Investigation the effect of Sb on phase boundary variation of 0.965(Na0.5K0.5)(Nb1-xSbx)-0.035BaZrO3 ceramics and the corresponding piezoelectric properties

Xing-Hua Ma*, Junjia Xia* and Zhenlu Zhangb

*School of Mechanical & Automotive Engineering, Qingdao University of Technology, Qingdao 266520, Shandong, China; bSchool of Science, Beijing University of Posts and Telecommunications, Beijing 100876, China

ABSTRACT
CuO-added 0.965(Na0.5K0.5)(Nb1-xSbx)-0.035BaZrO3 ceramics (0.00 ≤ x ≤ 0.10) were well prepared at 1070°C for 8 hours. And the effect of Sb2+ ions on the phase boundary variation and the corresponding piezoelectric properties were studied. It was found that the crystal structures varied from orthorhombic-tetragonal, orthorhombic-tetragonal-rhombohedral, orthorhombic-rhombohedral PPB and finally to rhombohedral structures of 0.965(Na0.5K0.5)(Nb1-xSbx)-0.035BaZrO3 with x value increasing, and the corresponding piezoelectric properties varied according to the variation of crystal structures. Particularly, the specimen with an Amm2 orthorhombic (11.1%) – R3m rhombohedral (88.9%) dominant PPB structure (x = 0.08) showed the highest d33 value of 415 pC/N and strain of 0.12% at 4.5 kV/mm.

1. Introduction

Due to their promising potential to replace Pb(Zr1-x
Ti)xO3 (PZT)-based piezoelectric ceramics, the environmentally friendly (Na0.5K0.5)NbO3 (NNK)-based ceramics have been extensively studied in recent years [1–6]. Normally, the NNN ceramics possess orthorhombic structure (Amm2 space group) at room temperature and exhibit various polymorphic phase transition temperatures including rhombohedral to orthorhombic transition temperature (TRO) at ~ 110°C, orthorhombic to tetragonal transition temperature (T0-T) at around 190°C and Curie temperature (Tc) at approximately 410°C [7]. To improve piezoelectric and electromechanical properties of the NNN ceramics, large amount of research has been performed, such as synthesizing textured ceramics [2,8–10], or shifting the phase transition temperatures to room temperature so that the so-called polymorphic phase boundary (PPB) is formed making the domain rotation easier at room temperature. For examples, orthorhombic-tetragonal PPB was constructed at room temperature by reducing T0-T of additives added NNN based ceramics and enhanced piezoelectric strain constants (d33 > 200 pC/N) were obtained [11–15]. rhombohedral-orthorhombic PPB structure was created by substituted the B6s site of KNN-based ceramics with Sb2+ ions to move TRO near room temperature, and a higher d33 value of ~230 pC/N was achieved [16]; rhombohedral-tetragonal PPB was induced via multi-elements doping to simultaneously move the TRO and T0-T close to room temperature (so that a T0-T can be formed) [17–20], due to their similarity with the morphotropic phase boundary (MPB) of PZT-based ceramics [21,22], d33 values could be promoted to more than 400 pC/N. Therefore, developing new type of morphotropic phase boundary in NNN based ceramics has attracted more and more attention.

Theoretically, the d33 value can be calculated with the equation of \( d_{33} = 2Q_{11} \times P_r \times E_{33}^T (Q_{11}: \text{electrostrictive coefficient}, P_r: \text{remnant polarization}) \) [23,24], and generally \( Q_{11} \) could be considered as constant so that \( d_{33} \) is proportional to the value of \( P_r \times E_{33}^T \). Furthermore, the electromechanical coupling coefficient, \( k_p \), is positively proportional to \( d_{33} \times g_{33} \) value (\( g_{33} = d_{33}/E_{33}^T \), piezoelectric voltage constant) [25]. Therefore, specimens with high \( P_r \) and \( E_{33}^T/E_{33} \) values could exhibit high \( d_{33} \) and \( k_p \) values. NNN based ceramics with pseudocubic structure are considered to display high dielectric constants (\( E_{33}^T/E_0 \)), because pseudocubic structure exits near \( T_C \). Moreover, if PPB structure is developed upon pseudocubic structure, a high \( P_r \) value could be also expected because of more possible spontaneous polarization directions during the poling process. Therefore, in recent years, there have been several studies reported to create orthorhombic-pseudocubic PPB structure or tetragonal-pseudocubic PPB structure near room temperature and promising piezoelectricity was also obtained [25–29]. As the research further developed, the pseudocubic structure was identified...
as tetragonal-cubic PPB structure in NK(Nb$_{1-x}$Sb$_x$)$_3$MTiO$_3$ (M = Ca, Ba) ceramics [25,28] and rhombohedral structure in NK(Nb$_{1-x}$Sb$_x$)-CaZrO$_3$ ceramics [29].

