

Structures and electrical properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--Li}(\text{Ta}_{0.5}\text{Nb}_{0.5})\text{O}_3$ lead-free piezoelectric ceramics

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Abstract Solid solutions of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) and $\text{Li}(\text{Ta}_{0.5}\text{Nb}_{0.5})\text{O}_3$ (LTN) were investigated as a potential candidate of lead-free piezoelectric ceramics. It was found that the Curie temperature of solid solutions increases slightly with increasing the LTN content and simultaneously the polymorphic phase transition temperature linearly decrease till below room temperature. An orthorhombic to tetragonal phase transformation at room temperature, or a morphotropic phase boundary, in NKN is induced by ~ 7 at% LTN addition, where the best dielectric, piezoelectric and electromechanical properties are achieved. The 0.94NKN–0.07LTN ceramics possess a dielectric constant of 765, a loss tangent of 0.04 at 1 kHz, a piezoelectric constant d_{33} of 253 pC/N and an electromechanical coupling factor k_p of 48%.

1 Introduction

In the past few years there has been a tremendous flurry of research interest in lead-free piezoelectric materials that show similar piezoelectric properties to those of lead zirconate titanate (PZT) based materials. The reason for this is that the PZT based ceramics contain approximately

60 wt% lead oxide that has brought serious threats to the environment and human health.

Unfortunately, there has not yet been a lead-free piezoelectric material possessing completely comparable properties to those of PZT based materials. Traditional lead-free ferroelectric ceramics, for example, barium titanate, bismuth sodium titanate, and their solid solutions, usually show relatively low piezoelectric properties [1–6]. Since Saito et al. reported their work in 2004, alkaline niobates have been a focus in this research field [7]. Sodium potassium niobate ceramics $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$, NKN near the morphotropic phase boundary (MPB) were actually investigated starting from last century [8, 9]. However, the difficulty in processing made them exhibit much weaker electrical properties than they could have intrinsically [10–14]. It is known that the MPB may play a crucial role in the enhancement of piezoelectric properties. LiTaO_3 (LT), LiNbO_3 (LN) and LiSbO_3 (LS) were added into NKN, forming solid solutions with new MPBs, although they have different crystalline structures from NKN matrix [7, 15–24]. It is believed that structural distortion due to the dissolution of Li, Ta and Nb into A- or B sites of perovskite lattices leads to an orthorhombic to tetragonal phase transition in NKN, which significantly enhances piezoelectric properties [15]. The addition of LS can effectively improve electrical properties; however, the Curie temperature of NKN apparently decreases [22–24]. Therefore, the amount of LS addition was usually limited. For the same purpose, other ferroelectric phases were also added, but satisfactory properties have not been reported yet and the Curie temperature was decreased [25–31].

In this study, a solid solution between LT and LN (LTN) in equal mole was used as one end member. It was mixed with NKN with a purpose to form a MPB composition. The crystalline structures, grain morphology and electrical

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properties of $(1-x)\text{NKN}-x\text{LTN}$ ceramics as a function of the LTN content were explored in detail. An ordinary sintering technique was employed to make dense materials.

2 Experimental

$(1-x)\text{NKN}-x\text{LTN}$ ceramics were manufactured via a conventional mixed-oxide processing route. High-purity raw materials used in this study were sodium carbonate (Na_2CO_3 , 99.8%), potassium carbonate (K_2CO_3 , 99.05%), lithium carbonate (Li_2CO_3 , 99.5%), niobium oxide (Nb_2O_5 , 99.9%), and tantalum oxide (Ta_2O_5 , 99.5%). The powders were mixed in a nylon jar with ZrO_2 balls in anhydrous ethanol for 18 h and then calcined at 900 °C for 4 h after drying. Before compaction, the calcined powder was milled again for 24 h to improve the sintering activity. Specimens with a thickness of ~ 2 mm and a diameter of ~ 12 mm were pressed using a stainless steel die. Samples were sintered under atmospheric condition in the temperature range of 1040–1100 °C for 2–4 h.

The microstructure of the sintered samples was observed by scanning electron microscopy (SEM, JEOL6301F, Tokyo, Japan). Powder X-ray diffraction (XRD, Rigaku, Tokyo, Japan) patterns of crushed pellets using a $\text{Cu K}\alpha$ radiation were recorded in the 2θ range of 20–60°.

Two major surfaces of each specimen were screen-painted with silver paste and then fired at 550 °C for 30 min after a careful polishing process. Dielectric constant at frequencies of 1 k to 1 M Hz was measured as a function of temperature by a LCR meter (HP 4980A, Agilent, USA). After a poling treatment taken in a silicone oil bath at 3 kV/mm for 20 min at 150 °C, the piezoelectric strain constant d_{33} and the planar electromechanical coupling factor k_p were measured by using a Belincourt-meter (YE2730, Sinocera, Yangzhou, China), and a resonance-antiresonance method through an impedance analyzer (HP 4192A, Hewlett-Packard, Palo Alto, CA), respectively.

