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# Phase structures, electrical properties and temperature stability of $(1-x)[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$–$x$BiFeO$_3$ ceramics

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ABSTRACT

The addition of BiFeO$_3$ in the ceramics shifts the PPT below room temperature to improve the temperature stability of KNN-based ceramics. The phase structure, microstructure, dielectric, piezoelectric properties and temperature stability of $(1-x)[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$–$x$BiFeO$_3$ piezoelectric ceramics were investigated. The phase structure of these ceramics changed from tetragonal phase to pseudo cubic phase with BiFeO$_3$ additives. The optimal piezoelectric properties were obtained at $x = 0.004$, which were listed as follows: $d_{33} = 261$ pC/N, tan $\delta = 0.016$, $K_p = 0.58$, $T_c = 345\,^\circ$C and $\varepsilon_r = 1116$. Especially, the results demonstrated that the PPT of $(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$ ceramics has been shifted below room temperature successfully by the addition of BiFeO$_3$. The time stability and ageing rate values of the ceramics with $x = 0.000$ were 15% and 7.8%. These values decrease to 4.97% and 6.09% at $x = 0.004$, respectively, showing that the ceramics have better temperature and time stability for the polymorphic phase transition below room temperature.

## 1. Introduction

Pb(Zr, Ti)O$_3$ (PZT) based piezoelectric ceramics are widely used because they have good piezoelectric properties. However, these ceramics with toxic lead element will cause a crucial environmental pollution and human health problems [1–3]. In recent years, environmental regulations (RoHS, etc.) have been enforced in the European Union. Some lead based piezoelectric devices may be forbidden in future. Therefore, the development of lead-free piezoelectric ceramics has recently attracted much attention [4].

Recently, lead-free (K, Na)NbO$_3$ (KNN-based) ceramics have attracted special attention for their excellent piezoelectric properties, high Curie temperature and environmental friendliness. A variety of additions have been added into KNN to form new KNN-based ceramics to improve the electrical properties [5–8]. The improved electrical properties of ceramics could be attributed to the existence of the polymorphic phase transition ($T_{o-t}$) near room temperature [9]. Therefore, in order to obtain excellent electrical properties in $(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$ (KNLNT) based ceramics, it is necessary to make the ($T_{o-t}$) approach room temperature. However, it has been found that these KNLNT ceramics possessed low temperature and time stabilities, which limited the practical applications. Therefore it will be useful to prepare KNLNT ceramics with high temperature and time stability along with high piezoelectric properties. In order to solve the above problems, the electrical properties and temperature stability of KNN-based ceramics are improved by using modifications (NiO, AgTaO$_3$, BiCoO$_3$, and CaTiO$_3$, etc.) but the favorable values can be hardly simultaneously obtained [10–16].According to our previous work, $[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$ ceramics obtain optimal properties by ordinary sintering in air and carefully control the process conditions [17]. In this work, BiFeO$_3$ was introduced to the KNLNT ceramics to form $(1-x)[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$–$x$BiFeO$_3$ ceramics in order to improve electrical properties, the temperature and time stabilities of KNLNT ceramics. The effects of the BF content on the phase structure, microstructure, density, dielectric, piezoelectric, temperature and time stability of the $(1-x)$KNLNT–$x$BF ceramics were investigated systemically.

## 2. Experimental

Na$_2$CO$_3$ (99.8%), K$_2$CO$_3$ (99%), Li$_2$CO$_3$ (98%), Nb$_2$O$_5$ (99.9%), Ta$_2$O$_5$ (99.99%), Bi$_2$O$_3$ (99%) and Fe$_2$O$_3$ (99%) were used to prepare $(1-x)[(K_{0.458}Na_{0.542})_{0.96}Li_{0.04}](Nb_{0.85}Ta_{0.15})O_3$–$x$BiFeO$_3$ ($x = 0$–$0.016$) ceramics by conventional mixed oxide method. The stoichiometry powders are mixed by ball milling in ethanol for 16 h, then dried and calcined at 850 °C for 9 h. The calcined powders are mixed with 5 wt% polyvinyl alcohol (PVA) solution and then pressed into pellets with a diameter of 1.5 cm under 100 MPa pressure. After burning off PVA at 500 °C for 2 h, the samples are sintered at 1130 °C for 3.5 h. Silver paste was fired at 800 °C on both faces of the samples as the electrodes. Samples for piezoelectric measurements were poled under 3.5 kV/mm for 15–20 min at 80 °C in a silicone oil bath. The electrical properties of all ceramics were measured more than 24 h later.

