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Domain structure of nonstoichiometric sodium potassium niobate-based ceramics for piezoelectric acoustic actuators

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ABSTRACT

In this work, three piezoelectric acoustic actuators are prepared by using multi-layer technology for lead-free $(Na_{0.48\text{-}x}K_{0.48\text{-}x}Li_{0.04})Nb_{0.89\text{-}x}Ta_{0.05}Sb_{0.06}O_3\text{-}xSrTiO_3$ (NKLNTS-xST) ceramics, $x = 0$ and 0.007, and commercial lead-based ceramic. The phase and domain structure are also investigated by using the XRD patterns and TEM images of the NKLNTS-xST ceramics. The $(Na_{0.473}K_{0.473}Li_{0.04}Sr_{0.007})Nb_{0.883}Ti_{0.007}Ta_{0.05}Sb_{0.06}O_3$ piezoelectric acoustic actuator has the best sound pressure level and d_{33} value of 650 pCN^{-1}. The response mechanisms suggest that the piezoelectric ceramic vibration amplitude was increased and the sound pressure level improved since the orthorhombic and tetragonal phases were found to coexist and the nanoscale domain increased for the $(Na_{0.473}K_{0.473}Li_{0.04}Sr_{0.007})Nb_{0.883}Ti_{0.007}Ta_{0.05}Sb_{0.06}O_3$ ceramic.

1. Introduction

In recent years, smartphones have been developing rapidly as portable devices, with the trend of becoming lighter and thinner. Dynamic speakers for smartphones generally have good performance; however, they are limited by their thickness in portable devices. Recently, piezoelectric acoustic actuators have received increasing attention due to the lighter, smaller size and immunity to electromagnetic interference. Piezoelectric material can be roughly divided into three types: (1) lead-based ceramics; (2) lead-free ceramics; and, (3) Polyvinylidene fluoride (PVDF) [1–4]. Among them, lead-free piezoelectric ceramics, for example sodium potassium niobate (NKN)-based materials, have been widely researched as substitutes for lead-based ceramics in view of health and environmental concerns [5–10].

Previous research has also indicated that the densification and piezoelectric properties of sodium potassium niobate-based ceramics can be improved by substituting $SrTiO_3$ dopants [11]. Further, the loss tangent for $(Na_{0.48\text{-}x}K_{0.48\text{-}x}Li_{0.04})Nb_{0.89\text{-}x}Ta_{0.05}Sb_{0.06}O_3\text{-}xSrTiO_3$ (NKLNTS-xST) ceramics can also be reduced when $x = 0.007$. The ceramics in this composition feature excellent piezoelectric properties due to the formation of the so-called polymorphic phase transition (PPT) near room temperature [12]. Since the orthorhombic (O) and tetragonal (T) phases are formed in the coexistence region, this region can be more appropriately called the polymorphic phase boundary (PPB) [13–16]. Many papers have discussed the domain structure of lead-free ceramics in the PPB region, but few have considered NKLNTS-xST-based samples, which is the motivation of the present work.

In the present study, the nonstoichiometric $(Na_{0.48\text{-}x}K_{0.48\text{-}x}Li_{0.04})Nb_{0.89\text{-}x}Ta_{0.05}Sb_{0.06}O_3\text{-}xSrTiO_3$ (NKLNTS-xST) ceramics were prepared by a solid-state reaction method based on our previous work [12]. The phase and domain structures were investigated systematically. Then, multilayer piezoelectric ceramics were fabricated by the tape casting method for application as piezoelectric acoustic actuators.