In this research, the effect of Sb$^{5+}$ substitution on the structural variation and piezoelectric properties of 0.965(Na$_{0.5}$K$_{0.5}$)(Nb$_{1-x}$Sb$_x$)$_3$-0.035BaZrO$_3$ (0.00 ≤ x ≤ 0.10) ceramics was explored. The corresponding results demonstrated that the addition of Sb$^{5+}$ ions squeezed (until eliminate) the tetragonal phase region and induced orthorhombic-rhombohedral PPB structure, leading to an enhanced piezoelectric property. This study is expected to be useful for developing new types of lead-free piezoelectric ceramics with high performance.

2. Experimental procedure

1.5 mol% CuO-added 0.965(Na$_{0.5}$K$_{0.5}$)(Nb$_{1-x}$Sb$_x$)$_3$-0.035BaZrO$_3$ ceramics (0.965CNKN$_{1-x}$Sb$_x$-0.035BZ in short) with 0.00 ≤ x ≤ 0.10 were synthesized via a conventional solid state method. K$_2$CO$_3$, Na$_2$CO$_3$, Nb$_2$O$_5$, Sb$_2$O$_3$, BaCO$_3$, and ZrO$_2$ (> 99%, High Purity Chemicals, Saitama, Japan) were stoichiometrically weighed and mixed for 24 hours with anhydrous ethanol as solvent in nylon jars with alumina balls. The well mixed and dried powders were calcined at 950°C for 3 hours. Then, the calcined powders added with 1.5 mol% of CuO (as sintering additive) were remilled for another 72 hours. At last, the resulted powders were pressed into disc-shaped green bodies under a pressure of 100 MPa and sintered at 1070°C for 8 hours in air. The densities of sintered bodies were measured using the Archimedes method. X-ray diffraction (XRD; Rigaku D/Max-RC, Tokyo, Japan) with Cu Kα radiation was used to analyze the crystal structure and calculate the theoretical density. In addition, XRD reflections at 45.5° and 66.5° were obtained via slow-scan mode with resolution of 0.01° and scanning rate of 0.3°/minute, respectively, and the corresponding XRD patterns were deconvoluted with Voigt function. The XRD patterns were further analyzed by using TOPAS-Academic Rietveld refinement method [30]. The microstructures of thermally etched (conducted at the temperature of 100°C lower than the sintering temperature) specimens were investigated using scanning electron microscopy (SEM; Hitachi S-4300, Tokyo, Japan). The specimens coated with silver

![Figure 1](image-url). XRD reflections at 66.5° measured via slow-speed scanning of 0.965CNKN$_{1-x}$Sb$_x$-0.035BZ ceramics sintered at 1070°C for 8 h: (a) x = 0.00, (b) x = 0.04, (c) x = 0.06, (d) x = 0.08, and (e) x = 0.10.
electrode were poled by a DC field of 4.5 kV/mm for 1 hour at room temperature in a silicon oil bath. A quasistatic $d_{33}$ meter (Micro-Epsilon Channel Product DT-3300, Raleigh, NC, USA) was employed to measure the piezoelectric constant ($d_{33}$) at room temperature. An impedance analyzer (Agilent Technologies HP 4194A, Santa Clara, CA, USA) was used to characterize the relative permittivity ($\varepsilon_{r}/\varepsilon_0$), dielectric loss (tanδ), electromechanical coupling factor ($k_p$), and mechanical quality factor ($Q_m$) at room temperature. The curves of relative permittivity against temperatures of the sintered specimens were obtained using an LCR meter (Agilent Technologies HP 4284A) in an automated temperature-controlled furnace equipped with a computer interface for data acquisition. The polarization vs. electric field (P-E) hysteresis loops were characterized using a modified Sawyer-Tower circuit. And strain vs. electric field (S-E) curves were measured using a laser displacement sensor (aixACCT System GmbH, Aachen, Germany) with spot size of 20 μm and resolution of 10 nm. To prevent electrical flashover, P-E and S-E curves were both measured in silicon oil at a fixed frequency of 1 Hz.