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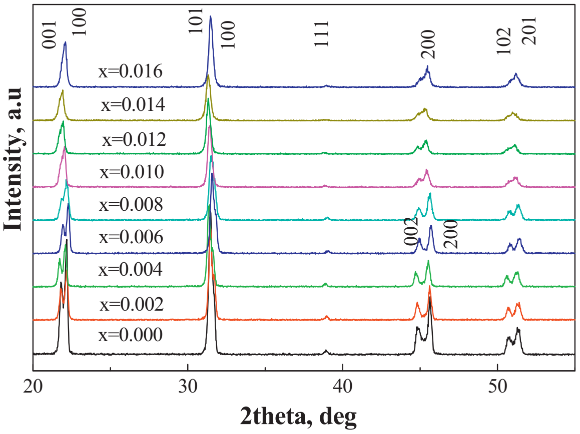

**Fig. 1.** The XRD patterns of the ceramics with different $BiFeO_3$ contents.

Phase structure of the ceramics was measured by X-ray diffraction (XRD) (*D*/max-2200, Rigaku, Japan, Cu Kα) at room temperature. Surface microstructures of the ceramics were observed using a scanning electron microscopy (SEM) (model Quanta200, FEI Co). Density is measured by the Archimedes method with distilled water. Dielectric properties were obtained using an Agilent E4980A by measuring the capacitance (*C*), dielectric constant $\varepsilon_r$ and dielectric loss $\tan\delta$ at 1 kHz, 10 kHz, and 100 kHz as a function of temperature. The piezoelectric constant $d_{33}$ was recorded at room temperature from one day aged samples using a quasi static piezoelectric $d_{33}$ meter (ZJ-3d, China). The planar electromechanical coupling coefficient ($K_p$) is determined at room temperature by the resonance and anti-resonance techniques using an impedance analyzer (4294A).

## 3. Results and discussion

Fig. 1 shows the XRD patterns of the KNLNT ceramics with different BF contents. It can be seen that pure perovskite structure is formed in the composition range of $x = 0.000$–$0.016$. Moreover, it is found that the positions of the diffraction peak of the ceramics shifted to higher angles with the increase of BF content. For the ceramics with $x = 0.000$, two diffraction peaks (0 0 2) and (2 0 0) can be observed, indicating the ceramics are of tetragonal phase. The split of the peaks (0 0 2) and (2 0 0) can also be seen by increasing *x* from 0.000 to 0.008. However, further increasing *x* to 0.010, those two peaks begin to merge into one peak. Only one peak (2 0 0) exists at $x = 0.016$, which suggests the ceramics may be of the pseudo cubic phase. The XRD pattern around $x = 0.010$–$0.016$ shows mixed phases. The results indicate that the BF has completely diffused into the KNLNT lattice to form a new solid solution when $x \leq 0.016$, and the transition point for the structural change can be confirmed to be around $x = 0.010$–$0.016$. These results indicate that the BF has completely diffused into the KNLNT lattice to form a new solution when the content of $0.000 \leq x \leq 0.016$. As a result, it is feasible that the KNLNT ceramics are prepared with a small amount of BF.

Fig. 2 shows SEM images of the surface of the ceramics with different BF contents. With increasing the BF amount, the grain size decreases. It can clearly be seen that the grain size is about 1.5 μm at $x = 0.000$ in Fig. 2(a), and decreases to 0.5 μm for the sample at $x = 0.008$ in Fig. 2(d). The ceramics with $x = 0.004$ possess the microstructure of well faceted and quite uniformly distributed fine grains. This uniform and fine grain microstructure is preferable as it will lead to higher mechanical strength. However, many large pores and inhomogeneous microstructure can be seen in the ceramics at $x = 0.008$ which may be the result of the abnormal grain growth behavior, while high amount of BF makes the microstructure of the ceramics deteriorate seriously. According to the above results, it is evident that the addition of $Bi^{3+}$ and $Fe^{3+}$ can assist the densification of the ceramics and improve the sinter ability of the ceramics. The may be related to the low melting point (930 °C) of BF compounds which promote the formation of a transitory liquid phase during sintering [18,19].

