# Improvement in the piezoelectric temperature stability of $(K_{0.5}Na_{0.5})NbO_3$ ceramics

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Through an analysis of the temperature stability of $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based ceramics and KNN solid solutions, we propose a method to enhance the temperature stability of KNN materials. These materials are valuable for their piezoelectric properties. To verify the feasibility of this method, $0.9 (K_{1-x}Na_x) NbO_3$-$0.06LiNbO_3$-$0.04CaTiO_3$ (KNLN-CaTiO_3) ceramics were designed, and their structure and properties were studied. The results show that KNLN-CaTiO_3($x = 0.54$) ceramics have a good temperature stability over a wide temperature range (25–320°C). Also, they have good piezoelectric properties ($d_{33}$=152 pC/N in $x$=0.54). This result confirms the feasibility of our proposed solution for improving the piezoelectric properties of KNN-based ceramics that have poor temperature stability.

$(K_{0.5}Na_{0.5})NbO_3$, morphotropic phase boundary, piezoelectric, temperature stability

Piezoelectric ceramics are a type of functional material that allow for the exchange between mechanical motion and electricity. Piezoelectric ceramics have been applied in military, automotive, commerce, and medical industries [1,2]. $Pb(Zr,Ti)O_3$ (PZT) has been applied widely because of its excellent piezoelectric properties. However, conventional piezoelectric ceramics or single crystals are primarily Pb-based perovskite materials. Lead poses a great threat to the environment. Thus, it is important to research and develop lead-free piezoelectric materials [3–5].

Recently, $(K_{0.5}Na_{0.5})NbO_3$ (KNN) based lead-free piezoelectric ceramics have attracted a great deal of attention. This is because KNN-based lead-free materials exhibit not only highly piezoelectric properties (200–300 pC/N) and high Curie temperatures (350–420°C) [6–17], but also good compatibility with the human body. Therefore, KNN based lead-free piezoelectric ceramics are an ideal substitution for PZT materials [2]. However, currently, a limiting factor for KNN-based ceramics is that they have poor temperature stability. Hollenstein et al. demonstrated that the piezoelectric properties of $0.94(K_{0.5}Na_{0.5})NbO_3$–$0.06LiNbO_3$ ceramics can decrease as much as 30% [18] when the working temperature deviates from room temperature. Low piezoelectric temperature stability limits the application of KNN-based ceramics. Therefore, improving the piezoelectric temperature stability has become a hot topic for research [19–21]. This paper presents a new approach to improving the piezoelectric temperature stability of $(K_{0.5}Na_{0.5})NbO_3$ ceramics. Also, we verified this approach experimentally.

## 1   Research idea

Studies have shown that the reason for the poor piezoelectric temperature stability of KNN based ceramics is their polymorphic phase transition (PPT) near room temperature

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[5,10–15]. For this reason, Zhang et al. and our research group [19,22] have both proposed shifting the PPT below room temperature by adding new components. These results show it is possible to improve the piezoelectric temperature stability. However, the piezoelectric constant decreases quickly with the addition of these new components. Therefore, we must seek a new approach for improving the piezoelectric temperature stability that maintains a high piezoelectric constant.

A recent study showed that the Na–K ratio has a large effect on the piezoelectric properties of KNN-based ceramics [23,24]. Zhang et al. showed that for pure KNN ceramics there is a phase boundary when the Na–K ratio is 52/48. This phase boundary separates two different orthorhombic phases and two different tetragonal phases when the temperature is higher than 200°C. This phase boundary is similar to the morphotropic phase boundary (MPB) in PZT ceramics. Therefore, pure KNN ceramics exhibit high piezoelectric properties [23]. Using the above analysis, we proposed a new approach to improving the piezoelectric temperature stability and maintaining the high piezoelectric constant. This new approach is to shift the PPT below room temperature by adding new components. Then, to improve the piezoelectric properties, we will identify the phase boundary separating the two different tetragonal phases by adjusting the Na–K ratio.