3. Results and discussion

A homogeneous perovskite phase without secondary phases was obtained in 0.965CNKN$_{1-x}$S$_x$-0.035BZ ceramics ($0.00 \leq x \leq 0.10$) sintered at 1070°C for 8 hours, as shown in Figure S1 of Supplementary Material. To have a detail analysis on the variation

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**Figure 2.** Rietveld refinement XRD profiles of 0.965CNKN$_{1-x}$S$_x$-0.035BZ ceramics sintered at 1070°C for 8 h: (a) $x = 0.00$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$, and (e) $x = 0.10$. 
of crystals as a function of x, high resolution XRD reflections at ~ 66.5° were measured via slow-speed scanning and the corresponding data was deconvoluted using the Voigt function analysis, as shown in Figure 1 (Note that the subscripts O, T, and R are the abbreviations of orthorhombic, tetragonal and rhombohedral, respectively. The solid peaks and dashed peaks in color originated from the Kα1 and Kα2 reflections, respectively). The orthorhombic (004)₀, (400)₀, (222)₀ and tetragonal (202)₉, (220)₉ reflections were observed in the specimens with x = 0.00, and the obvious different peak intensity indicated orthorhombic dominant-tetragonal PPB structure was formed (Figure 1(a)). With x value increasing, both of the orthorhombic and tetragonal phases decreased, and the rhombohedral phase (marked with (220)ᵣ and (2–20)ᵣ reflections) appeared as indicated by Figure 1(b) (x = 0.04). For x = 0.06, the rhombohedral phase further increased and coexisted with orthorhombic phase to form an orthorhombic dominant-rhombohedral PPB structure (Figure 1(c)). As x value further increased, rhombohedral became the dominant phase, such as x = 0.08 shown in Figure 1(d). And for the specimen with x = 0.10, as shown in Figure 1(e), only reflections of (220)ᵣ and (2–20)ᵣ could be found, demonstrating the rhombohedral phase became the single phase [29]. To further confirm the above analysis, slow scan analysis at 45.5° was performed, and similar conclusion could be drawn which is shown in Figure S2 of Supplementary Material.

To further clarify the structure variations of 0.965CNKNₓ₋₀.035BZ ceramics, Rietveld analysis was performed on XRD patterns of the specimens with x = 0.00, 0.04, 0.06, 0.08 and 0.10, respectively, as shown in Figure 2 (a)–(e). And the detail lattice parameters of the corresponding crystal structures are presented in Table 1. The crystal structure of the specimen with x = 0.00 was identified as a mixture of 71.1% Amm2 orthorhombic structure and 28.9% P4mm tetragonal structure with Rwp = 8.03 and GOF (goodness of fit) = 5.39 (Figure 2(a)). For the specimen with x = 0.04, rhombohedral phase (R3m, 4.4%) appeared and coexisted with orthorhombic (Amm2, 69%) and tetragonal (P4mm, 26.6%) phase to form a triphase PPB boundary with Rwp = 3.77 and GOF = 2.27, as shown in Figure 2(b). And the Rietveld analysis result of the specimen with x = 0.06 indicates the formation of orthorhombic (Amm2, 64.5%) dominant-rhombohedral (R3m, 35.5%) PPB structure with Rwp = 6.42 and GOF = 4.55 (Figure 2(c)). For the specimen exhibited the highest d₃₃ and strain value which will be demonstrated in the latter parts, the structure of x = 0.08 was further determined to be a mixture of Amm2 orthorhombic (11.1%) – R3m rhombohedral
Table 1. Refined lattice parameters of 0.965CNKN\textsubscript{1-x},S\textsubscript{x}-0.035BZ ceramics sintered at 1070°C for 8 h: x = 0.00, x = 0.04, x = 0.06, x = 0.08, and x = 0.10.