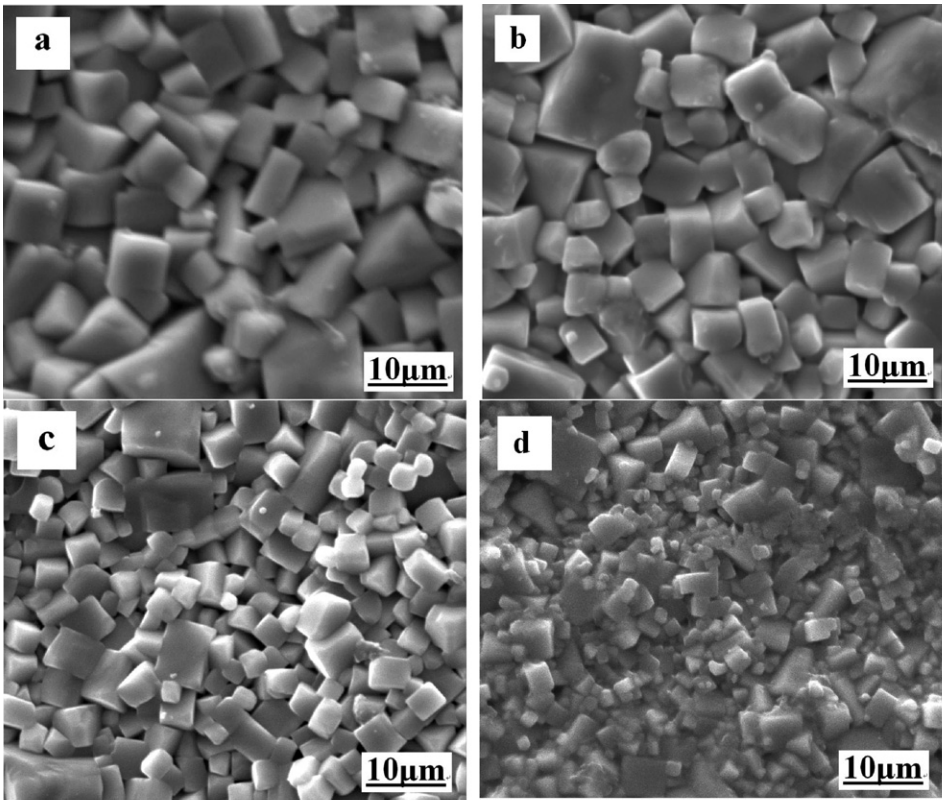

**Fig. 2.** The SEM photographs of the surface of the ceramics with different $BiFeO_3$ contents: (a) $x = 0.000$, (b) $x = 0.002$, (c) $x = 0.004$, (d) $x = 0.008$.

