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Journal

Phase Transition and Electrical Properties of Li-and Ta-Substituted $(Na_{0.52}K_{0.48})(Nb_{0.96}Sb_{0.04})O_3$ Piezoelectric Ceramics

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Lead-free $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics ($x = 0.0375$–0.0575) have been manufactured by a conventional solid-state method. All compositions form solid solutions with a pure perovskite structure. A morphotropic phase boundary (MPB) between orthorhombic ($x \leq 0.04$) and tetragonal ($x \geq 0.045$) ferroelectric phases was identified in the composition range of the $0.04 < x < 0.045$. The composition near the MPB ($x = 0.0425$) exhibits the best electrical properties with a dielectric constant of 1644, a piezoelectric constant of 310 pC/N, a planar-mode electromechanical coupling factor of 0.48, and a Curie temperature of 340°C. The results indicate that the materials studied could be a promising lead-free piezoelectric candidate for device applications.

I. Introduction

Lead-based piezoelectric ceramics, such as Pb(Zr,Ti)O$_3$, have been widely applied for sensors, actuators, and transducers owing to their excellent dielectric, piezoelectric, and electromechanical properties.[1] Considering the toxicity of lead oxide, lead-free alternatives to those lead-containing materials have been extensively searched and investigated throughout the world.

$(Na_{05}K_{0.5})NbO_3$ (NKN) ceramics were considered as a promising candidate to replace lead-based piezoelectric ceramics due to their attractive piezoelectric properties and Curie temperatures.[2] However, pure NKN ceramics are difficult to densify by ordinary sintering,[3–6] which has restricted the progress of research for quite a long time until Li, Ta, and Sb were utilized in the composition. Through the addition of Li, Ta, and Sb, several compositions with the so-called morphotropic phase boundary (MPB) have been produced with significantly improved piezoelectric properties, sintering behavior, and appropriate Curie temperatures.[7–13] However, there has been quite a broad distribution in the properties reported previously[13–16] even for the materials with the same compositions. This is not only because this system is highly sensitive to the processing conditions but also because the addition of Li, Ta, and Sb into NKN compositions makes different contributions to the improvement of electrical properties. For instance, the addition of Li and/or Ta tends to enhance piezoelectric properties through the development of MPBs[17–21] and to increase the Curie temperature as well. By comparison, the addition of Sb is believed to promote the piezoelectricity more strongly because its higher electronegativity makes the structure more covalent.[7] In fact, the Sb-doped NKN-based compositions usually exhibit better dielectric properties and electromechanical properties at the expense of the Curie temperature. Therefore, a suitable amount of Sb was sometimes used to modify pure NKN compositions.[9,22]

In this study, a fixed amount of Sb was added to NKN compositions considering the compromise between the property and Curie temperature. Taking into account the fact that Na tends to volatilize more drastically than K during sintering, slightly more Na was used in the initial composition. On the basis of the composition, $(Na_{0.52}K_{0.48})(Nb_{0.96}Sb_{0.04})O_3$, Li, and Ta were added in equal moles to develop a new composition with an MPB. Good electrical properties are expected. The phase transition behavior and composition dependence of the electrical properties were investigated in detail.

II. Experimental Procedures

Lead-free $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ($x =$ 0.0375, 0.040, 0.0425, 0.045, 0.0475, 0.050, 0.0525, 0.055, and 0.0575) piezoelectric ceramics were prepared by a conventional solid-state method. The raw materials used in this study were K_2CO_3 (99.0%), Na_2CO_3 (99.8%), Li_2CO_3 (99.9%), Nb_2O_5 (99.5%), Ta_2O_5 (99.9%), and Sb_2O_3 (99.9%). They were ball milled with ZrO_2 balls for 10 h using ethanol as the medium. After drying, they were calcined twice at 850°C for 5 h, and calcined powders were ball milled again for 24 h. Sintering was carried out in air in the temperature range of 1060°–1120°C for 3 h. Silver paste was fired on both sides of the disk samples at 550°C for 30 min as the electrodes for dielectric and piezoelectric measurements. The samples were poled at 110°C in a silicone oil bath with a dc electric field of ~2.0 kV/mm for 15 min.

The crystal structure of the specimens was examined by an X-ray diffractometer (XRD) (Philips X'pert, Almelo, the Netherlands) using Cu$K\alpha$ radiation. The microstructure was observed by a scanning electron microscope (SEM, JEOL JSM-6335F, Tokyo, Japan). The dielectric properties of the samples were determined as a function of temperature and frequency by an LCR meter (Agilent E4980A, Santa Clara, CA) equipped with a programmable temperature box. 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 (Impedance Analyzer PV70A, Beijing, China).