| Sample composition | Structural model (SG) | Site label | $x$ | $y$ | $z$ | Site occupancy | Lattice parameter (Å) |
|--------------------|----------------------|-----------|-----|-----|-----|----------------|----------------------|
| $x = 0.00$         | Orthorhombic (Amm2)  | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                 | a = 3.9740 (1) |
|                    | 71.1%                | Nb/Zr    | 0.5 | -0.5| -0.5| 0.0            | 0.5235 (31)         | b = 5.6705 (2) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.5235 (31)    | c = 6.5601 (2) |
|                    | Tetragonal (P4mm)    | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9705 (2) |
|                    | 28.9%                | Nb/Zr    | 0.5 | -0.5| -0.5| 0.0            | 0.5079 (43)         | b = 3.9998 (4) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.5079 (43)    | c = 3.9998 (4) |
| $x = 0.04$         | Orthorhombic (Amm2)  | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9705 (4) |
|                    | 65.0%                | Nb/Zr/Sb | 0.5 | -0.5| -0.5| 0.0            | 0.5482 (25)         | b = 5.6355 (10) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.5482 (25)    | c = 5.6339 (11) |
|                    | Tetragonal (P4mm)    | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9797 (4) |
|                    | 26.4%                | Nb/Zr/Sb | 0.5 | -0.5| -0.5| 0.0            | 0.5002 (43)         | b = 3.9797 (4) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.5002 (43)    | c = 3.9797 (4) |
| $x = 0.06$         | Orthorhombic (Amm2)  | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9840 (4) |
|                    | 64.5%                | Nb/Zr/Sb | 0.5 | -0.5| -0.5| 0.0            | 0.0                | b = 5.6201 (1) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.0            | c = 5.6207 (1) |
|                    | Rhombohedral (R3m)   | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9840 (3) |
|                    | 35.5%                | Nb/Zr/Sb | 0.5 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9840 (3) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.0            | a = b = 3.9840 (3) |
|                    | 43.2%                | Nb/Zr/Sb | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9840 (3) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.0            | a = b = 3.9840 (3) |
| $x = 0.08$         | Orthorhombic (Amm2)  | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9840 (3) |
|                    | 11.1%                | Nb/Zr/Sb | 0.5 | -0.0| -0.0| 0.0            | 0.5070 (22)         | b = 5.627 (3) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.5070 (22)    | c = 5.6269 (3) |
|                    | Rhombohedral (R3m)   | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9828 (4) |
|                    | 88.9%                | Nb/Zr/Sb | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9828 (4) |
|                    | 01/02                | 0.0      | -0.0| 0.0 | 0.0 | 0.0            | a = b = 3.9828 (4) |
| $x = 0.10$         | Orthorhombic (Amm2)  | K/Na/Ba   | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9828 (4) |
|                    | 100%                 | Nb/Zr/Sb | 0.0 | -0.0| -0.0| 0.0            | 0.0                | a = b = 3.9828 (4) |
(88.9%) dominant PPB structure ($R_{wp} = 6.56$ and GOF = 4.69), as shown in Figure 2(d). And for $x = 0.10$, the crystal structure turned into 100% rhombohedral structure with $R_{wp} = 6.12$ and GOF = 4 (Figure 2(e)). As reported by Lee et al. [29], this result could be further verified by the remained piezoelectric (ferroelectric) properties of the specimen with $x = 0.10$.