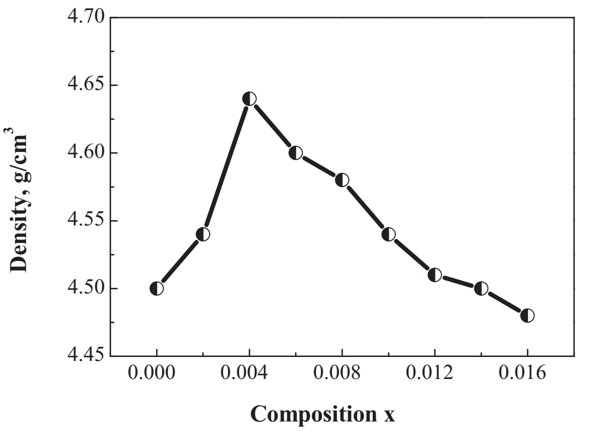

**Fig. 3.** Density of KNLNT ceramics with different BiFeO$_3$ contents.

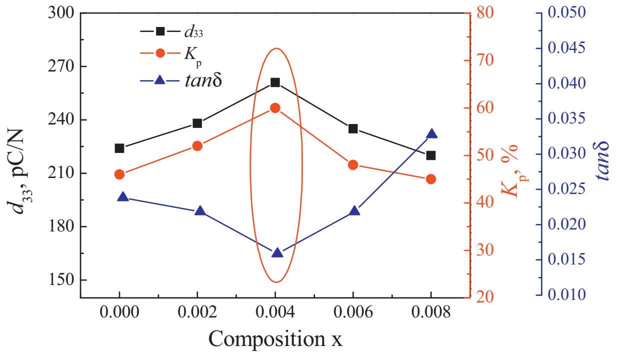

**Fig. 4.** $d_{33}$, $K_p$, $Q_m$ of KNLNT ceramics with different BiFeO$_3$ contents.

Fig. 3 shows the density of the KNLNT-based ceramics with different BF contents. The highest density ($\rho = 4.64\,g/cm^3$) is obtained at $x = 0.004$. Further increasing $x$ above 0.004 leads to the decrease of density. The variation of the density of BF doped ceramics is consistent with the SEM photographs results showed in Fig. 2. It is believed that a very small amount of addition promotes the formation of liquid phase and is helpful for densification of the ceramics.

$d_{33}$, $K_p$ and tan$\delta$ of the KNLNT ceramics with different BF contents are shown in Fig. 4. The electrical properties of $(1-x)$KNLNT–$x$BF ceramics show a strong dependence on compositions. By adding a small amount of BF to KNLNT ceramics, the piezoelectric properties increase clearly. However, further additions of BF makes the piezoelectric properties deteriorate markedly. $d_{33}$ and $K_p$ increase firstly, reach the maximum values at $x = 0.004$, and then decrease subsequently with further increasing BF contents. Besides, tan$\delta$ of the KNLNT ceramics show an opposite tendency with $d_{33}$ and $K_{p.}$ tan$\delta$ decreases gradually to the minimum value at $x = 0.004$, and then increases clearly with further increasing BF content to $x = 0.008$. The optimal properties are obtained at $x = 0.004$, which are as follows: $d_{33} = 261$ pC/N, $K_p = 0.58$ and tan $\delta = 0.016$.

The temperature dependence of $\varepsilon_r$ for $(1-x)$KNLNT–$x$BF ($x = 0.000$, 0.002, 0.004, 0.006, 0.008, 0.010, 0.016) ceramics measured at different frequencies is shown in Fig. 5. The tetragonal and cubic phase transition temperature ($T_c$) and the orthorhombic and tetragonal phase transition temperature ($T_{o-t}$) are observed in Fig. 5, and the $T_{o-t}$ of the ceramics appears (above room temperature) with the addition of BF. As shown in Fig. 5, for the ceramics with $x = 0.000$–0.008, the curves are relatively flat at low temperatures. $\varepsilon_r$ increase rapidly further increasing temperature and reach the maximum value, then $\varepsilon_m$ begins to decrease markedly. The peaks of $\varepsilon_m$ at higher temperature are associated to the tetragonal to cubic phase transition. Besides, pure KNN ceramics are known to undergo two phase-transitions, which are from orthorhombic to tetragonal ($T_{o-t}$) and from tetragonal to cubic ($T_c$), respectively [20]. Interestingly, a different variation trend can be observed at $x = 0.010$ and 0.016. As the temperature increases, $\varepsilon_r$ peak occurs at around 120 °C, and then another $\varepsilon_r$ peak related to tetragonal to cubic phase transition appears. The different phenomenon observed may result from the fact that the ceramics at $x = 0.016$ have a pseudo cubic phase structure, low density, and poor microstructure at room temperature. As also seen in Fig. 5, $T_c$ decreases gradually with increasing the BF contents. The $T_c$ of the ceramics decreases from 359 °C to 278 °C as BF increases from 0.000 to 0.016. As a result, the BF decreases the $T_c$ of the $(1-x)$KNLNT–xBF ceramics and shifts the orthorhombic and tetragonal phase transition above room temperature. Usually, the polymorphic phase transition (PPT) near or at room temperature is responsible for the improved piezoelectric properties of KNN-based ceramics [21]. The PPT of the ceramics was not observed for $x = 0.000$–0.0008. In other words, the PPT of the ceramics almost disappears (below room temperature and even to the extent that below zero). The addition of BiFeO$_3$ from 0.010 to 0.016 in the ceramics decreases the Curie temperature and shifts the PPT above room temperature,