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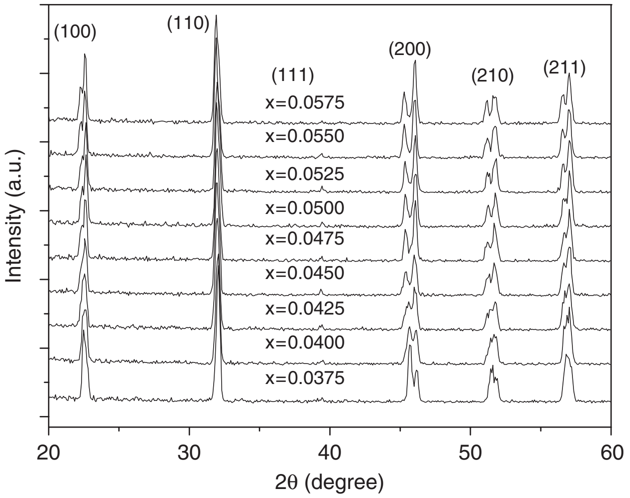

Fig. 1. X-ray diffractometer patterns of $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics with different x indicated.

III. Results and Discussion

Figure 1 shows the XRD patterns of $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics sintered at 1100°C for 3 h. It can be seen that all compositions show a pure perovskite structure within the composition range studied. The 4 mol% Sb-substituted $Na_{0.52}K_{0.48}NbO_3$ shows an orthorhombic structure like the undoped counterparts.[22] This symmetry remained until the 4 mol% LiTaO$_3$ was added. With a further increase in x, tetragonal symmetry appeared ($x>0.045$). Thus, an MPB between the orthorhombic and tetragonal ferroelectric phases can be identified in the composition range of $0.04<x<0.045$. Above the MPB, no other phase, except perovskite, could be detected, meaning that the amount of Li and Ta used was still within the solubility limit. Moreover, in the tetragonal zone, the increase of x caused an increase of tetragonality of solid solutions, which could be further verified in the subsequent measurement of dielectric properties.

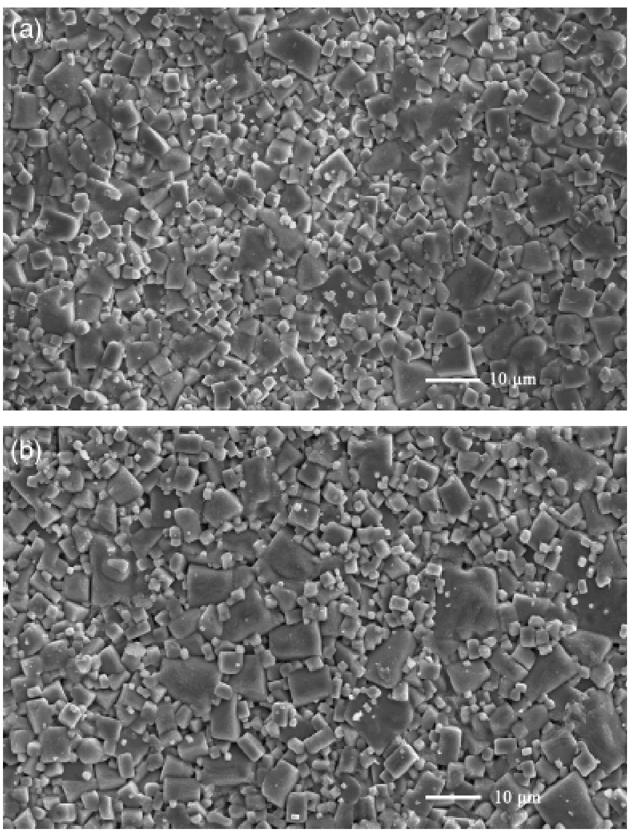

Fig. 2. Scanning electron microscope images of $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics with (a) $x=0.0425$ and (b) $x=0.0525$ sintered at 1100°C for 3 h.

