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# Temperature stability, phase structure and electrical behavior of Li-modified $0.99(K_{0.48}Na_{0.52})NbO_3$–$0.01BiCoO_3$ piezoelectric ceramics

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**Abstract**

High temperature applications of piezoelectric ceramics require not only high Curie temperature ($T_C$), but also good thermal stability in a wild temperature range. To achieve this goal, $0.99[(K_{0.48}Na_{0.52})_{1-y}Li_y]NbO_3$–$0.01BiCoO_3$ [KNLN-*y*-BC] piezoelectric ceramics have been prepared by a conventional solid-state sintering method. The effects of lithium on the phase structures, electrical properties, and thermal stability were investigated. A polymorphic phase boundary between orthorhombic and tetragonal phases has been found in the composition range of $0.02 \leq y \leq 0.03$ at room temperature. With the increasing content of Li, $T_C$ gradually raised while $T_{O\text{–}T}$ reduced, respectively. The $T_{O\text{–}T}$ value of KNLN-0.03-BC ceramic is close to room temperature, resulting in good electrical properties ($d_{33}$~180, $k_p$~0.326). Moreover, KNLN-*y*-BC ceramics possess a lower $T_{O\text{–}T}$ and higher $T_C$ ($>400$ °C) when $y \geq 0.03$, that means they have a better thermal stability and might be used in a broader temperature range.


*Keywords:* Sodium potassium niobate; Polymorphic phase transition (PPT); Curie temperature ($T_c$); Temperature stability

## 1. Introduction

Piezoelectric materials are technologically important because of their application in various kind of devices including ultrasonic medical imaging, ultrasonic nondestructive testing, speakers, resonators, gas igniters, gyroscope, and pressure sensors, etc. [1–3]. Some new applications have been demonstrated in piezoelectrics, such as micromotors, energy harvesting devices, magnetoelectric sensors, and high power transformers [4,5]. Sodium potassium niobate with the general chemical formula of $(K_{1-x}Na_x)NbO_3$ (KNN hereafter) is one of the most attractive lead-free materials which has been extensively investigated throughout the last decade. The composition near $x$=0.5 is of great interest because of superior piezoelectric and ferroelectric properties among different compositions in the KNN system [1–3].

It is well known that the polymorphic phase transition (PPT hereafter) plays an important role on the piezoelectric and dielectric properties of KNN-based ceramics [6–9]. A large number of dopants have proved to effect the temperature of orthorhombic to tetragonal polymorphic phase transition ($PPT_{O\text{–}T}$ hereafter), and dropping orthorhombic to tetragonal phase transition temperature ($T_{O\text{–}T}$ hereafter) close to room temperature could improve the piezoelectric properties [6–12]. In contrast, rhombohedral to orthorhombic polymorphic phase transition ($PPT_{R\text{–}O}$ hereafter) at a low temperature has been almost neglected for KNN-based ceramics. Recently, it has been reported that rhombohedral to orthorhombic phase transition temperature ($T_{R\text{–}O}$ hereafter) below room temperature of (Na, K)(Nb, Sb)$O_3$, KNN-$BaZrO_3$ and KNN-$BiScO_3$ ceramics can be tuned close to room temperature. As a result, these ceramics possess an excellent piezoelectric properties induced by the theory of two-phase coexistence [13–15].

In our previous work, $(1-x)(K_{0.48}Na_{0.52})NbO_3$-$x$$BiCoO_3$ piezoelectric ceramics have been prepared by a conventional