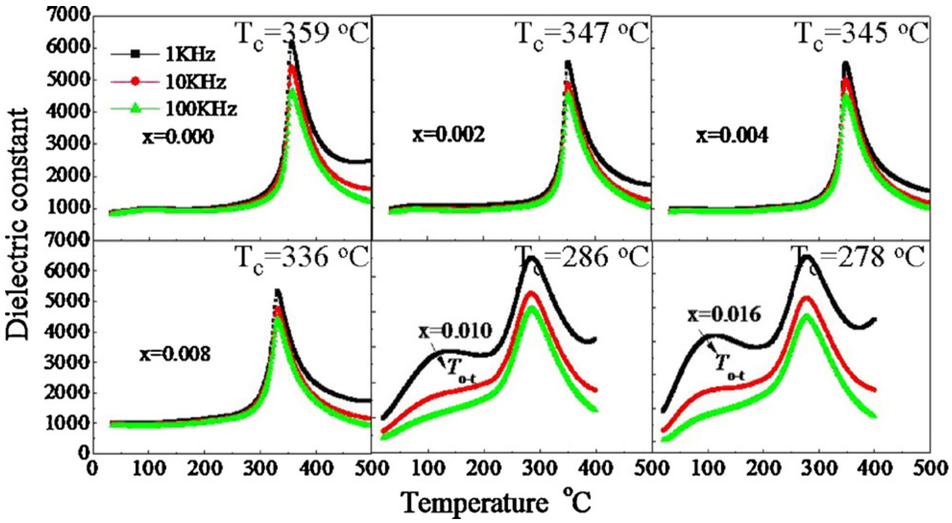

**Fig. 5.** The temperature dependence of $\varepsilon_r$ for $(1-x)$KNLNT–$x$BF ($x = 0.000$, 0.002, 0.004, 0.006, 0.008, 0.01, 0.016) ceramics measured at different frequencies.

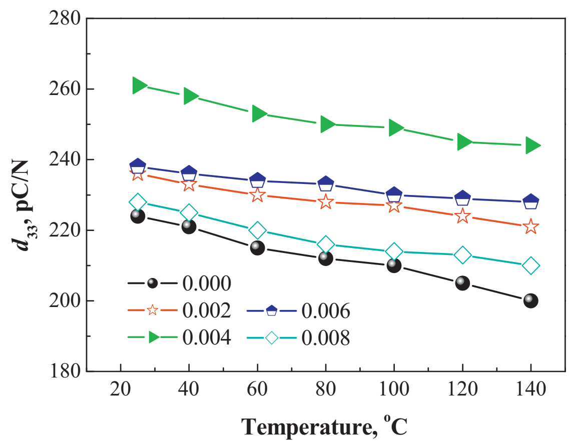

**Fig. 6.** Temperature dependence of $d_{33}$ for the ceramics with different $BiFeO_3$ contents.

owing to the Bi substitution for $K^+$ or $Na^+$ site and the decrease in grain size. As a result, good temperature stability and piezoelectric properties are obtained which should be attributed to the optimum $BiFeO_3$ content in the ceramics. But the orthorhombic and tetragonal phase transition above room temperature is not helpful to improve the temperature stability of KNN-based ceramics with $x = 0.010–0.016$ [22,23].

Fig. 6 shows the temperature dependence of $d_{33}$ for the ceramics with different BF contents. It can be seen that $d_{33}$ decreases gradually with increasing the temperature. $d_{33}$ values of the ceramics measured at 25 °C with $x = 0.000$ and $x = 0.004$ are 224 pC/N and 261 pC/N, respectively. By increasing the temperature to 140 °C, $d_{33}$ values decrease to 200 pC/N ($x = 0.000$) and 244 pC/N ($x = 0.004$). The ageing rate value of the ceramics with 0.004 is 6.5%, which is lower than that of the ceramics with $x = 0.000$ (10.7%). The results of Fig. 6 show that temperature stability of the ceramics is improved when adding a small amount of BF.

