

Phase Transformation and Tunable Piezoelectric Properties of Lead-Free $(\text{Na}_{0.52}\text{K}_{0.48-x}\text{Li}_x)(\text{Nb}_{1-x-y}\text{Sb}_y\text{Ta}_x)\text{O}_3$ System

Ruzhong Zuo,[†] Jian Fu, and Danya Lv

Institute of Electro Ceramics and Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, China

Lead-free $(\text{Na}_{0.52}\text{K}_{0.48-x})(\text{Nb}_{1-x-y}\text{Sb}_y)\text{O}_3$ - $x\text{LiTaO}_3$ (NKNS-LT) piezoelectric ceramics have been fabricated by ordinary sintering. A special attention was paid to the composition design through which the dielectric and piezoelectric properties of the (Li, Ta, Sb) modified NKN systems were significantly promoted. A property spectrum was generated with a particular discussion on the relationship between the Sb content, the LT content, the polymorphic phase transition, and the electrical properties and their temperature stability. Excellent and tunable electrical properties of $d_{33} = 242\text{--}400$ pC/N, $k_p = 36\%\text{--}54\%$, $\epsilon_{33}^T = 750\text{--}2500$, and $T_c = 230\text{--}430^\circ\text{C}$ demonstrate a tremendous potential of the compositions studied for device applications.

I. Introduction

THE research and development of lead-free piezoelectric ceramics have been a hot topic since Saito *et al.*¹ made good progress in the electrical properties in 2004. A flood of relevant publications have come forth in the last few years.^{2–4} A typical composition, $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN), near a morphotropic phase boundary (MPB) has absorbed much attention owing to its good electrical properties, together with a relatively high Curie temperature.⁵ Pure NKN compositions demonstrate a polymorphic phase transition (PPT) at $\sim 200^\circ\text{C}$, except for a ferroelectric–paraelectric phase transition at $\sim 420^\circ\text{C}$.⁵ Although it is well known in pure NKN materials for last 50 years, the PPT was reported in modified NKN-based lead-free materials in 2006⁶ where it was shifted below room temperature by the addition of Li, Ta, and/or Sb, such that a two-phase coexistence zone between orthorhombic and tetragonal phases was formed.⁷ This zone can be more appropriately called as the polymorphic phase boundary (PPB), not just a classical MPB, because this boundary is strongly dependent on temperature. However, similar to an MPB, two kinds of ferroelectric phases may coexist near a PPB. Therefore, the (Li, Ta, Sb) modified NKN compositions exhibit not only significantly improved sinterability but also enhanced electrical properties. However, the best properties reported so far for this system are still not as good as expected, in addition to both processing difficulties and temperature stability issues.^{2,8} Particularly, the piezoelectric constant d_{33} (~ 300 pC/N)¹ and the electromechanical coupling factor k_p ($\sim 45\%$) values have wandered at this level for quite a long time. Obviously, it is indispensable to further promote these properties in order to compete with lead-based piezoelectric ma-

terials. It has been realized that the relative content of Li, Ta, and Sb made a difference in changing the electrical properties of NKN-based systems,¹ although the existence of a PPB was believed to be the main reason for the enhanced electrical properties of this system.⁸ It was pointed out that more covalent elements, for example, Sb, owing to higher electronegativities, could contribute more to the dielectric and piezoelectric properties.¹

In this work, a special attention was paid to the composition design by prescribing a fixed amount of Sb in NKN compositions and then mixing with a changing amount of LiTaO_3 (LT). The phase transformation and various electrical properties as a function of the Sb and LT content were investigated. A property spectrum concerning this material system was reported, among which the compositions with significantly improved piezoelectric properties and/or tunable properties were demonstrated.

II. Experimental Procedures

Ceramics with compositions of $(\text{Na}_{0.52}\text{K}_{0.48-x})(\text{Nb}_{1-x-y}\text{Sb}_y)\text{O}_3$ - $x\text{LiTaO}_3$ (NKNS-LT _{x/y}) ($0 < x < 0.07$, $0 < y < 0.16$) were manufactured by a solid-state reaction method. Based on that Na volatilizes more drastically than K at high temperature, a bit more Na was used in the initial compositions. 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%) were used as raw materials. After mixing and drying, the powder mixtures were calcined twice at 850°C for 5 h, followed by a ball milling for 24 h. The dried powders were then compacted into disk samples with desired aspect ratios and then sintered in air at $1060\text{--}1120^\circ\text{C}$ for 3 h.