To check the effect of $x$ values on phase transition temperatures and Curie temperature, the temperature-dependent dielectric measurements were conducted on 0.965CNKN$_{1-x}$Sb$_x$0.035BZ ceramics with 0.00 $\leq x \leq 0.10$ in a temperature range of $-50^\circ$C to $350^\circ$C, and the corresponding results are shown in Figure 3. When $x = 0.00$, as shown in Figure 3(a), the specimen exhibited a $T_C$ at approximately $315^\circ$C with a $T_{O-T}$ of around $152^\circ$C. With the addition of Sb$^{5+}$, the $T_C$ quickly decreased with $x$ values increasing. For $x = 0.04$, the $T_C$ and $T_{O-T}$ declined to $208^\circ$C and $120^\circ$C, respectively, which is shown in Figure 3(b). The $T_C$ of $x = 0.06$ was around $146^\circ$C, leading to the tetragonal phase zone was quickly squeezed [29] and a $T_{O-R}$ emerged at approximately $92^\circ$C, indicating orthorhombic dominant-rhombohedral PPB structure was formed (Figure 3(c)). For the specimen with $x = 0.08$ (Figure 3(d)), the $T_C$ declined to $\sim 77^\circ$C, which induced the formation of rhombohedral dominant-orthorhombic PPB structure. And when $x = 0.10$ (Figure 3(e)), $T_C$ further fell to $\sim 62^\circ$C, leading to rhombohedral was left as the single phase. These results are consistent with those of the XRD analysis. In addition, the $T_{R-O}$ which could be shifted above $-50^\circ$C by the addition of Sb$^{5+}$ were not observed in all the specimens, demonstrating the rhombohedral phase reported here also originate from the pseudocubic structure that exist at temperature near $T_C$ as proposed by Lee, et al. [29]. After adding the Sb$_2$O$_5$, the Sb$^{5+}$ ions should substitute the Nb$^{5+}$ or Zr$^{4+}$ ions at the $B$ sites. As reported by Shannon [31], the $R_{Nb^{5+}}$ (VI) = 0.60 Å, $R_{Sb^{5+}}$ (VI) = 0.64 Å and $R_{Zr^{4+}}$ (VI) = 0.72 Å, respectively. Therefore, the substitution of Sb$^{5+}$ ions at the

Figure 4. $P$-$E$ hysteresis curves of 0.965CNKN$_{1-x}$Sb$_x$0.035BZ ceramics sintered at 1070°C for 8 h: (a) $x = 0.00$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$, and (e) $x = 0.10$. 
$B$ sites may cause a higher distortion of the crystal lattice (i.e. the Goldschmidt tolerance factor [32] was changed), leading to the variation of the phase transition temperatures.

Figure 4 plots the evolution process of $P-E$ hysteresis loops of 0.965CNKN$_{1-x}$Sb$_x$-0.035BZ (0.00 ≤ $x$ ≤ 0.10) ceramics. The specimen with $x = 0.00$ exhibited a $P_r$ of ~15 μC/cm$^2$ and an $E_c$ of ~0.8 kV/mm (Figure 4(a)). And with the addition of Sb$^{5+}$, the $P_r$ values were slightly promoted to approximately 15.5 μC/cm$^2$ ($x = 0.04$, Figure 4(b)) and 16 μC/cm$^2$ ($x = 0.06$, Figure 4(c)) probably because of the development of less amount of rhombohedral phase in the PPB structure [16]. Compared with the NKN-MTIO$_3$ (M: Ca, Sr, and Ba) ceramics [25,27,28], the $P-E$ hysteresis loops maintain square loops with low coercivity, probably due to the enhanced $B$-site cation (i.e. Zr) ordering [33]. The $P_r$ values started to decrease when $x$ exceeded 0.06, but the specimen with $x = 0.10$ still exhibited a $P_r$ value of ~4 μC/cm$^2$ (Figure 4(e)), further indicating that the rhombohedral phase existed with ferroelectricity rather than the pure cubic phase [29]. In contrast, the $E_c$ values decreased from 0.8 kV/mm ($x = 0.00$) to 0.15 kV/mm ($x = 0.10$) continuously with the addition of Sb$^{5+}$, probably because the domain rotation occurred more easily for the specimens with the development of rhombohedral phase [16].

The application of piezoelectric actuators normally requires piezoelectric ceramics or crystals to exhibit high electric-field-induced strain to produce large displacement [34,35]. Figure 5 shows the normal $S-E$ curves of 0.965CNKN$_{1-x}$Sb$_x$-0.035BZ ceramics with 0.00 ≤ $x$ ≤ 0.10 measured under the electric field of 4.5 kV/mm. When $x = 0.00$, the specimen displayed a relatively low strain of ~0.09% (Figure 5(a)). And the strain increased with the increase of $x$ values, for the specimen with $x = 0.08$ which exhibited the highest $d_{33}$ value (415 pC/N, this will be demonstrated in the latter part), the strain was further enhanced to the maximum value of ~0.12% (Figure 5(d)), which probably due to the large portion of rhombohedral phase in the orthorhombic-rhombohedral PPB structure since the highest strain is usually achieved near the phase
boundaries where two or more ferroelectric phase coexist with modified piezoelectric properties [36].
However, the strain of the specimen with $x = 0.10$ declined to approximately 0.08% which might because of the single rhombohedral phase (Figure 5(e)). Such variation can be further confirmed by the unipolar S-E curves as shown in Figure S3 (Supplementary Material).