2. Experimental process

The raw materials of Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_3, Ta_2O_5, $SrCO_3$ and TiO_2 powders (> 99% purity) were used to synthesize the nonstoichiometric $(Na_{0.48\text{-}x}K_{0.48\text{-}x}Li_{0.04})Nb_{0.89\text{-}x}Ta_{0.05}Sb_{0.06}O_3\text{-}xSrTiO_3$ (NKLNTS-xST), where $x = 0$ and 0.007 via a conventional solid-state reaction method. First, Na_2CO_3, K_2CO_3, Nb_2O_5, Li_2CO_3, Sb_2O_3, Ta_2O_5, $SrCO_3$ and TiO_2 powders were ball-milled together with ZrO_2 balls in a polyethylene jar for 24 h using ethanol (99% purity) as the medium. The resulting slurry was dried and then calcined at 890 °C in air for 4 h, and subsequently ball-milled again for 24 h. After drying, the mixed powder was uni-axially pressed into a disc (diameter: 11 mm) at a

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pressure of 100 MPa and subsequently sintered in air at 1100 °C for 3 h. Then, the specimens were poled in silicon oil at 60 °C for 30 min under a DC field of 3 kV/mm. The crystal structure was confirmed by XRD (D2 PHASER, Bruker, Germany) using Cu Kα (λ = 0.154 nm) radiation, while the piezoelectric constant d_{33} was measured using a d_{33} meter (90–2030, APC, USA). The microstructure was observed using both FE-SEM (SU8000, Hitachi, Japan) and TEM (JEM-2100F, JEOL, Japan).

The green sheet, with a thickness of 30 µm, were fabricated via the tape casting method using the calcined ceramic powders and commercial lead-based ceramic powders. The green sheet was printed with a 70Ag/30 Pd metal-paste, after which the printed sheets were stacked, pressed and dried. Subsequently, the laminated structure was obtained by hot isostatic pressing. After all the green chips were printed with external electrodes and sintered in air at 1100 °C for 3 h, and the commercial lead-based ceramic powders were sintered in air at 880 °C for 2 h, the specimens were poled in silicon oil at 60 °C for 30 min under a DC field of 3 kV/mm. The piezoelectric coefficient d_{33} was measured using a d_{33} meter (90-2030, APC, USA). The sound pressure level was measured in an anechoic chamber using a 1/2-in. microphone preamplifier (2669L, Brüel & Kjær, Denmark), a 1/2-in. microphone (4191, Brüel & Kjær, Denmark), and an amplifier measuring system 3560 C T02 Pulse analyzer (Brüel & Kjær, Denmark). The distance between the piezoelectric acoustic actuator and microphone was 10 cm.

3. Results and discussion

Fig. 1 shows the XRD patterns of the as-prepared NKLNTS-*x*ST (x = 0 and 0.007) at room temperature. To confirm the exact diffraction angles, silicon powders were used for calibration. It can be seen that both ceramics display the pure perovskite structures. Typically, the perovskite phase structure of NKN-based ceramics is initially judged by the relative intensities of the (002) and (200) Bragg peaks (about 45°) [17]. According to a previous report and the experimental results, it appears that the lattice structures show the orthorhombic phase when x = 0 [12]. The two reflection peaks, namely $(202)_O$ and $(020)_O$ using TOPAS software, are shown in the inset of Fig. 1(a), for which the O subscript represents orthorhombic structures. Fig. 1(b) shows the reflection patterns of the samples with x = 0.007, and the inset shows the detailed data obtained using the TOPAS software. More specifically, three peaks can be seen in the inset, namely $(202)_O$, $(020)_O$, and $(200)_T$, where the T subscript represents tetragonal structures. This result provides evidence for the coexistence of the orthorhombic and tetragonal phases of the samples when x = 0.007. The obtained lattice parameters derived from the Rietveld refinement with different composition are presented in Table 1.