3 Results and discussion

XRD patterns shown in Fig. 1 indicate that the crystal structure of $(1-x)\text{NKN}-x\text{LTN}$ ceramics changes with increasing LTN content. A small amount of LTN can dissolve into the perovskite lattice of NKN to form solid solutions and retain the original perovskite structure. A secondary phase can be detected only when x is larger than 0.1, because NKN and LTN have different crystal structures [15]. The secondary phase denoted as asterisks can be indexed as $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ (ICDD: 52–0157) with a tetragonal tungsten bronze structure. In addition, the transformation of crystal structure from an orthorhombic to tetragonal

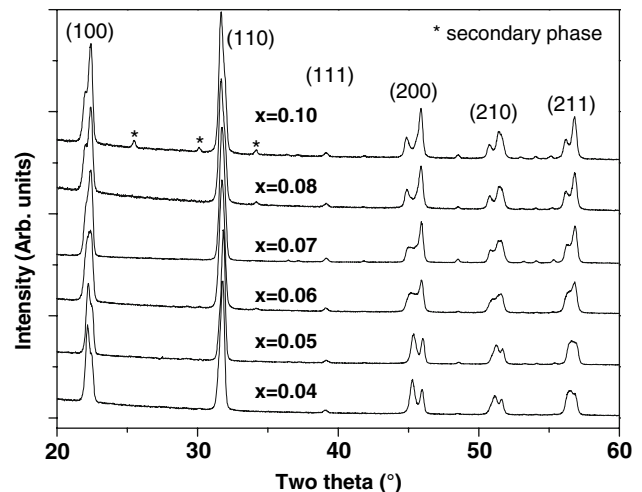


Fig. 1 XRD patterns of $(1-x)\text{NKN}-x\text{LTN}$ ceramics with x as indicated

symmetry can be detected when x is larger than 0.07. Therefore, a MPB between orthorhombic and tetragonal phase exists near $x = 0.07$ in $(1-x)\text{NKN}-x\text{LTN}$ ceramics. For $0.07 < x < 0.10$, the tetragonality c/a of the solid solution increases with increasing x , as calculated using the XRD data in Fig. 1.

The morphology of the samples sintered at 1070 °C is shown in Fig. 2. All samples show faceted grain morphology that is typical of the NKN based ceramics. The addition of LTN improves the sintering of NKN to a certain degree, but simultaneously promotes the grain growth. As known, pure NKN ceramics are difficult to be densified by ordinary sintering. However, for $0.04 < x < 0.10$ $(1-x)\text{NKN}-x\text{LTN}$ ceramics can be well densified at temperatures as low as 1070 °C. The use of lithium in the composition is believed to benefit the densification.

Figure 3 illustrates the temperature dependence of dielectric constant measured at 100 kHz for $(1-x)\text{NKN}-x\text{LTN}$ ceramics. There are two phase transition temperatures for the composition with $x = 0.04$. One corresponds to the transition between tetragonal and cubic phases (T_c) at ~ 431 °C; another one corresponds to the transition between orthorhombic and tetragonal phases (T_{O-T}) at ~ 126 °C. This observation is similar to that of pure NKN ceramics. However, T_c increases, but T_{O-T} decreases with increasing x . For $x = 0.07$, T_{O-T} is shifted below room temperature. These changes can be clearly seen in the inset in Fig. 3.

The electrical properties of $(1-x)\text{NKN}-x\text{LTN}$ ceramics as a function of the LTN content x are shown in Fig. 4. All compositions possess better electrical properties than pure NKN ceramics as previously reported [10–14]. This should be ascribed to both the improved densification and the changed crystal structure caused by the addition of LTN. Similar to other MPB systems, it was found that the electrical properties of $(1-x)\text{NKN}-x\text{LTN}$ ceramics show

Fig. 2 SEM micrographs of $(1 - x)\text{NKN}-x\text{LTN}$ ceramics sintered at $1070\text{ }^\circ\text{C}$ for x equals to (a) 0.04, (b) 0.06, (c) 0.08 and (d) 0.10, respectively