Silver paste was fired on major surfaces at 550°C for 30 min as the electrodes for dielectric and piezoelectric measurements. The samples were poled at 110°C in stirred silicone oil by applying a dc field of 2 kV/mm for 15 min. The crystal structure was examined by an X-ray diffractometer (D/Mzx-rB, Rigaku, Tokyo, Japan) using a $\text{CuK}\alpha$ radiation. Dielectric properties were measured as a function of temperature by a LCR meter (Agilent E4980A, Santa Clara, CA). The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, SINOCERA, Yangzhou, China). The planar electromechanical coupling factor k_p were determined by a resonance–antiresonance method with an impedance analyzer (PV70A, Band ERA Co. Ltd., Beijing, China).

III. Results and Discussion

Figure 1 shows the X-ray diffraction patterns of NKNS compositions. For $y < 0.09$, only phases with a perovskite structure are detected. A secondary phase $\text{K}_2\text{Sb}_2\text{O}_7$ (ICDD: 44-0927) starts to appear at $x = 0.1$, meaning that the solubility limit of Sb in the NKN lattice has been reached, owing to different structures of $(\text{Na,K})\text{SbO}_3$ (pseudoilmenite structure) and $(\text{Na,K})\text{NbO}_3$ (perovskite structure). A small amount of Sb can

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[†]Author to whom correspondence should be addressed. e-mail: piezolab@hfut.edu.cn

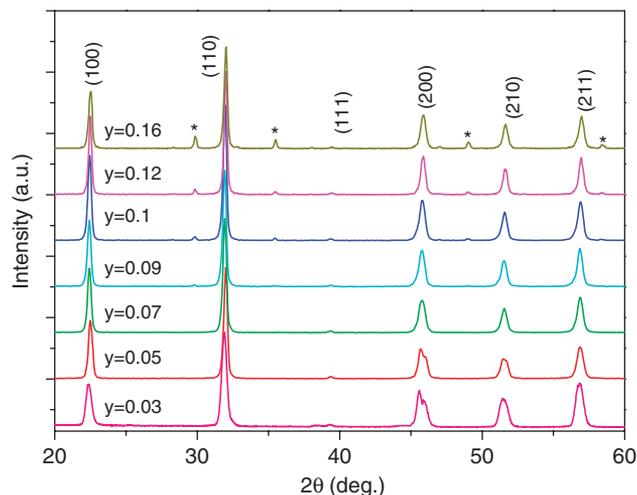


Fig. 1. X-ray diffraction patterns of $(\text{Na}_{0.52}\text{K}_{0.48})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3$ ceramics with different y values as indicated. The symbol of stars stands for the secondary phases.

diffuse into the NKN lattice but seems to reduce its orthorhombicity within the studied composition range at room temperature, probably due to the coexistence of orthorhombic and tetragonal phases in a PPT system.

The effect of the Sb substitution on the phase structures of NKN ceramics can be also clarified by measuring the curves of the dielectric constant versus temperature, as summarized in Fig. 2. Similar to pure NKN ceramics,^{3,9} the Sb substituted NKN ceramics exhibit two phase transition points above room temperature: the orthorhombic–tetragonal (T_{o-t}) polymorphic phase transition and the tetragonal–cubic ferroelectric phase transition (T_c). It can be seen that T_c rapidly drops with increasing y and T_{o-t} decreases with y as well but at a relatively low speed (average 20° and 15°C/mol\% Sb for T_c and T_{o-t} , respectively), such that the tetragonal zone has become narrow at the temperature scale. When $y=0.1$, the material becomes weakly orthorhombic at room temperature. On the one hand, it can be expected that further addition of Sb will not evidently influence these two transition points (Fig. 2), probably owing to the solubility limit of Sb in the NKN lattice. On the other hand, although the diffraction peaks (202) and (020) for NKNS ceramics with $y \geq 0.07$ seem to merge into a single peak (Fig. 1), their phase structures should belong to the coexistence of orthorhombic and tetragonal phases at room temperature (Fig. 2).