To verify the feasibility of this approach, an experiment was designed. There are three aspects to this experiment. First, according to [19], $Ca^{2+}$ substitution at the A site cannot significantly affect the Curie temperature, but the PPT temperature will decrease rapidly. Thus, we introduce $CaTiO_3$ into KNN, and shift the PPT temperature below room temperature. Second, $LiNbO_3$ is introduced into the KNN to improve the Curie temperature, because of the high Curie temperature of $LiNbO_3$ (~1210°C). Third, in the KNN phase diagram, a vertical line can be seen near $x$=0.52. The two ferroelectric phases separated by this line are slightly different. They have different orthorhombic phases (FO1 and FO2) and different tetragonal phases (FT1 and FT2). Because this line is similar to the MPB in PZT, we hope that the corresponding component, which can tune this parameter, can be found. Thus, a high piezoelectric constant and high temperature stability can be attained at the same time. Therefore, the optimal components can be found by adjusting the Na–K ratio. This will lead to a high piezoelectric constant and high temperature stability in KNN-based lead-free ceramics. According to the above analysis, the formula is $0.9(K_{1-x}Na_x)NbO_3$-$0.06LiNbO_3$-$0.04CaTiO_3$. The structure and properties of this compound are presented in this paper.

## 2 Experimental procedure

$0.9K_{1-x}Na_xNbO_3$-$0.06LiNbO_3$-$0.04CaTiO_3$ (KNLN–CaTiO₃,

$x$=0.50, 0.52, 0.54 and 0.56) ceramics were prepared using a conventional solid-state sintering method. Reagent-grade oxide and carbonate powders of $K_2CO_3$(≥99%), $Na_2CO_3$ (≥99.8%), $Li_2CO_3$(≥98%), $Nb_2O_5$(≥99.99%), $CaCO_3$(≥99%) (state chemical reagent group company, Hefei, China), and $TiO_2$(≥99%) were used as starting materials. Before being weighed, these powders were separately dried in an oven at 120°C for 5 h, milled for 24 h via planetary milling with a zirconia ball media and ethanol, and calcined at 860°C for 4 h in a crucible with a lid. Then, these powders were ball-milled again for 12 h, dried, and pressed into disks with diameters of 12 mm and thicknesses of 1 mm at 300 MPa. For the pressing, we used 5 wt% polyvinyl alcohol (PVA) as the binder. After the PVA was burned off, the pellets were sintered at 1140°C for 2 h in sealed $Al_2O_3$ crucibles with lids. Silver paste was sintered onto both sides of the samples at 810°C for 20 min to serve as electrodes for the measurements.

The microstructure evolution was observed using scanning electron microscopy (SEM) (model JSM-6360, JEOL, Tokyo, Japan). The dielectric spectral measurements were performed using a LCR meter (TH2816, Tonghui Electronics, Changzhou, China) at a heating rate of 2°C/min over the temperature range of 25–500°C and the frequency range of 1–100 kHz. The samples were painted with silver paste and poled in silicone oil at 3 kV/mm for 15 min at 80°C. The piezoelectric constant was measured using a piezoelectric $d_{33}$-meter (Chinese Academy of Sciences, Beijing, ZJ-3A).

