Structure and piezoelectric properties of lead-free $(Na_{0.52}K_{0.44-x})(Nb_{0.95-x}Sb_{0.05})O_3$-$x$LiTaO$_3$ ceramics

Jian Fu · Ruzhong Zuo · Danya Lv · Yi Liu · Yang Wu

Abstract Lead-free $(Na_{0.52}K_{0.48-x})(Nb_{0.95-x}Sb_{0.05})O_3$-$x$ LiTaO$_3$ ($x = 0.025$–0.05) piezoelectric ceramics in which the Sb content is kept constant, have been specially designed and successfully fabricated by a conventional solid state reaction method. The $(Na_{0.52}K_{0.48})(Nb_{0.95}Sb_{0.05})O_3$ ceramics can be well sintered after A-site and B-site cations are replaced by Li$^+$ and Ta^{5+}, respectively. A single-phase perovskite structure remains within the studied substitution concentration. An orthorhombic-tetragonal phase transition occurs with gradually increasing the content of Li$^+$ and Ta^{5+}, and was identified in the composition range of $0.0375 < x < 0.0425$ where two kinds of ferroelectric phases may coexist and simultaneously a strong compositional dependence of electrical properties was found out. An appropriate content of Sb effectively enhanced the piezoelectric properties of the materials. The optimum overall properties with a piezoelectric constant d_{33} of 321 pC/N, a dielectric constant ε_{33}^T of 1,780, a planar electromechanical coupling coefficient k_p of 0.52 and a Curie temperature T_c of 315 °C were obtained in the composition with $x = 0.0425$, indicating the ceramics studied have potentials for replacing lead-containing ceramics for device applications.

1 Introduction

Recent studies have demonstrated that the piezoelectric properties of Li- and Ta and/or Sb doped (Na,K)NbO$_3$ (NKN) ceramics are comparable to those of the most widely used lead zirconate titanate based ceramics [1, 2]. Particularly, the addition of Li, Ta and Sb significantly improves the sinterability of NKN ceramics under conventional processing conditions [3–6]. These outcomes have obviously stimulated systematical studies on alkaline niobates by optimizing the compositions and the processing conditions in order to achieve further enhancement of the piezoelectric activity. The optimization of processing conditions has been so far investigated through improving the compositional distribution [7, 8], reducing the volatilization of alkali elements [9], depressing the evolution of secondary phases [10], and even attempting different electric poling procedures [11]. By comparison, the innovation of compositions has still been around looking for new materials with a two-phase coexistence state by shifting an orthorhombic-tetragonal polymorphic phase transition (PPT) close to the ambient temperature through either adding other ferroelectric phases with a perovskite structure [12–14], or adjusting the combination of different components [1]. Particularly, an elaborate combination of NaNbO$_3$, KNbO$_3$, LiNbO$_3$, NaTaO$_3$, KTaO$_3$, LiTaO$_3$, NaSbO$_3$, KSbO$_3$ and LiSbO$_3$ (LS) has produced a couple of compositions with desirable electrical properties [1, 2, 15–19].

However, these compositions with different ratios of Li, Ta and Sb exhibit extremely different properties, for example, the piezoelectric constant d_{33} displays a broad distribution. The divergence of electrical properties may be partially ascribed to the processing sensitivity, yet the relative content of each element may also play a crucial role. For example, it has been believed that more covalent Ta and Sb tend to enhance the piezoelectric activities of alkaline niobates [1]. Particularly, the increase of Sb content obviously enhances the dielectric and piezoelectric constants of these systems [19, 20], although the Curie temperatures will be linearly

J. Fu · R. Zuo (✉) · D. Lv · Y. Liu · Y. Wu
Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, 230009 Hefei, People's Republic of China
e-mail: piezolab@hfut.edu.cn

lowered. Therefore, the addition of a suitable amount of Sb and Ta can be considered as a right way to achieve excellent overall properties for lead-free alkaline niobate systems.

In this study, a prescribed amount (5%) of Sb was added into $(Na_{0.52}K_{048})NbO_3$. Lead-free $(Na_{0.52}K_{0.48})(Nb_{0.95}Sb_{0.05})O_3$ (NKNS) compositions are expected to exhibit an orthorhombic structure [20]. A special K/Na ratio was arbitrarily used to compensate for more volatilization loss of Na during sintering. Solid solutions between $LiTaO_3$ (LT) and NKNS were then fabricated by a conventional solid state reaction method. Their phase transition behavior, microstructure and various electrical properties were investigated.