Figure 3 shows the effect of the LT and Sb content on the phase transition behavior of NKNS–LT ceramics. For all compositions with varying content of Sb, there exists a phase trans-

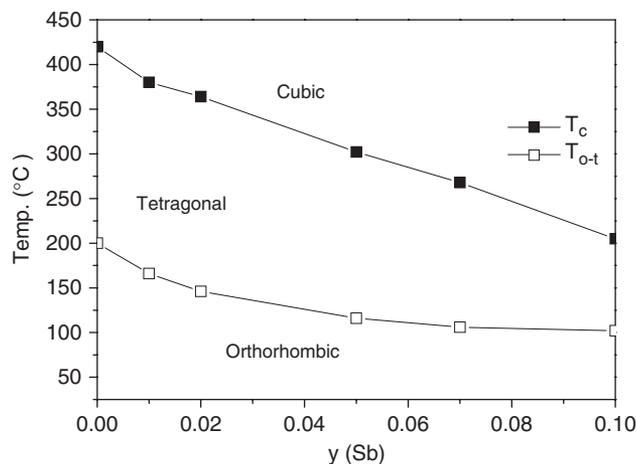


Fig. 2. Phase transformation of $(\text{Na}_{0.52}\text{K}_{0.48})(\text{Nb}_{1-y}\text{Sb}_y)\text{O}_3$ ceramics with changing the content of Sb.

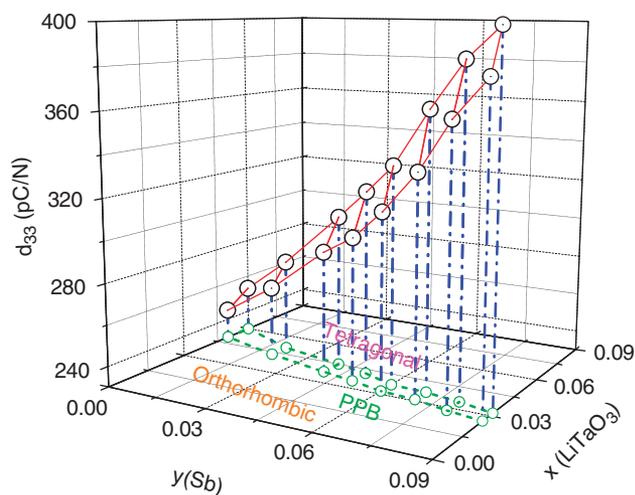


Fig. 3. Polymorphic phase transition of NKNS–LT _{x/y} ceramics with changing the content of Sb (y) and LiTaO₃ (x), together with d_{33} values for compositions within the polymorphic phase boundary (PPB) zone.

formation zone with a certain width between orthorhombic and tetragonal phases. The shadow in Fig. 3 corresponds to the PPB zone where there may coexist two kinds of ferroelectric phases with different symmetries.⁷ It can be seen that the phase structure of pure NKN ceramics ($y=0$) gradually transforms from an orthorhombic symmetry to a tetragonal symmetry as the LT content becomes more. With increasing the Sb content, the PPB zone slightly tilts down, meaning that less amount of LT is needed to induce a phase transformation. It can be realized that the formation of the PPB is actually through shifting a polymorphic phase transition T_{o-t} of NKNS compositions below room temperature. A small amount of LT with an ilmenite structure can diffuse into the perovskite NKN lattice to form solid solutions but tends to induce a change in the crystal symmetry of the matrix compositions.¹⁰

Various electrical properties as a function of the Sb content for poled PPB NKNS–LT ceramics are shown in Fig. 4. It can be seen that the dielectric, piezoelectric, and electromechanical properties almost linearly increase with increasing the Sb content in the compositions. It is noticeable that the d_{33} values increase averagely by 21 pC/N/mol\% Sb. The partial substitution of Sb for Nb induces a more pronounced piezoelectric activity, which can be partially attributed to the enhancement of the dielectric properties or the increase in the polarity due to higher electronegativity of Sb than Nb.¹¹ However, the Curie temperatures quickly decline with increasing the content of Sb. The

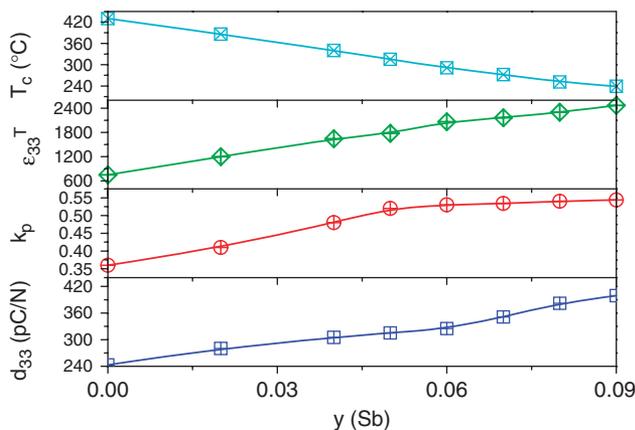


Fig. 4. Antimony concentration dependence of various electrical properties for poled polymorphic phase boundary (PPB) NKNS–LT _{x/y} ceramics. Note that for each PPB composition, the content of Sb (y) is different but fixed beforehand.