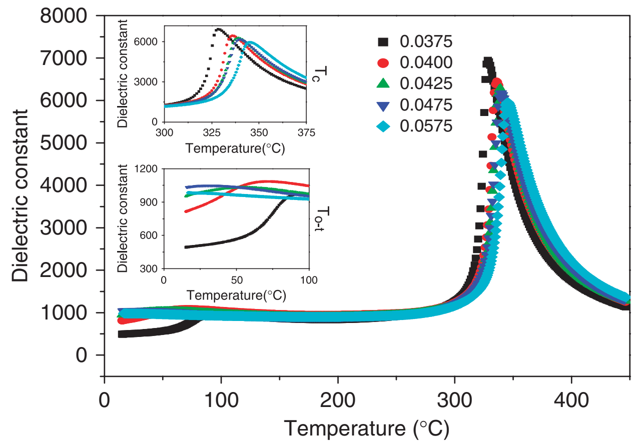

Fig. 3. Dielectric constant versus temperature measured at 10 kHz for $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics as indicated.

Figure 2 shows the SEM images on free surfaces of the samples sintered at 1100°C for 3 h. It can be seen that the grains are faceted and the average grain size does not show any significant change with increasing x, but shows a bimodal grain-size distribution. This phenomenon can often be found in NKN-based lead-free ceramics.[12,13,17–19] It was found that the addition of Li$^+$ tends to cause exaggerated grain growth in some cases.[17–19] Nevertheless, it can be seen from Fig. 2 that all samples have been well densified.

Dielectric constant versus temperature curves of unpoled samples measured at 10 kHz are shown in Fig. 3. It is obvious that samples with $x<0.04$ exhibit two-phase transitions: an orthorhombic–tetragonal transition ($T_{o-t}<100$°C) and a tetragonal–cubic transition ($T_c>300$°C). With increasing x, T_{o-t} shifts to lower temperatures but T_c shifts to higher temperatures. When x is >0.045, there is only one-phase transition left above room temperature. This also indicates that an MPB was developed due to the addition of LiTaO$_3$. The fact that the T_c becomes higher with increasing x indicates that the tetragonality increases when $x \geq 0.045$. These findings are consistent with the XRD results discussed above.

Figure 4 shows the dielectric, piezoelectric, and electromechanical properties of poled $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ samples. The electrical properties for the ceramics across the MPB display a strong compositional dependence. The best electrical property of this material system was obtained from the composition near the MPB with $x=0.0425$, which

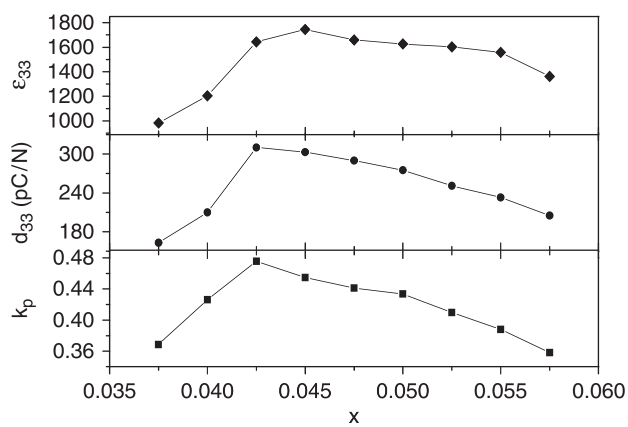

Fig. 4. Various electrical properties of poled $(Na_{0.52}K_{0.48-x})(Nb_{0.96-x}Sb_{0.04})O_3$–$x$LiTaO$_3$ ceramics as a function of x.

exhibits a piezoelectric constant, $d_{33,}$ of 310 pC/N, a planar-mode electromechanical coupling factor, $k_{p,}$ of 0.48, and a dielectric constant ε_{33}^{T} of 1644 and $T_c = 340°C$. Away from the MPB, the electrical properties deteriorate rapidly with either increasing or decreasing x. Therefore, it is obvious that the MPB plays an important role in improving the electrical properties. It can be seen that this material system has advantages in terms of the overall properties. The room temperature dielectric constant is significantly enhanced probably due to the addition of Sb compared with the Sb-free composition.[9,22] Additionally, a combination of good piezoelectric property and a relatively high Curie temperature makes the system an attractive candidate for device applications.[7]

IV. Conclusions

The phase transition behavior and electrical properties of Li- and Ta-substituted $(Na_{0.52}K_{0.48})(Nb_{0.96}Sb_{0.04})O_3$ lead-free piezoelectric ceramics were investigated. The MPB between orthorhombic and tetragonal phases was identified between $x = 0.04$ and 0.045. Good dielectric, piezoelectric, and electromechanical properties with $\varepsilon_{33}^{T} = 1644$, $d_{33} = 310$ pC/N, and $k_p = 0.48$ were obtained in the composition near the MPB, which also has a relatively high Curie temperature of 340°C. The overall properties show significant advantages over those of previously reported systems.

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