## 3 Results and discussion

### 3.1 Phase structure and microstructure

Figure 1(a) shows the XRD patterns for the KNLN-CT ceramics as a function of $x$ ($x$=0.50, 0.52, 0.54 and 0.56). Figure 1(b) shows the corresponding expanded XRD patterns of KNLiN and KNLaN ceramics over the range, $2\theta$ from 40° to 50°. For KNLN-CT ceramics, a pure perovskite structure can be obtained with different Na–K ratios. This material has been previously reported to have a changing symmetry with different Na–K ratios [22]. The characteristic peaks of the tetragonal phases can be seen for $x$=0.50, 0.52 and 0.56. Also, three peaks with different shapes can be seen among the 45° characteristic peaks. This demonstrates a change in lattice constant. When $x$=0.54, two characteristic peaks can be seen among the 45° characteristic peaks, and three peaks can be found for the other three components. This shows that the phase at $x$=0.54 is a mixed phase with different tetragonal phases. Also, this phase structure can be verified using the dielectric temperature figure. Figure 2(a)–(d) shows SEM micrographs of fractured surface of the KNLN-CT ceramics sintered at 1140°C for 2 h. It can be seen that the grain sizes of all the KNLN-CT ceramics change slightly, and that the average grain size is 1 μm. Pores cannot be seen and the crystal boundary is clear.
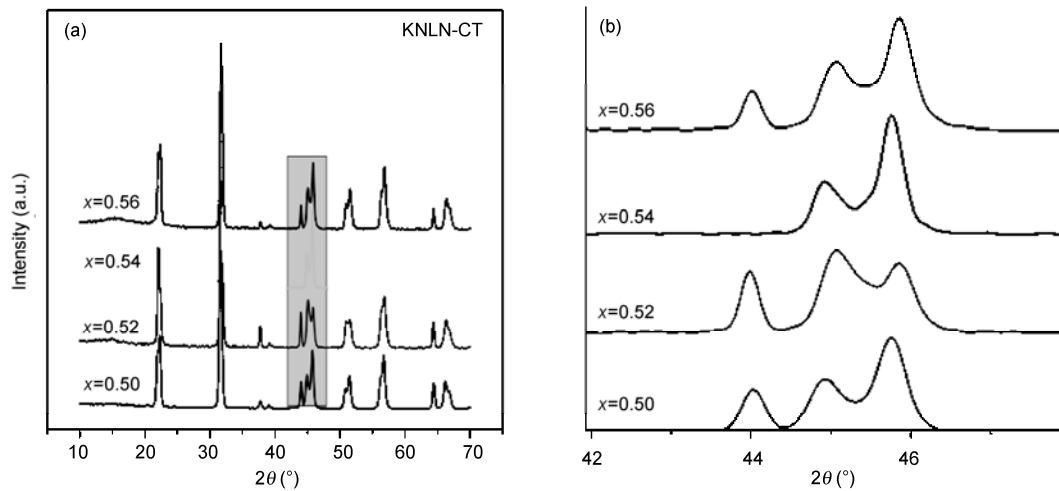
**Figure 1**   X-ray powder diffraction pattern of the KNLN-CT ceramics as a function of *x* (*x*=0.50, 0.52, 0.54 and 0.56) at room temperature (25°C).
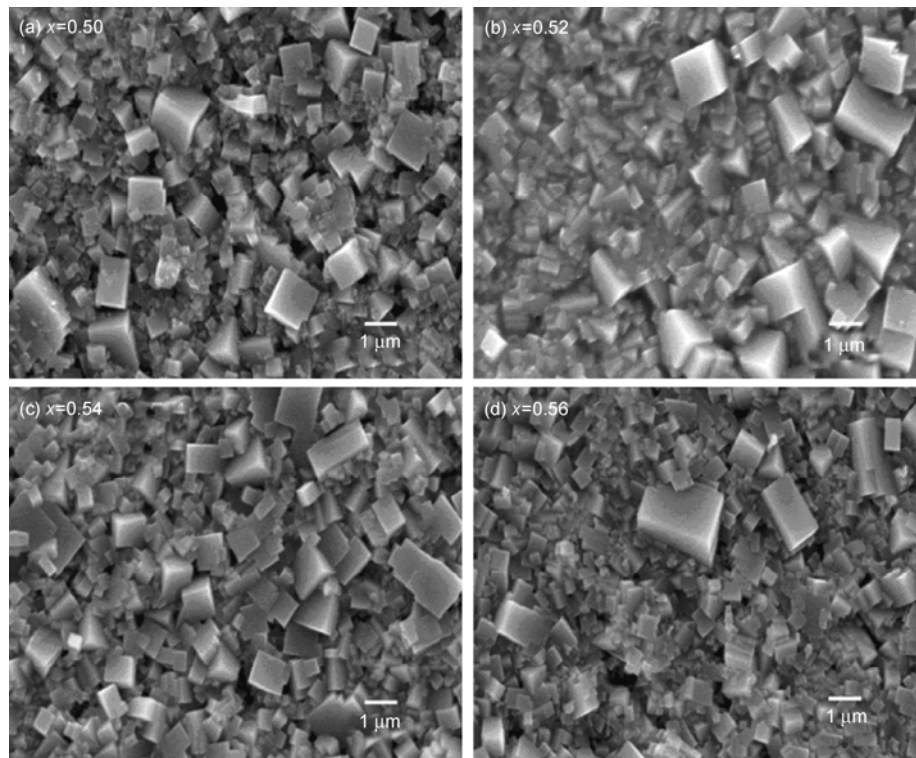


**Figure 2**   SEM micrographs of fractured surface of the KNLN-CT ceramics as a function of *x* (*x*=0.50, 0.52, 0.54 and 0.56).

This shows that all KNLN-CT ceramics are very dense.