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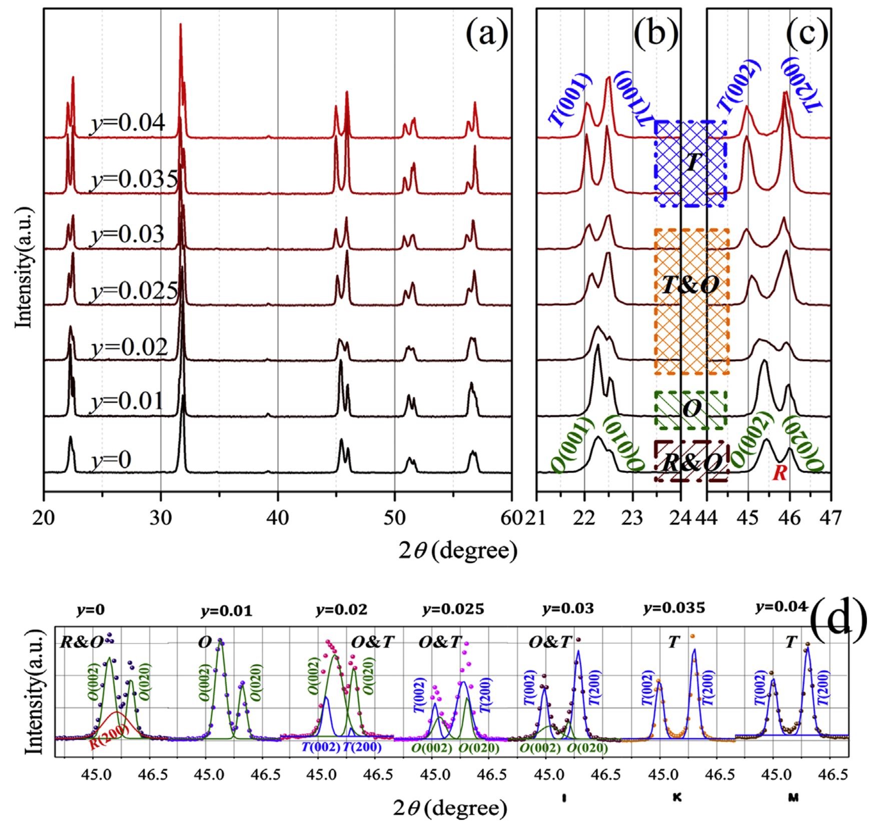


Fig. 1. (a) XRD patterns of KNLN-$y$-BC ceramics as a function of $y$, and enlarged XRD patterns in the $2\theta$ ranges of (b) $21^\circ < 2\theta < 24^\circ$ and (c) $44^\circ < 2\theta < 47^\circ$. (d) The (200) reflection lines of enlarged XRD patterns in the $2\theta$ ranges of 44°–47° fitted with Gaussian function.

solid-state sintering method, the phase structure and electrical properties are influenced by the content of $BiCoO_3$ [16]. $PPT_{R\text{–}O}$ has been identified in the composition range of $0.01 \leq x \leq 0.02$ at room temperature. The enhanced piezoelectric properties have been achieved by forming the coexistence of rhombohedral and orthorhombic (R&O) phases [16]. $T_{R\text{–}O}$ or $T_{O\text{–}T}$ of KNN-based piezoelectric ceramics near or at room temperature leads to some changes in domain wall structure, thus resulting in an enhanced piezoelectric behavior. In contrast, $T_C$ and temperature stability decrease [17]. For high temperature applications, piezoelectric materials require not only high $T_C$, but also good thermal stability. Therefore, it is more interesting to find a method to modify the electrical behavior of KNN-based ceramics, resulting in an excellent electrical properties or the improved temperature stability together with a high $T_C$ value.

In this work, $0.99[(K_{0.48}Na_{0.52})_{1-y}Li_y]NbO_3$–$0.01BiCoO_3$ [KNLN-$y$-BC hereafter] piezoelectric ceramics were prepared by a conventional sintering technique, and the lithium as an addition to KNLN-$y$-BC ceramics was selected for tailoring its phase structure and electrical properties. It is expected that KNLN-$y$-BC ceramics exhibit an excellent piezoelectric properties or improved thermal stability together with a high $T_C$ value.

## 2. Experimental

$0.99[(K_{0.48}Na_{0.52})_{1-y}Li_y]NbO_3$-$0.01BiCoO_3$ [KNLN-$y$-BC hereafter] ($y=0$, 0.01, 0.02, 0.025, 0.03, 0.035 and 0.04) ceramics were prepared by a conventional solid-state reaction technique, where $K_2CO_3$ (99%), $Na_2CO_3$ (99.8%), $Li_2CO_3$ (99.99%), $Nb_2O_5$ (99.5%), $Bi_2O_3$ (99%), and $Co_2O_3$ (99%) were used as the starting raw materials. The stoichiometric powders were mixed by ball milling for 24 h with zirconia balls media in anhydrous ethanol, and then dried. The dried powders were calcined at ~850 °C for 6 h, and the calcined powders were pressed into disks at ~10 MPa using polyvinyl alcohol (PVA) as a binder with diameters of ~10 mm and thicknesses of ~0.8–1.0 mm. After burning off PVA, the ceramic disks were sintered in the temperature range of 1080–1120 °C for 2 h in air. Silver paste was sintered on both sides of the specimens at ~700 °C for 10 min to form electrodes for the dielectric and piezoelectric measurements. The specimens were pooled in a silicon oil bath at 30 °C by applying a dc electric field of 4 kV/mm for 20–30 min. All the electrical measurements were conducted on aged specimens (24 h after poling).

