Influence of A-site non-stoichiometry on structure and electrical properties of $K_{0.5}Na_{0.5}NbO_3$-based lead-free piezoelectric ceramics

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The coexistence zone of orthorhombic and tetragonal phases, which is dependent on non-stoichiometry, appears at $-0.010 \leqslant x \leqslant 0.0125$ in $0.94(K_{0.5+x}Na_{0.5+x})NbO_3-0.06LiNbO_3$ (K_xN_xN–6LN) ceramics. K_xN_xN–6LN ceramics with $x = -0.0125$ are of orthorhombic structure. This coexistence zone plays an important role in achieving the desired electrical properties, but an optimum range of tetragonal phase fraction exists in which the significantly enhanced piezoelectric constant d_{33} is attained. These findings are of importance for guiding the design of KNN-based lead-free ceramics with enhanced electrical properties.
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Lead-based perovskite piezoelectric ceramics have dominated the commercial market of the electronic industry, with applications in actuators, sensors and ultrasonic transducers, owing to their excellent piezoelectric properties [1]. The high piezoelectric response is related to the morphotropic phase boundary (MPB) between rhombohedra, tetragonal or monoclinic phases [2,3]. These compositions near the MPB show significantly enhanced piezoelectric properties. However, the lead-based PZT piezoelectrics contain >60 wt.% toxic lead, which leads to various environmental problems. KNN-based ceramics are being widely studied and emerging as promising candidates for lead-free piezoelectrics, owing to their relatively high piezoelectric constant and phase transition temperature [4]. Unlike lead-based piezoelectrics, the enhanced properties are usually due to a shift in the tetragonal–orthorhombic phase transition temperature (PPT) to near room temperature in KNN-based lead-free piezoelectrics [5]. A major drawback of KNN-based ceramics is that A-site Na and K are volatile during elevated temperature sintering. This makes it difficult to control the sintering process and stoichiometry of KNN-based ceramics [6]. Previous studies have shown that the sintering behavior, crystal structure, microstructure and electrical properties can be affected profoundly by a small deviation from stoichiometry in the electroceramics [7,8]. There have been several reports recently which confirmed the importance of adjusting the K/Na ratio and amount of excess A-site alkali to attain enhanced dielectric and piezoelectric properties [9,10]. It was reported that a high piezoelectric constant d_{33} can be achieved by optimizing the sintering temperature for Li-modified $(Na,K)NbO_3$ ceramics [11]. The present authors believe that this is actually realized by indirectly controlling the stoichiometry of KNN-based ceramics, since the amount of loss of volatile Na_2O and K_2O is temperature dependent. In contrast, little attention has been paid to KNN-based ceramics with nominal A-site deficiency. Therefore, some questions remain for understanding how the A-site non-stoichiometry influences the densification, structure and electrical properties of KNN-based ceramics. In the present work, the dependence of structure, dielectric and piezoelectric constant d_{33} on A-site non-stoichiometry (excess or deficiency) for $0.94K_{0.5}Na_{0.5}NbO_3-0.06LiNbO_3$ (KNN–6LN) was symmetrically investigated. The nominal non-stoichiometry of KNN–6LN with enhanced electrical properties is determined.

A series of $0.94K_{0.5+x}Na_{0.5+x}NbO_3-0.06LiNbO_3$ (K_xN_xN–6LN) ceramics ($x = 0$, ±0.0025, ±0.0050,

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± 0.0075, ± 0.01 and ± 0.0125) were fabricated via a conventional mixed-oxide route. Starting materials were sodium carbonate (Na_2CO_3, 99.8%), potassium carbonate (K_2CO_3, 99%), lithium carbonate (Li_2CO_3, 99.99%) and niobium oxide (Nb_2O_5, 99.5%). They were wet-milled by mixing a certain amount of raw material and ZrO_2 milling balls for 24 h. Several papers [6,11,12] have documented the influence of the sintering temperature on the final structure and properties, and reported that the KNN ceramics calcined between 700 and 850 °C and sintered between 1000 and 1100 °C showed high density and good piezoelectric properties. However, in the present study, since the main focus is on the influence of A-site non-stoichiometry on the structure and electrical properties of KNN–6LN ceramics, the calcination and sintering temperatures were selected as 750 and 1080 °C, respectively. After calcination at 750 °C for 3 h, the powders were ball milled and then pressed into disk samples with a 100 MPa pressure, followed by sintering at 1080 °C for 3 h in air. The samples were poled in 130 °C silicon oil by applying a 30 kV cm^{-1} DC electric field for 30 min. The structure was determined by X-ray diffraction (XRD, D/max 2500PC, Rigaku, Japan). The Raman spectra were measured by Renishaw micro-Raman spectroscopy (Renishaw InVia Reflex) using a 514.5 nm Ar$^+$ blue laser as the exciting source in the wave number range 1000–100 cm^{-1}. The temperature dependence of the dielectric constant (ε_r) and loss tangent (tan δ) was measured by LCR meter (E4980A, Aglient). The piezoelectric constant d_{33} was measured using a quasi-static d_{33} meter (Model ZJ-6A, Institute of Acoustics Academic Sinica). Microstructures were examined using scanning electron microscopy (SEM).