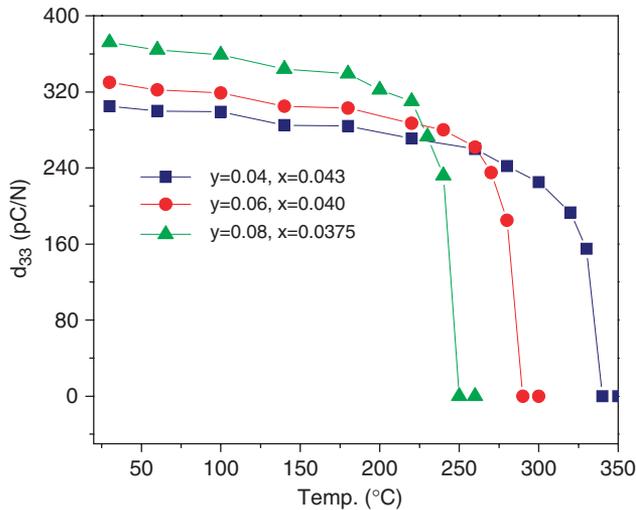


Fig. 5. Piezoelectric constants d_{33} as a function of temperature for poled polymorphic phase boundary (PPB) NKNS-LT_{x/y} ceramics with x and y indicated.

average rate was estimated to be 20°C/mol% Sb. The results indicate that the tunability of the piezoelectric properties for NKNS-LT ceramics can be realized through a special composition design. The d_{33} values in the range of 242–400 pC/N can be achieved. By comparison, k_p exhibits a different change, being saturated at ~7% Sb, and then reaching a plateau. The different behaviors of d_{33} and k_p account for two effects existed in the compositions: the enhancement of the dielectric properties owing to the addition of Sb, and the formation of the PPB. The change in k_p can be believed to have less correlation with the dielectric properties. Therefore, k_p will not obviously benefit from the addition of more Sb. However, both the enhancement of dielectric constants and the formation of the PPB can significantly promote the piezoelectric activity. Moreover, it can be seen from Fig. 3 that d_{33} exhibits a curved surface distribution and is relatively high at the tetragonal side for the PPB compositions, although it always reaches the optimum values near the PPB owing to the phase coexistence.⁷

The thermal de-poling behavior of poled PPB NKNS-LT ceramics is shown in Fig. 5. The d_{33} values were measured at room temperature after annealing the samples at varying chosen annealing temperatures (T_a) for 20 min. Samples are open circuited during annealing but short circuited before d_{33} is remeasured. It can be found that the d_{33} values for three compositions show a slight variation when T_a is $< T_c$ and vanish rapidly as T_a gets close to T_c . The first stage can be ascribed to the existence of the PPB, which may induce the temperature instability of piezoelectric properties.^{8,12} However, it is not serious for these three compositions probably because they lie close to the tetragonal side. This explains why the best values of d_{33} do not appear in the middle of the PPB but close to the tetragonal phase side (see Fig. 3). The poled compositions within the PPB will undergo a polymorphic phase transition during annealing,

such that part of polarization vectors may vanish. This can be considered as one reason for the temperature instability of the (Li, Ta, Sb) modified NKN compositions. However, the post-poled compositions at the tetragonal side will not undergo a tetragonal-orthorhombic polymorphic phase transition during cooling to room temperature or reheating above room temperature. Furthermore, the second stage is just typical of a ferroelectric material whose piezoelectric properties should disappear above the Curie temperature where it becomes a paraelectric state. Therefore, the thermal depoling behavior reveals a relationship between the phase structure of compositions and the reliability of electrical properties.

IV. Conclusions

Lead-free NKNS-LT piezoelectric ceramics were successfully manufactured with a special attention to the composition design. Excellent and tunable dielectric, piezoelectric, and electro-mechanical properties of $d_{33} = 242$ –400 pC/N, $k_p = 36\%$ –54%, $\epsilon_{33}^T = 750$ –2500, and $T_c = 230$ –430°C were achieved. The property spectrum was provided with a detailed discussion on the effect of the Sb content and the PPB on the piezoelectric properties and the temperature stability. The results demonstrate a tremendous advantage of this material system for device applications.

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