## 3.2   Dielectric properties

The dielectric temperature spectrum is an effective tool for studying the ferroelectric phase transformation. This is because a peak can be seen in dielectric temperature spectrum when the ferroelectric phase structure changes. Figure 3(a) is dielectric temperature spectrum (100 kHz) for the KNLN-CT ceramics. It can be seen that the Na–K ratio has a slight effect on the Curie temperature of the KNLN-CT

ceramics, and that the Curie temperature is near 360°C. This Curie temperature is higher than that of previous reports [19]. This is because $LiNbO_3$ has a high Curie temperature (1210°C), and its introduction improved the Curie temperature of the KNN ceramics. It can be also seen that dielectric peak increases and then decreases with increasing Na–K ratio. When *x*=0.54, the dielectric constant reaches its maximum at $\varepsilon_{max}$=2323. Figure 3(b) shows the expanded PPT patterns of the KNLN-CT ceramics. It can be seen that all the PPT temperatures are about –40°C. This demonstrates that it is a tetragonal structure at room temperature,
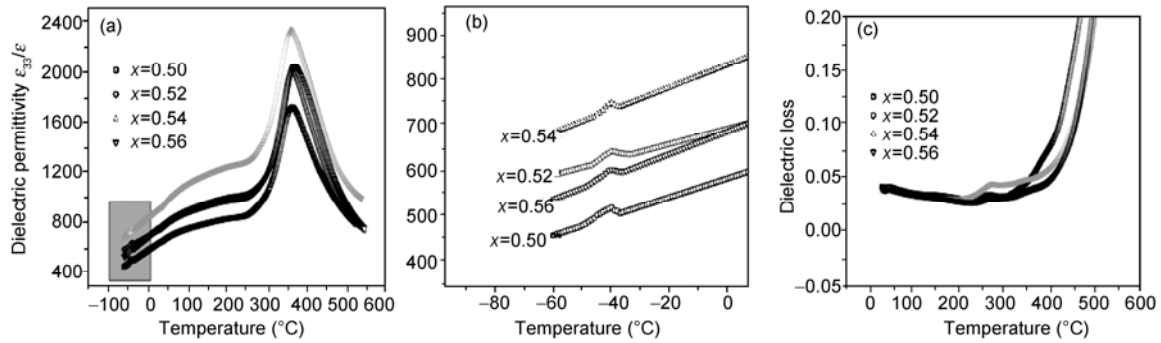
**Figure 3** Dielectric permittivity and loss for the KNLN-CT ceramics as a function of temperature.

which is consistent with the analysis from Figure 1. The shift of the PPT temperature below room temperature was effective in improving the piezoelectric temperature stability. Figure 3(c) shows the dielectric loss of the KNLN-CT ceramics with different Na–K ratios. In this figure, it can be seen that the dielectric loss tanδ is below 0.05 between 25–350°C, which is important for engineering applications.
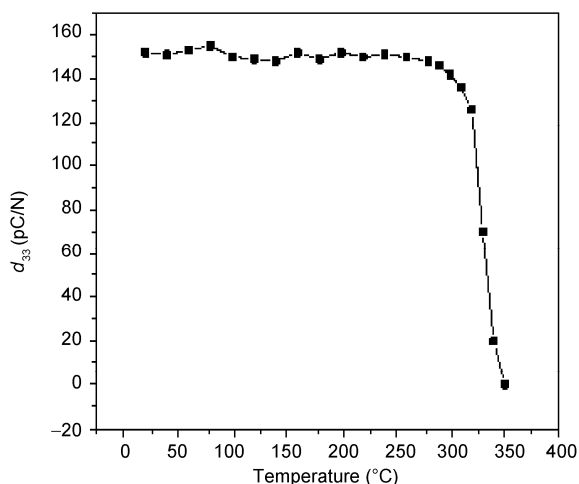
### 3.3 Piezoelectric properties