The crystal structure of the specimens was examined by the X-ray diffraction (XRD) using Cu $K\alpha$ radiation ($\lambda = 1.54178$ Å) in the $\theta$–$2\theta$ scan mode (DX1000, Dandong, China). Their piezoelectric constant ($d_{33}$) was measured using a piezo-$d_{33}$ meter (ZJ-3A, China). Their electromechanical coupling factor ($k_p$) were determined by an precision impedance analyzer (Agilent 4294A, Santa Clara, CA) using the resonance–antiresonance technique. The dielectric constant as a function of temperature was obtained using an $LCR$ meter (HP 4980, Agilent, USA).

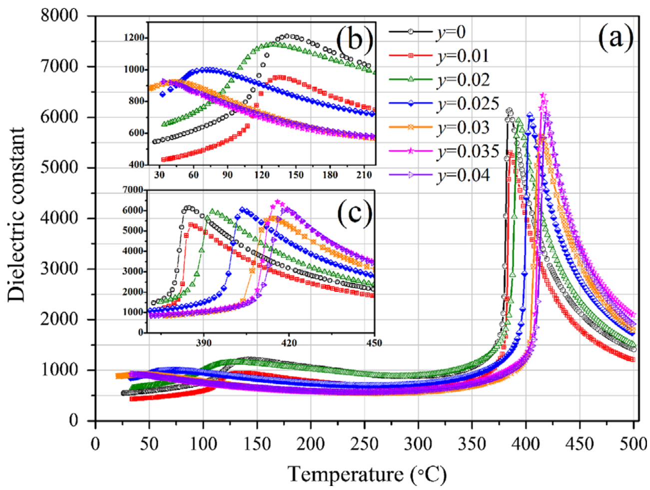


Fig. 2. $\varepsilon_r$ as a function of temperature for KNLN-*y*-BC ceramics at 100 kHz.

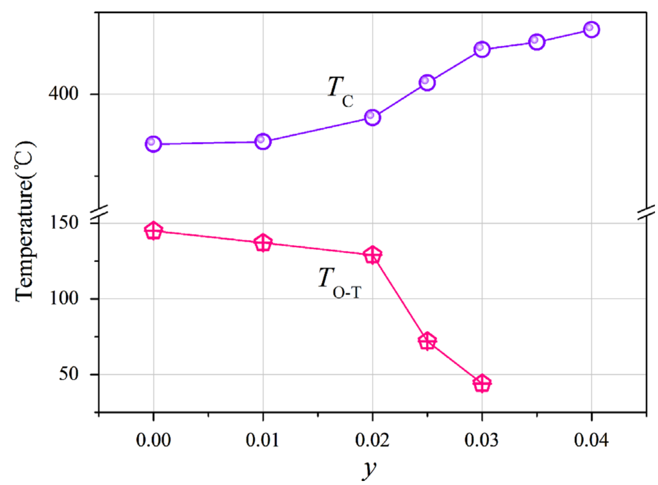


Fig. 3. Variation of $T_C$ and $T_{O-T}$ of KNLN-*y*-BC ceramics with *y*.