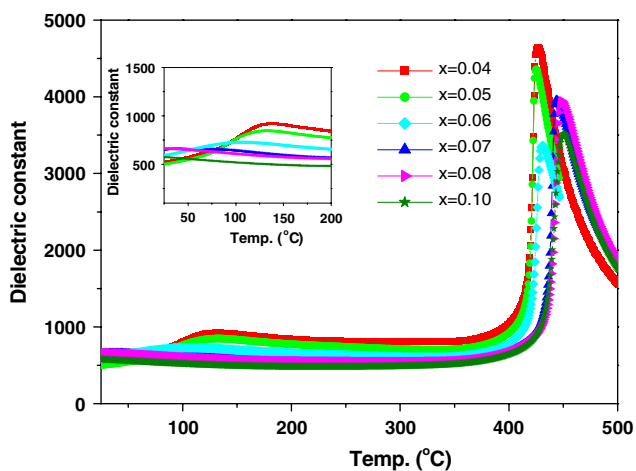
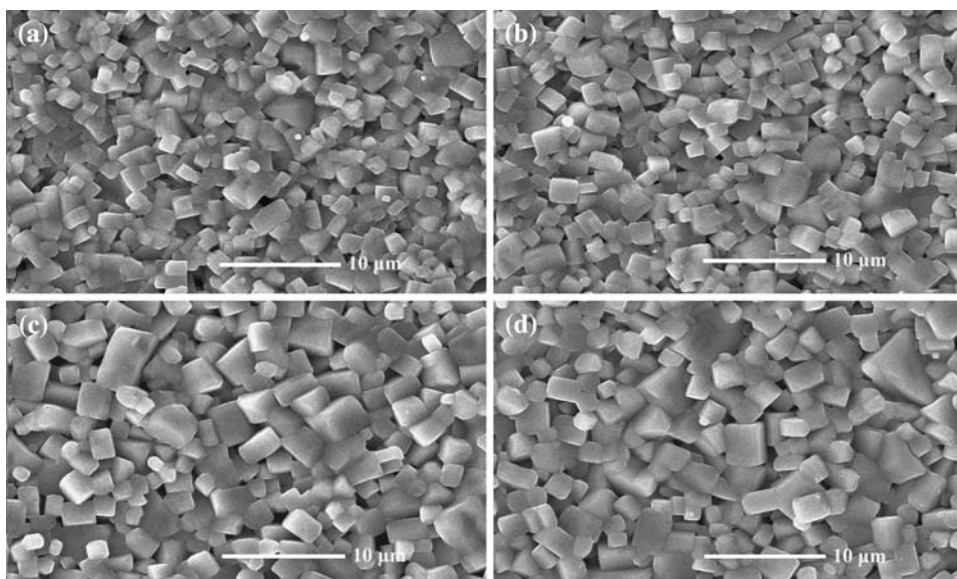


Fig. 3 Dielectric constant measured at 100 kHz as a function of temperature for $(1 - x)\text{NKN}-x\text{LTN}$ ceramics

a strong compositional dependence near the MPB. The best properties of $d_{33} \sim 253\text{ pC/N}$, $k_p \sim 48\%$, dielectric constant of ~ 765 and loss tangent of ~ 0.04 at 1 kHz appear in the composition with $x = 0.07$, which lies in the tetragonal side of the MPB. Therefore, it is clear that the MPB between orthorhombic and tetragonal phases plays an important role in the enhancement of piezoelectric properties of solid solution systems. Moreover, these systems show a bit better piezoelectric properties than NKN-LT or NKN-LN, however lower Curie temperatures [15, 16].

4 Conclusion

$(1 - x)\text{NKN}-x\text{LTN}$ solid solution ceramics were fabricated by ordinary sintering. LTN can be dissolved into the lattice of

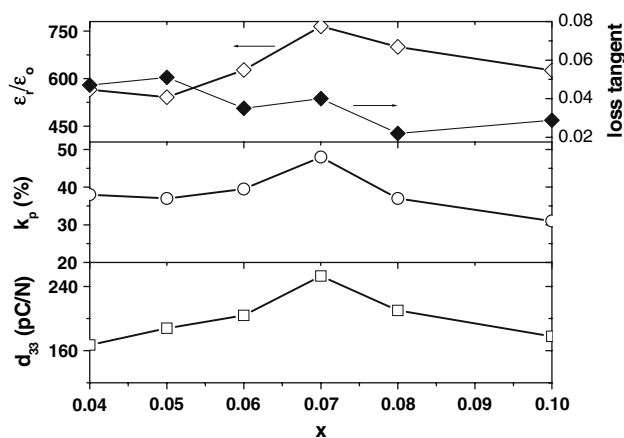


Fig. 4 Electrical properties of $(1 - x)\text{NKN}-x\text{LTN}$ ceramics as a function of the LTN content x

NKN to form solid solutions with a pure perovskite structure, till it reaches the solubility limit of $\sim 10\%$. The addition of a small amount of LTN induces a structure change from orthorhombic to tetragonal phase. A morphotropic phase boundary between orthorhombic and tetragonal phases was confirmed approximately at $x = 0.07$. Enhanced electrical properties of d_{33} of 253 pC/N , k_p of 0.48 , dielectric constant of 765 , and loss tangent of 0.04 were achieved for the sample with $x = 0.07$. This composition has a relatively high Curie temperature of $\sim 440\text{ }^\circ\text{C}$, showing a potential as a lead-free material for a wide range of electromechanical applications.

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