The XRD patterns of K_xN_xN–6LN ($-0.0125 \leqslant x \leqslant 0.0125$) at room temperature are shown in Figure 1. All ceramics are of perovskite structure. As shown, the phase transition behavior of KNN–6LN with excess (Na + K) is significantly different from that of KNN–6LN with deficient (Na + K). Coexistence of tetragonal and orthorhombic phases is observed in the nominal stoichiometric KNN–6LN ceramics. For K_xN_xN–6LN with $x = 0$–0.05 excess (K + Na), the diffraction peaks shift slightly to a lower 2θ angle. This indicates that the crystal parameters increase because Na_2O is more

volatile than K_2O and the radius of K$^+$ (1.33 Å) is larger than that of Na$^+$ (0.97 Å) [12]. In addition, the intensity of tetragonal peaks increases with increasing excess (K + Na), and the diffraction peaks begin to shift slightly to a higher 2θ angle. This suggests that KNN–6LN ceramics are overcompensated by excess (K + Na), and the B-site vacancies are induced to maintain the charge neutrality. In contrast, the intensity of tetragonal peaks weakens with increasingly deficient (K + Na) at $0 \leqslant x \leqslant -0.010$, accompanied by increasing intensity of orthorhombic peaks. K_xN_xN–6LN ceramics with deficient (K + Na) $x = -0.0125$ only exhibit orthorhombic structure. Lin et al. [13] reported a phase transition to an orthorhombic system by adjusting A-site non-stoichiometry with excess (Na + K + Li) of Li-modified KNN-based ceramics. However, the phase transition in the present study has an inverse trend to theirs. It is likely that the addition of excess Li may play a role, since it has been shown [14] that the phase transition from orthorhombic to tetragonal phase in $(K_{0.5}Na_{0.5})NbO_3-xLiNbO_3$ ceramics is due to the large distortion caused by Li$^+$ [14]. While Raman spectroscopy is sensitive to the occurrence of phase transition [15], it was used to determine the structure change of these samples. Figure 2 shows the room temperature Raman spectra for K_xN_xLN–6LN ceramics with $-0.0125 \leqslant x \leqslant 0.0125$ between 100 and 1000 cm^{-1}. In addition to two strong peaks at ~625 and 265 cm^{-1}, there are distinct shoulders in the Raman spectra on the low-frequency side of the Raman mode at ~625 cm^{-1}, which appear in both the orthorhombic and tetragonal phases [16]. Furthermore, there is a broad weak peak in the range 400–500 cm^{-1}, which is indicative of the orthorhombic phase [16]. As shown, the characteristic shoulder in Raman spectra of all K_xN_xN–6LN is obviously visible. However, there is a loss in Raman intensity in the range 400–500 cm^{-1}, and the peak becomes almost flat for K_xN_xN–6LN with deficient (K + Na), $x = -0.0125$, indicating that they are of orthorhombic structure. This result is consistent with that of XRD. These observations show that the coexistence of orthorhombic and tetragonal phases is dependent on the deviation from the A-site stoichiometry of KNN–6LN piezoelectrics and appears in the
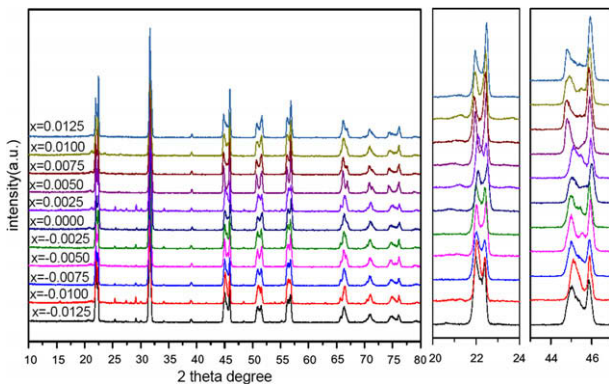

Figure 1. XRD patterns in the range 2θ from 10° to 80° of $0.94K_{0.5+x}Na_{0.5+x}NbO_3-0.06LiNbO_3$ (K_xN_xN–6LN) ($-0.0125 \leqslant x \leqslant 0.0125$) at room temperature.
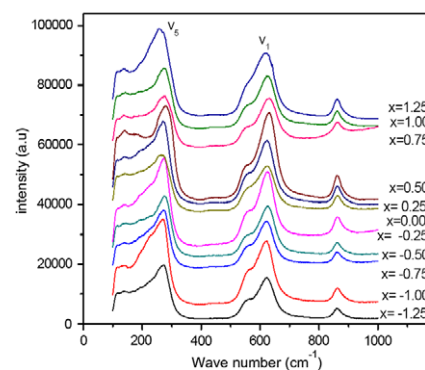
Figure 2. Room temperature Raman spectra for $0.94K_{0.5+x}Na_{0.5+x}NbO_3-0.06LiNbO_3$ (K_xN_xN–6LN) ceramics with $-0.0125 \leqslant x \leqslant 0.0125$ between 100 and 1000 cm^{-1}.