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Polymorphic phase transition and enhanced piezoelectric properties of LiTaO₃-modified (Na$_{0.52}$K$_{0.48}$)(Nb$_{0.93}$Sb$_{0.07}$)O₃ lead-free ceramics

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Abstract

Lead-free (Na$_{0.52}$K$_{0.48-x}$)(Nb$_{0.93-x}$Sb$_{0.07}$)O₃–xLiTaO₃ (NKNS7–xLT) solid solution piezoelectric ceramics were investigated in terms of their phase transition behaviour and various electrical properties. The polymorphic phase transition of NKNS7 compositions with an orthorhombic structure was shifted downwards with the addition of a small amount of LT; however, the tetragonal ferroelectric to cubic paraelectric phase transition was moved slightly upwards. The polymorphic phase boundary between the orthorhombic and the tetragonal phases was thus formed near room temperature among the compositions with $0.03 \leqslant x \leqslant 0.0375$ where enhanced piezoelectric and electromechanical properties were achieved. The compositions close to the tetragonal side exhibit better piezoelectric properties and temperature stability. The optimum electrical properties of $d_{33} = 362$ pC N^{-1}, $k_p = 53\%$, $\varepsilon_{33}^T = 2165$, $Q_m = 37$ and $T_c = 271\,^\circ$C were obtained in the composition with $x = 0.0375$. The results indicate that the materials studied could be an excellent candidate for replacing the widely used lead-based piezoelectric ceramics.

In recent years considerable attention in the field of piezoelectric ceramics has been focused on (Na$_{0.5}$K$_{0.5}$)NbO₃ (NKN) based compositions owing to their good electrical properties and relatively high Curie temperatures. As known, pure NKN is a composition near a morphotropic phase boundary (MPB) between two orthorhombic ferroelectric phases [1]. Therefore it can have good piezoelectric and electromechanical properties. In addition, pure NKN ceramics have a polymorphic phase transition between the orthorhombic and the tetragonal phases at ∼200 °C [2]. This polymorphic phase transition can be shifted around room temperature by adding a couple of different compositions,

such as (Bi$_{0.5}$Na$_{0.5}$)TiO₃, (Bi$_{0.5}$K$_{0.5}$)TiO₃, Ba(Ti$_{0.95}$Zr$_{0.05}$)O₃, LiTaO₃, LiNbO₃, LiSbO₃, generating a few new lead-free solid solution compositions with improved sinterability and enhanced piezoelectric activities [3–10]. Therefore, a polymorphic phase boundary (PPB), not just a classical MPB, can be formed near room temperature where two kinds of ferroelectric phases may coexist [11]. The PPB here is similar to the frequently used MPB to some extent but the crystal structure of the compositions near a PPB seems more sensitive to temperature, leading to the temperature instability issues of this system [12].

Among those solid solution compositions, the (Li, Ta, and Sb) modified NKN ceramics show the most significant

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enhancement in the electrical properties. However, the properties rely obviously on the relative content of Li, Ta and Sb in the compositions [3, 8]. This is probably because these three elements play different roles in the piezoelectric properties based on their respective physical properties. It has been realized that Sb^{5+} tends to promote the dielectric and piezoelectric properties owing to its higher electronegativity [3], compared with Ta^{5+} and Nb^{5+}. On further considering the several times higher prices of Ta^{5+} than Sb^{5+}, it is essential to reduce the content of Ta^{5+} but to increase the content of Sb^{5+}. Of course, it is also a fact that an increase in the content of Sb^{5+} is usually accompanied by a rapid drop in the Curie temperature. In this letter, a special composition was designed where a fixed amount of Sb^{5+} was employed in the total composition by taking into account the compromise between the property and the Curie temperature, and then a small amount of $LiTaO_3$ was added into the Sb^{5+} substituted NKN compositions. The phase transition behaviour and the dielectric and piezoelectric properties were investigated. The relationship between the phase structure and the properties was discussed.

