\) recorded from dielectric measurements.32 At \(T_d\), the peak value of the pyroelectric coefficient reaches as high as \(400 \times 10^{-8} \text{ C cm}^{-2}\text{K}^{-1}\). Although this large \(P\) itself is unusable for practical pyroelectric applications due to the irreversibility of the depolarization transition during cooling, the sharp pyroelectric coefficient indicates the undispersed ferroelectric-ergodic relaxor phase transition process, which is helpful for stabilizing the pyroelectric properties when \(T\) is lower than \(T_d\).

The inset of Fig. 4 presents the calculated remanent polarization \(P_r\) of poled BNT-BA-KNN ceramics as a function of temperature. \(P_r\) is achieved by integration of depolarization current according to the following equation:

\[
P_r = \int_{T_1}^{T_2} PdT = \int_{T_1}^{T_2} \frac{I(T)}{A \cdot (dT/dt)} dT,
\]

where \(P\) is the pyroelectric coefficient of the poled BNT-BA-KNN ceramics with the increasing temperature rate of 2 °C/min. The inset shows the remanent polarization as a function of temperature.
where $T_1$ and $T_2$ represent the lower and the upper temperature, respectively. At room temperature, $P_r$ is determined to be 34.6 $\mu$C/cm$^2$, which is consistent with the values recorded from $P-E$ loops in Fig. 2(b). Also, it can be seen that $P_r$ slightly decreases from 34.6 $\mu$C/cm$^2$ to 29.5 $\mu$C/cm$^2$, when temperature increases from 5 $^\circ$C to 100 $^\circ$C. Note that the variation of $P_r$ is less than 15% during this temperature scope. This shows that the ceramics can maintain a stable poled state in a wide temperature window. This is desirable for pyroelectric materials to be used as infrared thermal detectors. When $T$ further increases to near 120 $^\circ$C, a sudden decline of $P_r$ occurs due to the temperature induced ferroelectric-relaxor phase transition, accompanied by the above-discussed sharp pyroelectric peak.

Figure 5 displays the temperature dependent $p$ and FOMs of BNT-BA-KNN ceramics on heating at 1 kHz in the range of RT to 85 $^\circ$C. The $p$ and calculated FOMs of BNT-BA-KNN ceramics at 1 kHz, 100 Hz, and 20 Hz are also given in Table I. Note that an average $p$ value of $3.7 \times 10^{-8}$ Ccm$^{-2}$K$^{-1}$ on heating and cooling is used in this table to calculate the FOMs at different frequencies. Besides BNT-BA-KNN, pyroelectric parameters of other lead-free materials and lead-containing pyroelectric ceramics are also summarized in Table I for comparison.

![FIG. 5. Pyroelectric coefficient $p$ and figures of merit $F_r$, $F_v$, and $F_d$ as a function of temperature on heating at 1 kHz during the range of RT to 85 $^\circ$C.](image)

### TABLE I. A comparison of pyroelectric parameters of the BNT-BA-KNN ceramics, other lead-free materials, and lead-containing ceramics.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\varepsilon_r$</th>
<th>$\tan \delta$</th>
<th>Freq. (Hz)</th>
<th>$T_d$ ($^\circ$C)</th>
<th>$T_m$ ($^\circ$C)</th>
<th>$p$ (10$^{-8}$ Ccm$^{-2}$ K$^{-1}$)</th>
<th>$F_r$ (10$^{-10}$ mV)</th>
<th>$F_v$ (10$^{-2}$ m$^2$/C)</th>
<th>$F_d$ (10$^{-5}$ Pa$^{-1/2}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>BNT-BA-KNN$^a$</td>
<td>514</td>
<td>0.029</td>
<td>1k</td>
<td>118</td>
<td>282</td>
<td>3.7</td>
<td>1.32</td>
<td>2.89</td>
<td>1.15</td>
<td>This work</td>
</tr>
<tr>
<td>BNT-BA-KNN$^a$</td>
<td>536</td>
<td>0.028</td>
<td>100</td>
<td>118</td>
<td>282</td>
<td>3.7</td>
<td>1.32</td>
<td>2.78</td>
<td>1.14</td>
<td>This work</td>
</tr>
<tr>
<td>BNT-BA-KNN$^a$</td>
<td>551</td>
<td>0.030</td>
<td>20</td>
<td>118</td>
<td>...</td>
<td>3.7</td>
<td>1.32</td>
<td>2.70</td>
<td>1.09</td>
<td>This work</td>
</tr>
<tr>
<td>CSBN$^b$</td>
<td>328.7</td>
<td>0.033</td>
<td>1k</td>
<td>200</td>
<td>218</td>
<td>1.24</td>
<td>0.60</td>
<td>2.03</td>
<td>0.61</td>
<td>14</td>
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<tr>
<td>SBN$^c$</td>
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<td>100</td>
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<td>90</td>
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<td>0.98</td>
<td>1.08</td>
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<td>...</td>
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<td>11</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>34</td>
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<td>0.035</td>
<td>100</td>
<td>...</td>
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<td>0.994</td>
<td>1.14</td>
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<td>100</td>
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<td>1.90</td>
<td>0.931</td>
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<td>5.7</td>
<td>2.03</td>
<td>2.18</td>
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<td>...</td>
<td>665</td>
<td>2.3</td>
<td>0.72</td>
<td>17</td>
<td>35.2–4.9</td>
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<tr>
<td>PZT-PMN$^m$</td>
<td>196</td>
<td>0.014</td>
<td>33</td>
<td>118</td>
<td>258</td>
<td>3.16</td>
<td>...</td>
<td>7.3</td>
<td>4.33</td>
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<tr>
<td>PZ-based$^n$</td>
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<td>0.0027</td>
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<td>...</td>
<td>230</td>
<td>3.7</td>
<td>...</td>
<td>6</td>
<td>5.8</td>
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</table>