The favorable properties, optimal temperature and time stability are very important. To satisfy the requirement of piezoelectric devices, piezoelectric materials should combine high properties and good stability (time stability, temperature stability, and so on) simultaneously because characteristics of the piezoelectric devices deteriorate with increasing time. This means that the piezoelectric materials with time stability improved enjoy having a good application value. The piezoelectric ceramics was ageing about 240 days at room temperature in order to measured and calculated degree of ageing for the application of the piezoelectric materials. Formula (1) states ageing rate of the ceramics. $d_{33}$ shows some parameter of the electrical properties, $d_{33t_1}$ shows piezoelectric properties of unit time (one day) that the ceramics was poled, $d_{33t}$ shows piezoelectric properties of days (240 days) that the ceramics was poled. $t_1$ shows unit time that the ceramics was poled, $t$ shows days that the ceramics was poled. $A$ shows degree of ageing that is constant. $|A|$ shows that the value is lower, the better.

$$\frac{d_{33t} - d_{33t_1}}{d_{33t_1}} = A_1 g \frac{t}{t_1} \qquad (1)$$

Fig. 7 shows time stability ($|A|$) and ageing rate ($d_{33} - d_{33t}/d_{33}$) of the ceramics with different BF contents. Time stability and ageing rate decrease firstly and increase subsequently with increasing BF contents. The time stability and ageing rate values of the ceramics with $x = 0.000$ are 15% and 7.8%, while the values decrease to 4.97% and 6.09% respectively when increasing $x$ to 0.004, showing that the ceramics with $x = 0.004$ have better time stability. In summary, a small amount of BF can improve time stability of the KNLNT ceramics.

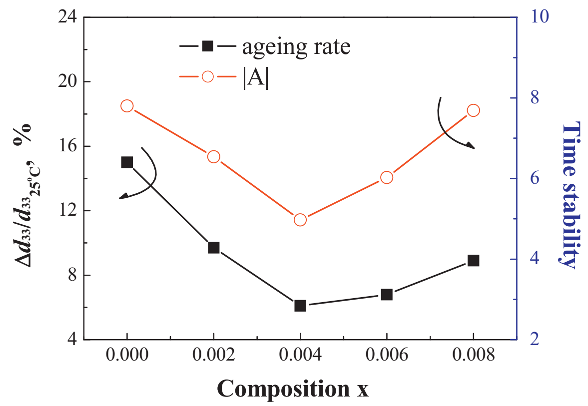

**Fig. 7.** The time dependence of $|A|$ and ageing rate for the ceramics with different $BiFeO_3$ contents.

## 4. Conclusions

The effects of the BF content on the phase structure, microstructure, density, dielectric, piezoelectric and stability of the $(1 - x)$KNLNT–$x$BF ceramics were investigated. The 0.004 $BiFeO_3$ substitutions not only increased the electrical properties of the ceramics, which enabled us to observe the changed phase from tetragonal phase to pseudo cubic phase but also led to the increase of the temperature and time stabilities of the ceramics. The phase structure changed from the tetragonal to pseudo cubic phase by increasing $x$ from 0.000 to 0.016. But for the ceramics with $x \geq 0.010$, except for the $\varepsilon_r$ peak related to tetragonal to cubic phase transition at $T_c$, another $\varepsilon_r$ peak could also be observed at around 120 °C due to the pseudo cubic phase structure, low density, and poor microstructure of the ceramics. By adding a small amount of BF to KNLNT ceramics, the piezoelectric properties increased clearly. However, further additions of BF makes the piezoelectric properties deteriorate markedly. The optimized electrical properties at $x = 0.004$ were as follows: $d_{33} = 261$ pC/N, $\tan\delta = 0.016$, $K_p = 0.58$, $T_c = 345$ °C, $\varepsilon_r = 1116$. The addition of $BiFeO_3$ in the ceramics shifted the PPT below room temperature even zero. And a small amount of $BiFeO_3$ could improve the time and temperature stability of KNLNT-based ceramics. The results showed that $BiFeO_3$ was a promising addition for obtaining optimized properties in KNLNT ceramics for applications in devices.

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