A conventional solid-state method was used to fabricate lead-free piezoelectric ceramics with compositions of $(Na_{0.52}K_{0.48-x})(Nb_{0.93-x}Sb_{0.07})O_3-xLiTaO_3$ (NKNS7–xLT) $(0.025 \leqslant x \leqslant 0.05)$. High-purity oxides and carbonates, Nb_2O_5 (99.5%), Ta_2O_5 (99.9%), Sb_2O_3 (99.9%), Na_2CO_3 (99.8%), K_2CO_3(99.0%) and Li_2CO_3 (99.9%), were used as the starting materials and weighed according to the nominal compositions. After mixing, the powder mixtures were calcined twice at 850 °C for 5 h. The calcined powders were then milled again for 24 h together with a 0.5 wt% PVB binder. After compaction, disc specimens were sintered in air at 1060–1120 °C for 3 h. For electrical measurements, silver paste was screen printed and then fired at 550 °C for 30 min. Electric poling was performed at 110 °C in a silicone oil bath by applying a dc field of ~ 2 kV mm^{-1} for 15 min.

The crystal structure was examined by an x-ray diffractometer (XRD, D/Mzx-rB, Rigaku, Japan) using Cu K$_\alpha$ radiation. Dielectric properties were measured as a function of temperature by an LCR meter (Agilent E4980A, USA). The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance–antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd China).

Figure 1 shows XRD patterns of NKNS7–xLT ceramics. It can be seen that all compositions have a pure perovskite structure, meaning that Li, Ta and Sb have completely entered into the NKN lattice within the studied composition range, although $NaSbO_3$, $KSbO_3$ and $LiTaO_3$ have a lithium niobate structure. When $x = 0.025$, the material has an orthorhombic structure at room temperature, similar to a pure NKN. This structure can remain till $x = 0.03$. With a further increase in x, the phase structure changes to a single tetragonal symmetry $(x > 0.0375)$, due to a large distortion caused by LT, based on different crystal structures. The structural distortion should increase by increasing the content of LT within the solubility
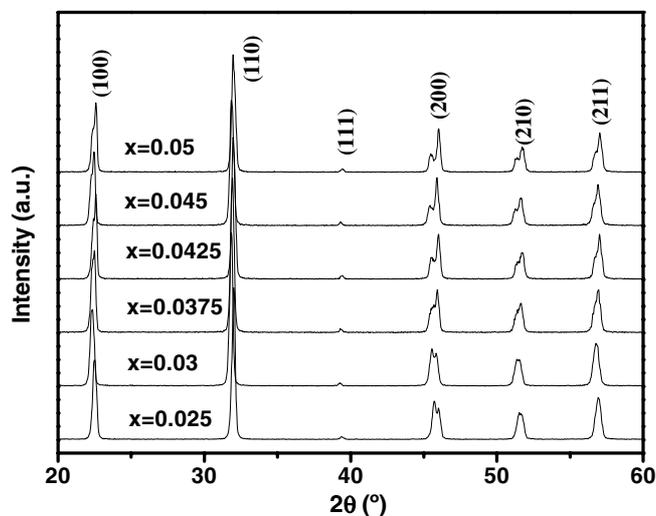

Figure 1. XRD patterns of NKNS–xLT ceramics with different LT contents as indicated.
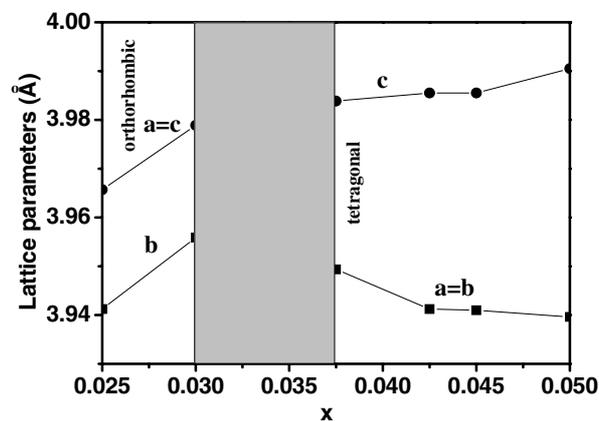

Figure 2. Lattice parameters of NKNS–xLT ceramics as a function of the LT content.

limit. Therefore, a two-phase coexistence zone between an orthorhombic symmetry and a tetragonal symmetry can be identified in the composition range of $0.030 < x < 0.0375$. In addition, it can be seen that the addition of LT tends to increase the tetragonality of the compositions as a result of increased distortion. The lattice parameters of NKNS–xLT ceramics were calculated by fitting the diffraction peak profile, as shown in figure 2. Clearly, there is a transition zone between the orthorhombic and the tetragonal phases in the range of $0.03 < x < 0.0375$. When $x > 0.0375$, the materials become pure tetragonal phases. The tetragonality c/a is ~ 1.009 for NKNS–0.0375LT and increases to ~ 1.013 for the composition with $x = 0.05$. An increase in tetragonality usually corresponds to a rise in the Curie temperature for a couple of perovskite solid solution ceramics, such as $Pb(Zr,Ti)O_3$ and $Pb(Mg_{1/3}Nb_{2/3})O_3-PbTiO_3$ [13, 14].