*0.97(0.9Bi$_0.5Na$_0.5TiO$_3$-0.01BiAlO$_3$)-0.03K$_0.5$Na$_0.5$NbO$_3$ ceramics.
*Ca$_0.2$Sr$_0.1$Ba$_0.7$Nb$_2$O$_6$ ceramics.
*Sr$_0.5$Ba$_0.5$Nb$_2$O$_6$ ceramics.
*Mn-doped 0.97K$_0.5$Na$_0.5$TiO$_3$-0.03(Bi$_0.5$K$_0.5$)TiO$_3$ ceramics.
*(K$_0.5$Na$_0.5$)$_{1-x}$Li$_x$Nb$_2$O$_6$ ceramics.
*K$_0.5$Na$_0.5$TiO$_3$-0.025Pb(Mg$_0.3$Nb$_0.7$)O$_3$ ceramics.
*0.93(Bi$_0.5$Na$_0.5$)$_3$Ti$_0.3$Zr$_0.7$O$_2$ ceramics.
*0.71(Bi$_0.5$Na$_0.5$)$_3$Ti$_0.3$Zr$_0.7$O$_2$ ceramics.
*La$_2$Ta$_2$O$_7$ ceramics.
*K$_0.5$Na$_0.5$TiO$_3$-0.05BaTiO$_3$ crystals.
*LiTaO$_3$ crystals.
*Mn-doped 0.975Pb(Zr$_{0.52}$Ti$_{0.48}$)$_2$O$_3$-0.025Pb(Mg$_{0.3}$Nb$_{0.7}$)O$_3$ ceramics.
pyroelectric ceramics. At room temperature, the obtained $F_r$, $F_v$, and $F_d$ of BNT-BA-KNN can be as high as 1.32 $\times$ 10$^{-16}$ m/V, 2.89 $\times$ 10$^{-2}$ m$^2$/C, and 1.15 $\times$ 10$^{-5}$ Pa$^{-1/2}$ at 1 kHz and 1.32 $\times$ 10$^{-16}$ m/V, 2.70 $\times$ 10$^{-2}$ m$^2$/C, and 1.09 $\times$ 10$^{-5}$ Pa$^{-1/2}$ at 20 Hz, respectively. The high pyroelectric coefficient and the relatively lower dielectric constant ($\sim$50) and lower dielectric loss ($\sim$0.03) compared with other lead-free ceramics all contribute to the enhancement of FOMs. More importantly, the values of $p$, $F_r$, $F_v$, and $F_d$ can remain relatively stable in the studied temperature scope of RT to 85 °C. Specifically, $F_v$ and $F_d$ vary only $\pm$2%. It should be stressed that although the room temperature $p$ is a bit smaller than those obtained in 0.93BNT-0.07BZT$^{22}$ and La-doped BNT-BT,$^{23}$ the good temperature stability during the wide temperature range together with the higher FOMs of BNT-BA-KNN pyroelectric ceramics is powerfully in favor of their applicability.

In summary, the microstructure, dielectric, and pyroelectric properties of ternary lead-free 0.97(0.99Bi$_{0.5}$Na$_{0.5}$TiO$_3$-0.03K$_{0.5}$Na$_{0.5}$NbO$_3$) compared with 0.93BNT-0.07BZT$^{22}$ and BNT-BT$^{23}$ can reach 3.7 $\times$ 10$^{-8}$ C cm$^{-2}$K$^{-1}$, 1.32 $\times$ 10$^{-10}$ m/V, 2.89 $\times$ 10$^{-2}$ m$^2$/C, and 1.15 $\times$ 10$^{-5}$ Pa$^{-1/2}$ at 1 kHz, respectively. At depolarization temperature, a large and sharp pyroelectric coefficient of 400 $\times$ 10$^{-8}$ C cm$^{-2}$K$^{-1}$ was also obtained due to the ferroelectric-ferroelastic relaxor phase transition. The sharp $p$ peak and high $T_d$ contribute to the temperature stability of pyroelectric properties. The values of the voltage responsivity and detectivity can maintain good stability with a variation of $\pm$2%. The overall excellent pyroelectric performance of the BNT-BA-KNN indicates that the ceramics should be promising lead-free alternatives which have great potential for uncooled infrared detector applications.

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