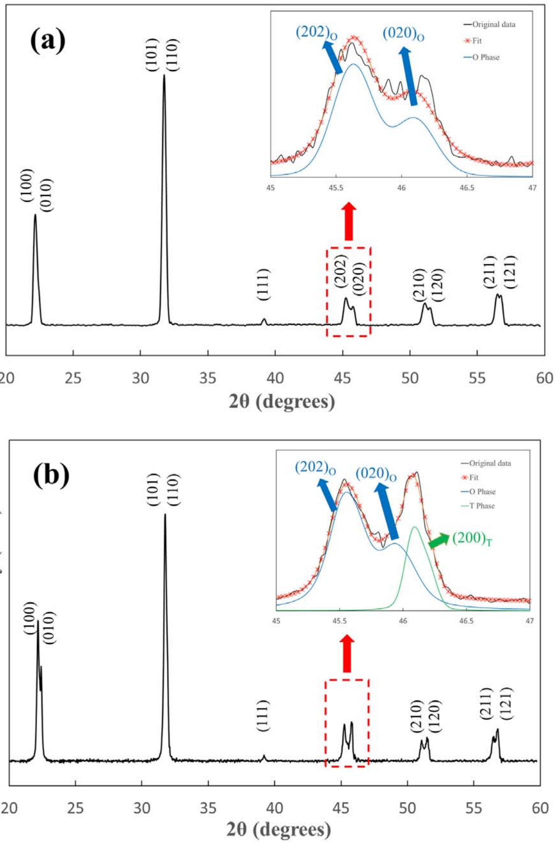

Fig. 1. XRD patterns of the NKLNTS-*x*ST ceramics, where x = (a) 0, and (b) 0.007.

Table 1
Refined structural parameters of the NKLNTS-*x*ST ceramics.

	x = 0	x = 0.007	
Parameters	O phase	O phase	T phase
a (Å)	5.5493	5.5911	4.0662
b (Å)	3.8103	3.9259	4.0662
c (Å)	5.5635	5.6056	3.9136
R_{wp} (%)	7.850	8.361	

R_{wp} is the weighted profile agreement factor.

It is well known that apart from the lattice contribution, the domain morphology also has an important role in the improvement of piezoelectric properties of ferroelectric materials. Therefore, we used acid-etching technology and transmission electron microscopy (TEM) imaging to observe the domain-wall structure. Fig. 2(a) and (b) show the bright field TEM image of the NKLNTS-*x*ST ceramics with x = 0 and 0.007, respectively. The irregularly shaped domain boundaries and rectangular domain stripes are clearly visible in Fig. 2(a). In Fig. 2(b), the stripe and herringbone domains morphology and increased domain wall density are clearly observed when the orthorhombic and tetragonal phases coexist for the NKLNTS-*x*ST (x = 0.007) ceramic. According to a previous report, the stripe and herringbone domains are typical features of domain configuration for NKN-based ceramics with orthorhombic-tetragonal phase coexistence [18]. In addition, when the orthorhombic and tetragonal phases coexist, the domain was found to have nanoscale dimensions. According to Qin et al., samples with nanoscale domains can enhance the electrical properties [19].

Fig. 3 shows a schematic diagram of the multilayer piezoelectric ceramics with 9 laminated layers. The cross-sectional SEM image of the multilayer ceramics is shown in Fig. 4. The thicknesses of the ceramic layers and electrode layers are about 30 µm and 5 µm, respectively. It was noted that the electrode did not diffuse into the ceramic layer. Table 2 compares the piezoelectric coefficient d_{33} values of the disc and multilayer NKLNTS-*x*ST (x = 0 and 0.007) and lead-based samples. It can be seen that there is a significant improvement in d_{33} values when x = 0.007 due to the O and T phase coexistence [12]. According to the reported data by Damjanovic, the free-energy distribution in the phase-transition region can be flattened and favors polarization rotation [20]. Therefore, the polarization anisotropy between two polar phases can be eliminated in the PPB region, leading to the decrease of domain wall energy and consequently reduce the dimension of domain, resulting in lower free energy and favoring polarization rotation [21]. Therefore, the energy of domain-wall is inherently lower and the mobility of the domain wall is enhanced when the domain enters the nanometer scale. They would be more easily reoriented under the applied electric field, thereby leading to high piezoelectric coefficients [21–23]. The piezoelectric coefficients shown in Table 2 suggest that the proposed NKLNTS-*x*ST ceramic is suitable for use in piezoelectric devices. To investigate the practical applications of this material, we fabricated a prototype piezoelectric acoustic actuator. Fig. 5 shows the main design-component diagram of the piezoelectric acoustic actuator developed for this research.