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Crystal structure and properties of $K_{0.5}Na_{0.5}NbO_3$–$Bi_{0.5}Na_{0.5}TiO_3$–$LiSbO_3$ lead-free piezoelectric ceramics

Yixiong Liu [a,b], Yanqiu Huang [a,b,*], Haiwei Du [a,b], Huilin Li [a,b], Guoxi Zhang [a,b]

[a] Engineering Research Center of Nano-Geomaterials of Ministry of Education, China University of Geosciences, Wuhan 430074, China
[b] Faculty of Materials Science and Chemical Engineering, China University of Geosciences, Wuhan 430074, China

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ABSTRACT

$(1-x)(0.99K_{0.5}Na_{0.5}NbO_3-0.01Bi_{0.5}Na_{0.5}TiO_3)-xLiSbO_3$ (KNN–BNT–LS100x, x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.1) lead-free piezoelectric ceramics were fabricated by conventional ceramic technique. The crystal structure, dielectric and piezoelectric properties of the ceramics were investigated. The X-ray diffraction (XRD) analysis revealed that the ceramics sintered in air at 1040–1080 °C for 3–4 h possessed a pure perovskite structure when $LiSbO_3$ content was 0–5 mol%. A morphotropic phase boundary (MPB) between the orthorhombic and tetragonal phases was identified in the composition range of $0.01 < x < 0.04$. The Curie temperature (T_c) and the orthorhombic–tetragonal transition temperature (T_{O-T}) shifted to lower temperature with increasing $LiSbO_3$ content. The ceramics close to the MPB exhibited enhanced dielectric and piezoelectric properties. The highest piezoelectric constant $d_{33} = 250$ pC/N, electromechanical coupling factors, $k_p = 0.29$, $k_t = 0.35$ and $k_{33} = 0.447$, mechanical quality factor, $Q_m = 33$, $T_c = 339\,°C$, $T_{O-T} = 65\,°C$, dielectric constant, $\varepsilon_{33}^T/\varepsilon_0 = 640$ and loss tangent, $\tan\delta = 0.031$ were obtained for the KNN–BNT–LS4 ceramic which has a tetragonal phase near the MPB.

1. Introduction

Potassium sodium niobate $(K_{0.5}Na_{0.5})NbO_3$ (KNN) has drawn significant attention in recent years due to its high piezoelectric properties, high Curie temperature (T_c) and environmental friendliness [1,2]. It is considered to be an excellent candidate for use in lead-free piezoelectric ceramics. However, the pure KNN is difficult to process into dense ceramics using conventional sintering methods because of the high volatility of alkaline elements at elevated temperatures [3,4]. In order to obtain well-sintered and dense KNN ceramics with good electrical performance, various ABO_3-type compounds have been added into KNN to form KNN-based solid solutions, such as KNN–$BaTiO_3$ [5], KNN–$SrTiO_3$ [6], KNN–$Bi(Zn_{0.5}Ti_{0.5})O_3$ [7], KNN–$LiTaO_3$ [8], KNN–$LiNbO_3$ [9], KNN–$BiAlO_3$ [10], KNN–$LiSbO_3$ [11–14], KNN–$(Bi_{0.5}Na_{0.5})TiO_3$ [15] and KNN–$(Bi_{0.5}Li_{0.5})TiO_3$ [16].

The sintering behavior of the KNN–$(Bi_{0.5}Na_{0.5})TiO_3$ ceramics could be improved significantly by adding a small amount of $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) [15]. It was found that the ceramics with 3 mol% $(Bi_{0.5}Na_{0.5})TiO_3$, which formed a tetragonal phase near the morphotropic phase boundary (MPB) region, exhibited good piezoelectric properties. In addition, previous studies have confirmed that the dielectric and piezoelectric properties of KNN-based ceramics could remarkably be improved by adding $LiSbO_3$ [12,13]. Our research indicated that the KNN–$(Bi_{0.5}Na_{0.5})TiO_3$ ceramics with small amounts of $LiSbO_3$ exhibited the excellent piezoelectric properties when 1 mol% $(Bi_{0.5}Na_{0.5})TiO_3$ was added. Many researches have been focused on the KNN–$LiSbO_3$ systems [17–21]. But few reports are involved with the solid solutions of $K_{0.5}Na_{0.5}NbO_3$–$Bi_{0.5}Na_{0.5}TiO_3$–$LiSbO_3$ system, and the effect of $LiSbO_3$ on the properties of the $K_{0.5}Na_{0.5}NbO_3$–$Bi_{0.5}Na_{0.5}TiO_3$–$LiSbO_3$ ceramics remains unclear. In this work, the ceramics of $(1-x)(0.99K_{0.5}Na_{0.5}NbO_3-0.01Bi_{0.5}Na_{0.5}TiO_3)-xLiSbO_3$ (abbreviated as KNN–BNT–LS100x) were fabricated by conventional ceramic technique. The crystal structure, phase transition, dielectric and piezoelectric properties of the ceramics were studied.