Figure 6(a) shows relative densities, $\varepsilon'_{33}/\varepsilon_0$, $d_{33}$, $k_p$, and $Q_m$ values of 0.965CNKN$_1$S$_x$-0.035BZ (0.00 $\leq x \leq 0.10$) ceramics. All the specimens exhibited high relative densities (around or higher than 95%), indicating that they were sintered well under the condition of 1070°C for 8 hours. The $\varepsilon'_{33}/\varepsilon_0$ value of the specimens with $x = 0.0$ was just approximately 500, and it was enhanced as $x$ values increased probably because of the $T_C$ dropped lower with continuously addition of Sb$^{5+}$ as discussed in the former part. The $d_{33}$ values of the specimens with $0.00 \leq x \leq 0.04$ ranged between 150 and 210, and then they increased from 293 pC/N ($x = 0.06$) to 415 pC/N ($x = 0.08$) with rhombohedral dominant-orthorhombic PPB structure. This maximum $d_{33}$ value could compete with some of those PZT based ceramics and are higher than many other lead-free piezoelectric ceramics. However, the specimen with $x = 0.10$ exhibited low $d_{33}$ value of approximately 185 pC/N due to the formation of single rhombohedral phase. According to the SEM observation, as shown in Figures S4(a)–(e), all the specimens exhibit dense and similar microstructures. Therefore, the effect of microstructural properties (such as the grain size) on the $d_{33}$ values should not be significant. Generally, the $d_{33}$ values can be calculated using the following equation:

$$d_{33} = 2Q_{11} \times P_r \times \varepsilon'_{33}$$

Where $Q_{11}$ is the electrostriction coefficient, and it can be recognized as a constant. Therefore, $d_{33}$ is considered to be proportional to the value of $P_r \times \varepsilon'_{33}$. Figure 6 (b) shows the correlation curves between $P_r \times \varepsilon'_{33}$ and $d_{33}$ of 0.965CNKN$_1$S$_x$-0.035BZ. And the similar variation trend displayed by both curves indicates the reasonable evolution process of $d_{33}$ values. Particularly, the specimen with $x = 0.08$ exhibits the highest $d_{33}$ value, which probably because its high $\varepsilon'_{33}$ value due to its low $T_C$ and still maintain a large $P_r$ value owing to the existence of the rhombohedral-orthorhombic PPB structure. Theoretically, $k_p$ values are proportional to $d_{33} \times g_{33}$ ($g_{33} = d_{33}/\varepsilon'_{33}$, piezoelectric voltage constant) [25]. Figure 6(c) shows the value curves of $(d_{33} \times g_{33}) - x$ and $k_p - x$, respectively, and the corresponding variation process matches well with each other. Here, the maximum value of $k_p$ occurred at $x = 0.06$ not at $x = 0.08$, which also probably because of the much higher $\varepsilon'_{33}$ value of $x = 0.08$ than that of $x = 0.06$ owing to its low $T_C$. With the Sb$^{5+}$ addition, the $Q_m$ values of all the specimens showed a downward tendency, which should be due to the declined $E_c$ as discussed in the former part.
4. Conclusions

With the addition of Sb$^{5+}$ ions, the crystal structures of 0.965CNKN$\varepsilon_{S_0}$-0.0358ZB with 0.00 ≤ x ≤ 0.10 varied from orthorhombic-tetragonal, orthorhombic-tetragonal-rhombohedral, orthorhombic-rhombohedral PPB structures and finally to single rhombohedral crystal structure. A high $\chi_{33}$ value of ~ 415 pC/N which could be comparable to many of the as reported high performance piezoelectric ceramics and a strain of ~ 0.12% was obtained when x = 0.08. The good piezoelectric behavior could be attributed to the formation of a rhombohedral dominant-orthorhombic PPB structure as well as enhanced dielectric and piezoelectric properties (such as the $P_x \times \varepsilon_{33}$ value). Therefore, CuO-added $0.965\text{Na}_{0.9}K_{0.1}\text{Sb}_{0.08}$-0.0358$\text{ZrO}_2$ could be a promising candidate to replace the lead based piezoelectric ceramics.

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Disclosure statement

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