Figure 4 shows the piezoelectric properties of the KNLN-CT ceramics as a function of composition at room temperature. It can be seen that the Na–K ratio affects the piezoelectric constant. The piezoelectric constant increases and then decreases with increasing $x$. The piezoelectric constant reaches its maximum $d_{33}$=152 pC/N at $x$=0.54. This is because the KNLN-CT ceramic is at the MPB of the tetragonal phases when $x$=0.54, and at this position, the domains can be easily oriented. Therefore, they possess high piezoelectric activity. In addition, compared with previous studies, this piezoelectric constant is not very high and can be explained from two facts. First, when $x$=0.54, the MPB of KNLN-CT ceramics is different from that of PZT. The MPB of PZT ceramics is in a mixed phase with rhombohedral and tetragonal phases. However, the MPB of KNLN-CT ceramics is in a mixed phase of different tetragonal phases. These two phases are both tetragonal phases, and only differ slightly in their lattice constant. This can be extracted from the XRD trace in Figure 1. Therefore, no additional polarization is produced, and the improvement of piezoelectric activity is limited. Second, the low piezoelectric constant is related to the introduction of $CaTiO_3$. Part of the $K^+$ and $Na^+$ ions at the A site are replaced by $Ca^{2+}$, and this donor substitution produces A vacant site. According to Cochran theory [25], A-site cations have a large coupling effect on the $BO_6$ octahedra in the $ABO_3$ perovskite structure, and the $Ca^{2+}$ donor substitution at the A-site produces a vacancy. This is detrimental to the coupling effect, limits the growth of nanosized polar regions and weakens spontaneous polarization, which leads to low piezoelectric activity. Also, introducing $CaTiO_3$ to KNN can induce relaxor

characteristics, which would contribute to this process [19]. Figure 5 shows the piezoelectric properties of KNLN-CT ($x$=0.54) as a function of temperature. It can be seen that the change in the piezoelectric constant is small over the temperature range, 25–320°C, which shows high piezoelectric temperature stability in this KNLN-CT($x$=0.54) ceramic.

According to the above analysis, KNLN-CT($x$=0.54) ceramic can have both high piezoelectric temperature stability and optimal piezoelectric constants (152 pC/N). The primary reason is that the introduction of $LiNbO_3$ and $CaTiO_3$ shifted the PPT temperature below room temperature (–40°C). Thus, KNLN-CT($x$=0.54) ceramics possesses high piezoelectric temperature stability. When $x$=0.54, KNLN-CT ceramics possess an MPB similar to PZT. Thus, KNLN-CT($x$=0.54) has a relatively high piezoelectric constant. However, although the piezoelectric constants (152 pC/N) of KNLN-CT($x$=0.54) ceramics is lower than that of other KNN based ceramics and possesses high piezoelectric temperature stability. Therefore, KNLN-CT($x$=0.54) ceramics have a large value for potential applications. This result also shows that the approach we used is feasible.
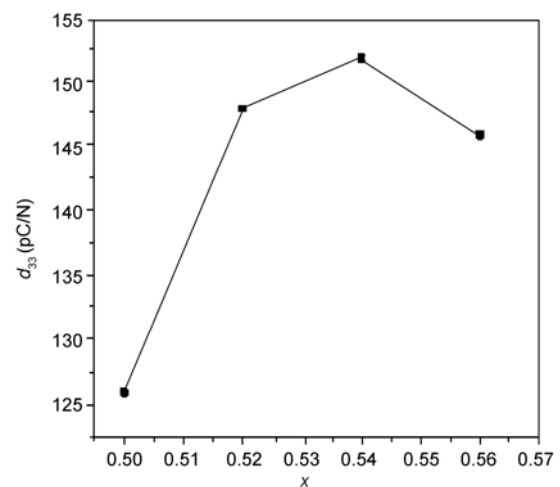


**Figure 4** Piezoelectric properties of KNLN-CT ceramics as a function of composition.

**Figure 5**  Piezoelectric properties of the KNLN-CT ceramics as a function of temperature.

## 4    Conclusions

$0.9(K_{1-x}Na_x)NbO_3$-$0.06LiNbO_3$-$0.04CaTiO_3$ ceramics were prepared using a conventional solid-state sintering method. The introduction of $LiNbO_3$ and $CaTiO_3$ shifted the PPT temperature below room temperature (–40°C), which led to high piezoelectric temperature stability in KNLN-CT ($x$=0.54) over a wide temperature range. A MPB similar to that of PZT was found in KNLN-CT($x$=0.54) ceramics by adjusting the Na–K ratio. This led to a high piezoelectric constant ($d_{33}$=152 pC/N). This result shows that although the piezoelectric constant (152 pC/N) of KNLN-CT($x$=0.54) ceramics is lower than that (200–300 pC/N) of other KNN based ceramics, it possesses a high piezoelectric temperature stability. Therefore, KNLN-CT($x$=0.54) ceramics have a high potential value for future applications.

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