2 Experimental

Ceramics with compositions of $(Na_{0.52}K_{0.44-x})(Nb_{0.95-x}Sb_{0.05})O_3$-$xLiTaO_3$ (NKNS-xLT) ($0.025 \leq x \leq 0.05$) were synthesized by a conventional solid state method. The raw materials in this study were Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Li_2CO_3 (99.9%), Nb_2O_5 (99.5%), Ta_2O_5 (99.9%) and Sb_2O_3 (99.9%). These powders were weighed according to the above chemical formula and then ball mixed in nylon jars with ZrO_2 balls for 6 h using ethanol as the medium. After drying, the powder mixtures were calcined at 850 °C for 5 h. Each calcined powder then underwent the mixing and calcination twice for homogenization. Afterwards, the calcined powders were ball-milled for 24 h with a 0.5 wt% PVB binder solution. The disk specimens were sintered in air in the temperature range of 1,060–1,120 °C for 3 h. Electrodes were made on major surfaces of each sample by firing silver paste at 550 °C for 30 min. The electric poling was performed at 110 °C in a silicone oil bath by applying a dc field of ~2 kV/mm for 15 min.

The phase structure of the samples was examined by an X-ray diffractometer (XRD-7000, Shimadzu, Japan) using a Cu Kα radiation. The microstructure was observed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). Dielectric properties of the sintered compacts were measured as a function of temperature and frequency by a LCR meter (Agilent E4980A, USA). The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China), and the planar electromechanical coupling factor k_p was determined by a resonance-antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd. China).

3 Results and discussions

The XRD patterns of NKNS-xLT ceramics are shown in Fig. 1. It can be seen that all compositions show a pure
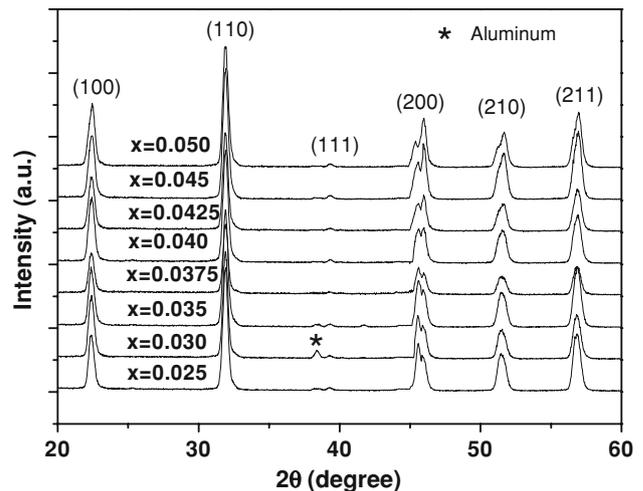
Fig. 1 XRD patterns of NKNS-xLT ceramics with different LT content as indicated

perovskite structure, indicating that Li^+ and Ta^{5+} have entirely entered the $(Na_{0.52}K_{0.48})(Nb_{0.95}Sb_{0.05})O_3$ lattice to form a solid solution within the studied composition range, although NKNS has a perovskite structure and yet LT owns a lithium niobate structure which can be described as a heavily distorted perovskite structure [21]. The additional peaks in the plot marked by the star were considered to be from the aluminum frame for powder stay. An orthorhombic perovskite structure remains till $x = 0.0375$. With further increasing x, a tetragonal symmetry starts to appear ($x \geq 0.0425$). Therefore, a phase structure transition owing to the composition change occurs in the range of $0.0375 < x < 0.0425$. It is known that LT has a totally different structure from NKN perovskite. Therefore a small amount of LT entering the lattice of NKN perovskite tends to induce a distortion of oxygen octahedral of NKN. This kind of structure distortion may promote the phase structure transition from orthorhombic to tetragonal symmetry. The distortion degree tends to be enhanced as more LT diffuses into the lattice. The structure transition induced by a continuous change in the composition is prone to produce a two-phase coexistence zone, which plays an important role in high-performance piezoelectric ceramics. These changes can also be seen from Fig. 2 where the lattice parameters of the NKNS-xLT ceramics were calculated as a function of the LT content. The two-phase coexistence zone just corresponds to the shadow part of Fig. 2. At the tetragonal side, it can be found that the tetragonality c/a increases with x. For the composition with $x = 0.0425$, the c/a ratio reaches ~1.007, and then increases to ~1.012 when $x = 0.05$.