## 3. Results and discussions

Fig. 1(a) shows the XRD patterns of KNLN-*y*-BC ($y=0$, 0.01, 0.02, 0.025, 0.03, 0.035 and 0.04) ceramics. All the ceramics show a pure perovskite structure, and no secondary phases are observed in the range detected. Fig. 1 (b) and (c) plot the enlarged XRD patterns for KNLN-*y*-BC ceramics in the $2\theta$ ranges of 21°–24° and 44°–47°, respectively. 0.99 $(K_{0.48}Na_{0.52})NbO_3$–$0.01BiCoO_3$ ceramic with $y=0$ has a coexistence of orthorhombic and rhombohedral (O&R) phase structures, as indicated by the special diffraction peaks {*O*(001)(010), *R*(200)&*O*(002)(020)} [16]. KNLN-0.01-BC ceramic maintains an orthorhombic structure at room temperature, similarly to the pure KNN ceramic resulting from the splitting of (200) peak [10]. KNLN-*y*-BC ceramics with a high Li content ($y>0.03$) are of a tetragonal structure (*T*(002)(200)), and $PPT_{O-T}$ between orthorhombic and tetragonal ferroelectric phases was identified in the composition range of $0.02\leq y\leq 0.03$. These (200) diffraction lines were fitted by the Gaussian function, as shown in Fig. 1(d). It can be found that the integrated intensities of *T*(002) and *T*(200) increase with an increase in *y*, while the intensities of *O*(200) and *O*(002) decrease remarkably. These results indicate that a coexistence of orthorhombic and tetragonal (O&T) structures is formed at room temperature in the composition range of $0.02\leq y\leq 0.03$. Therefore, phase structure of KNLN-*y*-BC ceramics is modified by controlling the Li content.

Fig. 2 shows the dielectric constant ($\varepsilon_r$) of KNLN-*y*-BC ceramics as a function of temperature, measured at 100 kHz. KNLN-*y*-BC ($x\leq 0.03$) ceramics have two phase transition temperatures, corresponding to the ferroelectric orthorhombic–tetragonal polymorphic phase transition ($T_{O-T}$) and the tetragonal–cubic transition (Curie temperature, $T_C$). $T_{O-T}$ shifts downward with increasing Li content, while $T_C$ increases gradually, as shown in Fig.2 (b) and (c). At $x>0.03$, the tetragonal–cubic phase transition was only observed in the range of temperature investigated. It is reveal that these ceramics possess a solely tetragonal structure, which is consistent with the XRD analysis. On the other hand, it is noticeable that KNLN-*y*-BC ceramics with a coexistence phase (O&T or O&R) show a higher dielectric peak and a broader phase transition as compared to the feeblish phase transition peak for KNLN-0.01-BC ceramic with an orthorhombic phase. These special dielectric behavior may originate from a more complex occupation of A and B sites in the $ABO_3$ perovskite structure.

Fig. 3 shows $T_C$ and $T_{O-T}$ values of KNLN-*y*-BC ceramics ($f=100$ kHz) as a function of *y*. The $T_C$ value increases gradually from ~385 °C to ~420 °C with the *y* increased from 0 to 0.04. With Lithium as additions to KNLN-*y*-BC ceramics, Li mainly occupies the A sites of $ABO_3$ perovskite structure, leading to a linear shift of $T_C$ to a higher temperature [10]. The ceramic without Lithium possesses a coexistence of orthorhombic and rhombohedral phases and a higher $T_{O-T}$ (145 °C). $T_{O-T}$ value decreases slightly with increasing Li content, and greatly shifts to a low temperature for the ceramics with $y\geq 0.02$. Moreover, $T_{O-T}$ value of KNLN-0.03-BC ceramic with a higher $T_C$ value (~414 °C) closed to room temperature lead to an excellent electrical properties, as following discussion.

The piezoelectric constant ($d_{33}$) and electromechanical coupling factor ($k_p$) values for KNLN-*y*-BC ceramics are shown in Fig. 4. The ceramic with $y=0$ shows a good piezoelectric properties ($d_{33}=165$ pC/N, $k_p=0.40$) because it lies in the $PPT_{R-O}$ composition. However, KNLN-0.01–BC ceramic with an orthorhombic phase possesses reduced electrical behavior. With increasing Li content, $d_{33}$ and $k_p$ values enhance and then decrease rapidly. The best piezoelectric properties with $d_{33}$~180 pC/N and $k_p$~0.326 appear in the $PPT_{O-T}$ composition with $y=0.03$. The results indicate that KNLN-*y*-BC ceramics have an enhanced properties owing to the formation of PPT at room temperature. Moreover, it is evident that $PPT_{O-T}$ between the orthorhombic and tetragonal phase plays a more important role than $PPT_{R-O}$ in the enhancement of electrical properties in KNLN-*y*-BC ceramics.