Dielectric properties at 10 kHz as a function of temperature for unpoled NKNS–xLT ceramics are shown in figure 3. Similarly to pure NKN materials [2], NKNS-xLT samples still exhibit two dielectric peaks above room temperature when $x < 0.03$. One is associated with the

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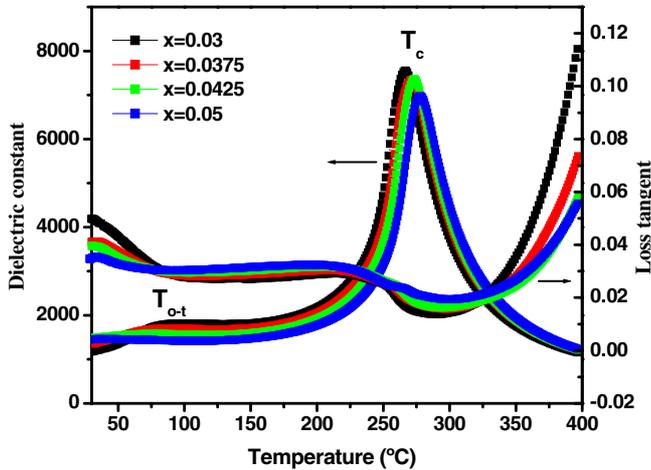
Figure 3. Dielectric constants and loss tangents at 10 kHz versus temperature curves for NKNS–xLT ceramics as indicated.

(This figure is in colour only in the electronic version)

Figure 4. Compositional dependence of various electrical properties of poled NKNS–xLT ceramics.

Figure 5. Temperature dependence of the piezoelectric constants and electromechanical coupling factors of poled NKNS–0.0375LT ceramics.

tetragonal–cubic ferroelectric phase transition (T_c) at high temperatures. Another corresponds to the orthorhombic–tetragonal polymorphic phase transition ($T_{O–t}$) at relatively low temperatures. However, with increasing content of LT, T_c was found to shift slightly upwards but $T_{O–t}$ shifts to a lower temperature. When $x = 0.0375$, $T_{O–t}$ locates near room temperature, such that a two-phase coexistence can be identified by XRD, as discussed in figures 1 and 2. A further increase in x ($x > 0.0375$) will bring $T_{O–t}$ below room temperature such that a pure tetragonal phase can be observed. It can be realized that the formation of the two-phase coexistence zone is caused by shifting a polymorphic phase transition close to room temperature; thereby this transition zone should be called a PPB rather than a MPB traditionally. The fact that T_c gradually increases with x matches with an increased distortion or tetragonality. The same phenomenon can be observed in the loss tangent versus temperature curves as shown in figure 3. Moreover, the loss values become smaller with increasing x at a low temperature, partially because the addition of LT slightly improves the sinterability. It can also be found that there is an anomaly in loss values near room temperature. The compositions with a pure tetragonal symmetry tend to have lower loss values than those with a PPB. This anomaly is associated with the polymorphic phase transition from orthorhombic to tetragonal structures. Above T_c, the high-temperature conductivity contributes to a rapid increase in the loss values.