The SEM images on free surfaces of the samples sintered at 1,100 °C for 3 h are shown in Fig. 3. It is evident that all samples show typical morphology of alkaline niobate systems. Grains are faceted and slightly inhomogeneous in grain
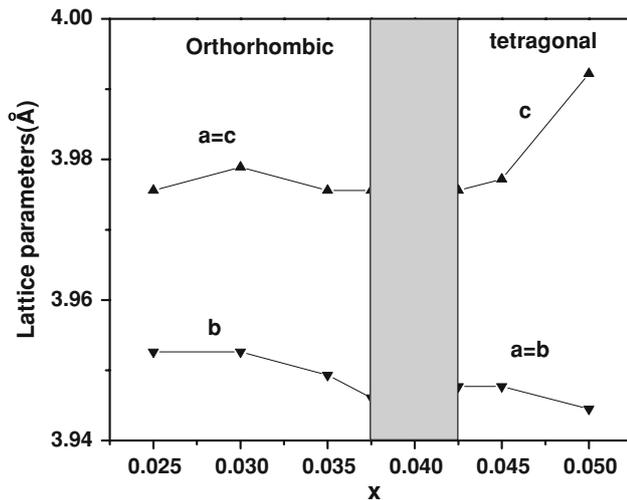
Fig. 2 Lattice parameters of NKNS-xLT ceramics as a function of the LT content

size. However, the average grain size does not obviously change with varying the content of LT. In addition, all samples have been dense with little porosity. Compared to pure NKN ceramics, the densification behavior has been greatly promoted by the addition of Li, Ta or Sb. However, these three elements seem to play different roles. Li tends to promote the sintering and influence the grain growth as well. Li is usually considered as an effective sintering aid for a few material systems due to a low melting point of Li_2O; however, an abnormal grain growth is prone to be induced [22, 23]. Because of the volatilization during sintering, Li more easily leaves away from the lattice sites to form high vapor pressure or liquid phases at high temperature, which makes the Li substituted NKN ceramics easily densified. Of course, the Li evaporation at high temperature will cause a certain deviation of chemical composition from the starting materials. Therefore, a low-temperature sintering processing will become more focused in future for this kind of compositions. By comparison, Ta and Sb have much less influence on the microstructure of NKN based materials and the Ta or Sb substituted NKN ceramics become difficultly sintered [20, 24]. As known, Ta and Sb have higher eletronegativities than Nb. Therefore, the Ta or Sb substituted NKN ceramics tend to have higher melting points because of their stronger covalency. This may require a higher sintering temperature. Therefore, the change in the sintering and microstructure of (Li, Ta, Sb) modified NKN systems is mainly attributed to the addition of Li.

Figure 4 shows the dielectric constants at 10 kHz as a function of temperature for chosen unpoled samples. Similar to pure NKN ceramics, the NKNS-xLT ceramics ($x \leq$ 0.0375) exhibit two-phase transitions: the tetragonal-cubic ferroelectric phase transition (T_c) and the orthorhombic-tetragonal (T_{o-t}) PPT. When $x = 0$, T_{o-t} and T_c are 126 and

302 °C, respectively [20]. However, T_{o-t} was shifted to room temperature with increasing the content of LT. Further increase in x caused T_{o-t} to lie below room temperature so that only a tetragonal structure can be identified at room temperature. Therefore, the formation of two-phase coexistence zone is caused by shifting a diffuse PPT close to room temperature. This kind of diffuse PPT, which behaviors like a relaxor ferroelectric phase transition, is probably attributed to the locally fluctuated compositions or coexisted multiphases with varying PPT temperatures. On the contrary, the addition of LT slightly moved T_c toward higher temperature. This should be correlated to an increase in tetragonality as shown in Fig. 2. The ceramics with $x = 0.0425$ own a T_c of 315 °C approximately.

Various electrical properties of poled NKNS-xLT ceramics as a function of the LT content are shown in Fig. 5. It can be seen that the piezoelectric strain constant d_{33}, the planar electromechanical coupling factor k_p and the dielectric constant ε_{33}^T first slightly go up with increasing x, reaching the maxima approximately at = 0.0425, and then drop down with further increase of x. The loss $\tan\delta$ at 10 kHz just fluctuates in the range of 2.8–3.5% with changing x. A strong compositional dependence of dielectric and piezoelectric properties of NKNS-xLT ceramics appears at $x = 0.0375 < x < 0.0425$ where two ferroelectric phases probably may coexist. This would be explained by an increase of possible polarization states. The optimum electrical properties were obtained in NKNS-0.0425LT ceramics, concerning a d_{33} of 321 pC/N, a k_p of 0.52, an ε_{33}^T of 1,780 and a T_c of 315 °C. It can be seen that the overall properties show advantages over those previously reported for random ceramics. The significance lies on a combination of a larger d_{33} and a relatively high T_c in the materials. Sb with a higher electronegativity was used in a fixed amount in the total composition, helping improve the permittivity. LT was used to substitute NKNS instead of LS, benefiting to the increase of the Curie temperature in addition to shift the T_{o-t} to room temperature. In previous works, although Sb is used in the composition, yet with the increase of LT content, the content of Sb is actually reduced. Moreover, LS used to be applied but it tends to decrease the Curie temperature although it can also move the T_{o-t} to room temperature. The more covalent Sb ions make a contribution to the enhancement of dielectric and further piezoelectric properties by increasing the polarizability of total perovskite unit cells. As an appropriate amount of Sb is added, the electrical properties can be enhanced while the Curie temperature is kept at a high level.