The thermal stability and temperature stability of piezoelectric ceramics are the important factors for the practical application of such ceramics in devices. Their electrical

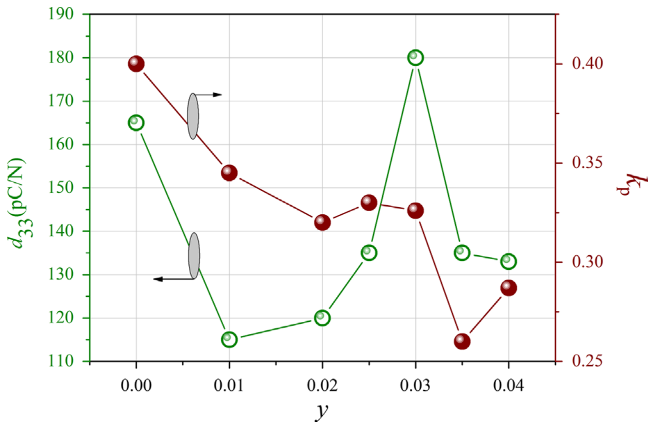


Fig. 4. $d_{33}$ and $k_p$ of KNLN-$y$-BC ceramics as a function of $y$.

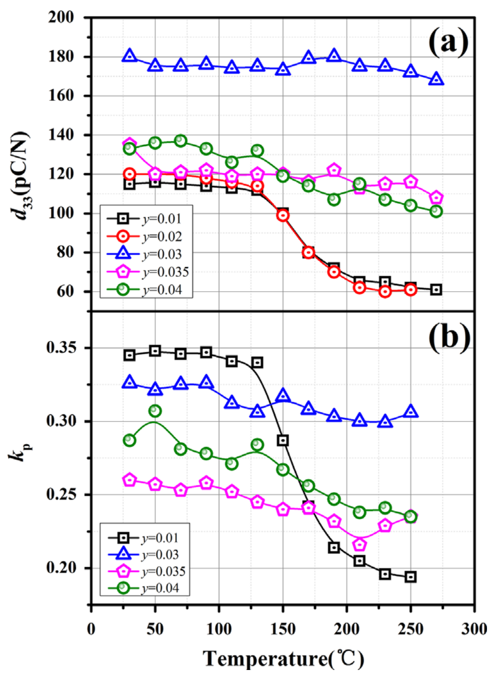


Fig. 5. Thermal-depoling behavior of (a) $d_{33}$ and (b) $k_p$ for KNLN-$y$-BC ceramics.

properties were measured at room temperature after annealing for 60 min at each chosen annealing temperature. Fig. 5 (a) gives $d_{33}$ value for KNLN-$y$-BC ceramics as a function of annealing temperature in the range from room temperature to 270 °C. $d_{33}$ value for KNLN-$y$-BC ceramics with $y=0.01$ and 0.02 remains almost unchanged below 120 °C and then decreases with increasing annealing temperature. Piezoelectric properties of KNLN-$y$-BC ($y \leq 0.02$) ceramics possess temperature dependence near $T_{O-T}$ (~120 °C). The temperature stability for KNLN-$y$-BC ceramics enhances with $y \geq 0.03$, owing to $T_{O-T}$ below the room temperature. As show in Fig. 5(b), the thermal stability of $k_p$ possesses analogous situation. As a result, KNLN-0.03-BC ceramic has an enhanced electrical properties ($d_{33}$~180 pC/N, $k_p$~0.326) and a good thermal stability in the detected temperature range.

## 4. Conclusion

Lithium modified KNN-based ceramics, 0.99 $[(K_{0.48}Na_{0.52})_{1-y}Li_y]NbO_3$–$0.01BiCoO_3$, were prepared using a conventional solid-state sintering. KNLN-$y$-BC ceramics with $PPT_{R-O}$ (the composition with $y=0$) and $PPT_{O-T}$ (the composition with $0.02 \leq y \leq 0.03$) at room temperature were synthesized. KNLN-$y$-BC ceramics have an enhanced properties owing to the formation of PPT at room temperature. Because $T_{O-T}$ is near room temperature, KNLN-0.03–BC ceramic shows an enhanced electrical properties ($d_{33}$~180 and $k_p$~0.326). Moreover, the introduction of lithium results in $T_C$ increase and $T_{O-T}$ decrease in KNLN-$y$-BC ceramics. KNLN-$y$-BC ceramics with $y \geq 0.03$ show an improved temperature stability and a high $T_C$ (>400 °C) should allow a wide temperature range of operation.


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