The various electrical properties of poled NKNS–xLT ceramics as a function of x are shown in figure 4. It can be seen that the electrical properties are obviously dependent on the composition. The best properties appear in the compositions near a PPB, meaning that the PPB plays an important role in improving the dielectric and piezoelectric properties, similar to an MPB in this respect. Both of them are based on a two-phase coexistence zone where there are more spontaneous polarization states. The piezoelectric strain constant d_{33}, the planar electromechanical coupling factor k_p and the dielectric constant ε_{33}^T first increase with x, reach the maxima approximately at $x = 0.0375$ and then decrease with
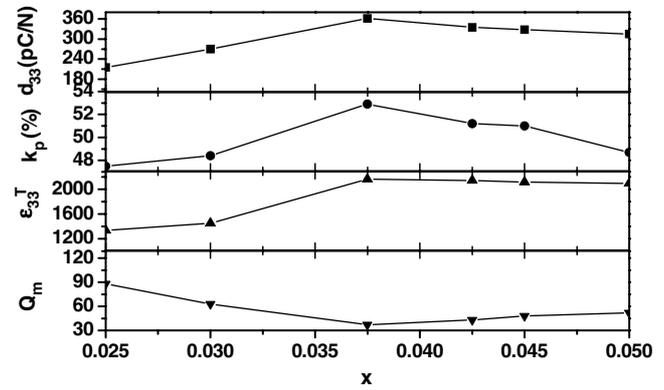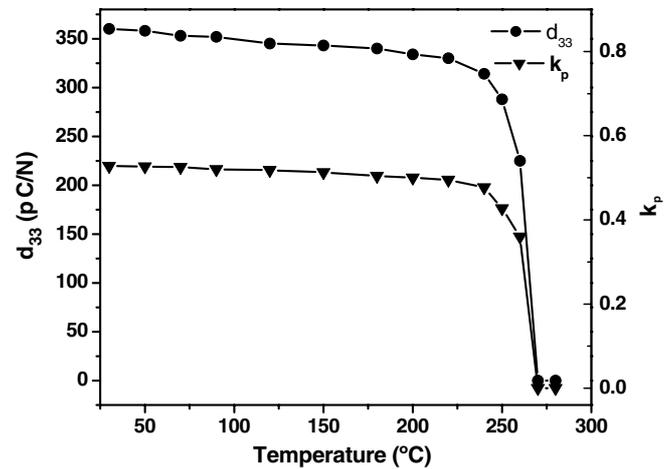
a further increase in x. By comparison, the mechanical quality factor Q_m shows a slight variation with x. It seems a little higher in the orthorhombic phase zone, reaches the minimum near the PPB and then slightly rises in the tetragonal zone. The change in Q_m seems opposite to that of the loss tangent. The optimum electrical properties with a d_{33} of 362 pC N^{-1}, a k_p of 53%, an ε_{33}^T of 2165, a Q_m of 37 and a T_c of 271 °C were obtained in the composition with $x = 0.0375$. Compared with Sb-free NKN based systems, these materials show significantly improved dielectric and piezoelectric properties. Therefore, the addition of a suitable amount of Sb^{5+} decreases the Curie temperature, but obviously promotes the piezoelectric activity.

Figure 5 shows the variation of the piezoelectric constant and the electromechanical coupling factor of the poled NKNS7–0.0375LT samples during annealing. It can be seen that both d_{33} and k_p show a slight variation when the annealing temperature (T_a) is lower than T_c and drop rapidly as T_a is close to T_c. The second stage is easily understood because the ferroelectricity will disappear above T_c. The first stage can be attributed to the existence of a PPB, which causes the material to undergo a phase transition between the orthorhombic and the tetragonal phases during annealing. During the phase transition, some polarization states or oriented domains will

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vanish. This is also the reason why NKN based systems tend to have a temperature instability of piezoelectric properties [12]. However, the composition with $x = 0.0375$ shows a weak temperature dependence of electrical properties probably owing to the fact that it locates close to the tetragonal side within a PPB. Therefore, it is necessary to choose the composition near the tetragonal side or to shift its $T_{\mathrm{O-t}}$ below room temperature [15–17] in order to improve the stability of the piezoelectric properties.

In conclusion, the polymorphic phase transition and various electrical properties of NKNS7–xLT lead-free piezoelectric ceramics were investigated. A PPB between the orthorhombic and the tetragonal phases was identified in the range of $x = 0.030$–0.0375, which plays an important role in improving the electrical properties. The addition of Sb^{5+} obviously increases the dielectric and piezoelectric activities based on its higher electronegativity. However, the PPB induces a slight variation of electrical properties with changing temperature. The compositions close to the tetragonal side show better piezoelectric properties and temperature stability. The excellent electrical properties of $d_{33} = 362 \, \mathrm{pC\,N^{-1}}$, $k_{\mathrm{p}} = 53\%$, $\varepsilon_{33}^{T} = 2165$, $Q_{\mathrm{m}} = 37$ and $T_{\mathrm{c}} = 271\,^{\circ}\mathrm{C}$ were obtained in the composition with $x = 0.0375$. The results indicate that this material has tremendous potential to replace the widely used lead-based piezoelectric ceramics.

Acknowledgments

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