4 Conclusions

Lead-free NKNS-xLT piezoelectric ceramics were specially designed and manufactured by ordinary sintering. Their

Fig. 3 SEM images on free surfaces of NKNS-xLT with different LT content: **a** $x = 0.03$, **b** $x = 0.0375$, **c** $x = 0.0425$ and **d** $x = 0.05$
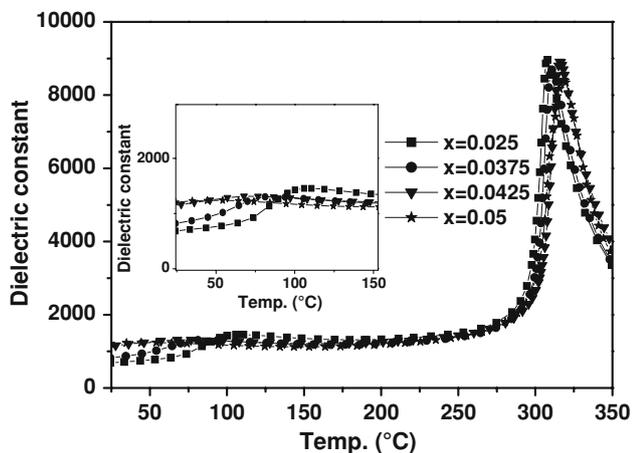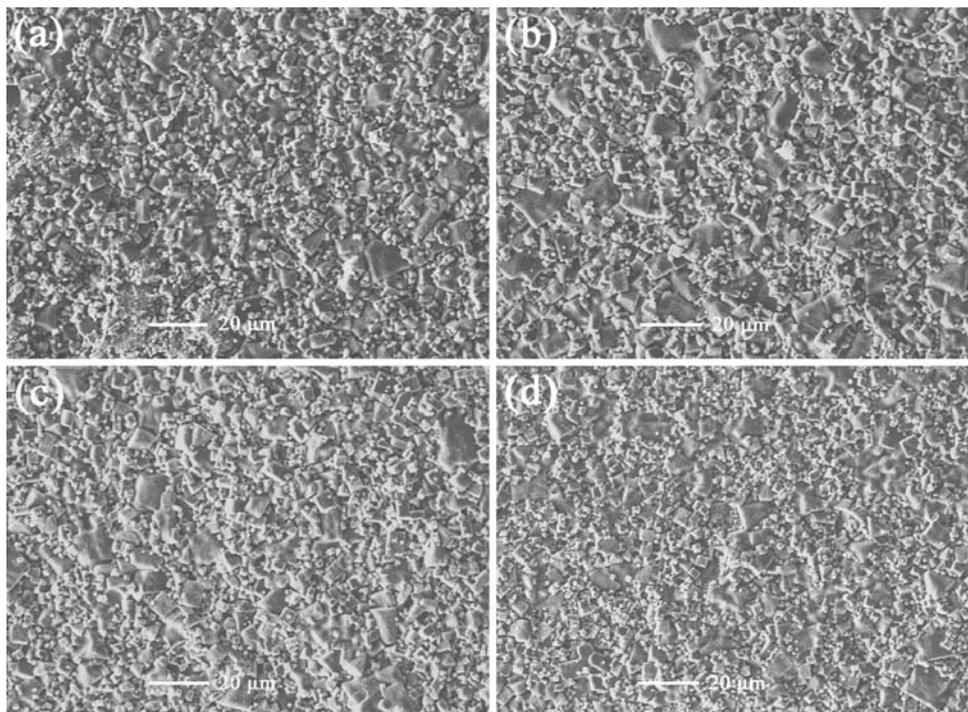
Fig. 4 Dielectric constants at 10 kHz versus temperature curves of NKNS-xLT ceramics as indicated

Fig. 5 Compositional dependence of various electrical properties of poled NKNS-xLT ceramics

phase transition behavior, microstructure and various electrical properties were investigated. The addition of LT not only promotes the sinterability of NKNS ceramics, but also induces a significant advancement of piezoelectric properties. The main change in the properties is considered to correlate with a possible two-phase coexistence zone formed by shifting a PPT T_{o-t} close to room temperature. This phase transition zone was identified in the composition range of $0.0375 < x < 0.0425$. The addition of an appropriate amount of Sb tends to enhance the electrical properties but keeps the Curie temperature at a relatively high level.

Excellent overall properties of $\varepsilon_{33}^T = 1,780$, $d_{33} = 321$ pC/N, $k_p = 0.52$ and $T_c = 315$ °C were obtained in the composition with $x = 0.0425$, indicating the ceramics studied have potential for replacing lead-containing ceramics for device applications.

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