2. Experimental details

The KNN–BNT–LS100x (x = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.1) ceramics were prepared by conventional solid-state reaction technique. Reagent-grade carbonate and oxide powders of K_2CO_3, Na_2CO_3, Li_2CO_3, Bi_2O_3, TiO_2, Nb_2O_5 and Sb_2O_3 were used as starting raw materials. The powders were mixed in stoichiometric proportions and milled in ethanol for 12 h, then dried and calcined at 850 °C for 4 h. The calcined powders were reground and mixed with 5 wt% polyvinyl alcohol (PVA) solution as binder, and then pressed into discs with a diameter of 20 mm. The green discs were finally sintered in air at 1040–1080 °C for 3–4 h. The electrodes were printed on the surfaces of the discs by firing silver paste at 600 °C for 10 min. The

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[*] Corresponding author at: Faculty of Materials Science and Chemical Engineering, China University of Geosciences, Wuhan 430074, China. Tel.: +86 27 87483374.
E-mail address: y.q.huang@163.com (Y. Huang).

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specimens were poled in silicone oil at 120 °C for 15 min by applying a dc field of 3 kV/mm.

The crystal structure of the sintered samples was determined by X-ray diffraction (X' Pert PRO) with a Cu Kα radiation. The bulk densities were measured by the Archimedes method. Dielectric measurements were carried out by a TH2819 Precision LCR Meter at 10 kHz from room temperature to 420 °C. The piezoelectric constant d_{33} was measured by a quasistatic piezoelectric constant testing meter (ZJ-3A). The electromechanical coupling factors, k_p, k_t, and the mechanical quality factor Q_m were determined by a resonance–antiresonance method using an impedance analyzer (Agilent 4294A). The longitudinal electromechanical coupling factor, k_{33}, was estimated from the electromechanical coupling factors, k_p, k_t [22].

3. Results and discussion

Fig. 1 shows the X-ray diffraction (XRD) patterns of the KNN–BNT–LS100*x* ceramics with 0, 1, 3, 4, 5, 6, and 8 mol% $LiSbO_3$. It is found that the ceramics show a pure perovskite structure when $LiSbO_3$ content is 0–5 mol%, suggesting that $LiSbO_3$ has diffused into the KNN lattices to form a homogeneous solid solution. When $LiSbO_3$ content is ≥6 mol%, a trace amount of extra phases $LiSbO_3$ and $K_3Li_2Nb_5O_{15}$ can be detected. This result is similar to the previous reports [12], where the pure perovskite phase of $(1-x)$KNN–xLiSbO$_3$ ceramics were obtained when the content of $LiSbO_3$ was <6 mol%. Additionally, the KNN–BNT–LS100*x* ceramics exhibit the orthorhombic symmetry at room temperature when $x \leq 0.01$. As $LiSbO_3$ content increases, the phase structure of the ceramics transforms from orthorhombic symmetry to tetragonal symmetry. When $LiSbO_3$ content reaches 4 mol%, the ceramic possesses the tetragonal symmetry only. These characteristics suggest that the KNN-BNT–LS100*x* system has an orthorhombic–tetragonal morphotropic phase boundary (MPB) at $0.01 < x < 0.04$. This differs from the $(1-x)$KNN–xLiSbO$_3$ ceramics, in which the MPB exists at $0.05 < x < 0.10$ [12,13].

Fig. 2 shows the bulk densities of the ceramics as a function of $LiSbO_3$ content. The bulk density increases with increasing $LiSbO_3$ content, reaching the maximum value of 4.2 g/cm^3 when $LiSbO_3$ content is 5 mol%. As $LiSbO_3$ content is >5 mol%, the bulk density decreases slightly with further increasing $LiSbO_3$. These results suggest that the density of the KNN–BNT–LS100*x* ceramics can be improved by addition of $LiSbO_3$.

Fig. 3 shows the temperature dependence of the relative permittivity, ε_r, and loss tangent, $\tan\delta$, of the KNN–BNT–LS100*x* ceramics. It is found that the KNN–BNT ceramic undergoes two-phase transitions from orthorhombic to tetragonal at 150 °C (T_{O-T}) and from tetragonal to cubic at 391 °C (T_c), respectively. When $LiSbO_3$ is added, T_c and T_{O-T} shift to lower temperature. The peaks of the ε_r–T curves near T_c and T_{O-T} broaden, and the highest ε_r values of KNN–BNT–LS100*x* ceramics at T_c decrease with increasing $LiSbO_3$ content. The broad shape of ε_r–T curves near the T_{O-T} indicates that the diffuse phase transition from orthorhombic to tetragonal takes place, which implies that the phase transition may take place in a wide range of temperature. These phenomena may be attributed to the more complex occupations of the A and B sites in an ABO_3 perovskite structure and heterogeneous compositions. The variations of T_c and T_{O-T} versus the content of $LiSbO_3$ are summarized in Fig. 4. T_c shifts rapidly from 391 to 312 °C when $LiSbO_3$ content increases from 0 to 6 mol%, and then almost remains unchanged with further increasing $LiSbO_3$. Meanwhile, T_{O-T} drops from 150 to 65 °C as $LiSbO_3$ content increases from 0 to 4 mol%. The samples with 0–10 mol% $LiSbO_3$ show low and stable dielectric loss characteristics, which the $\tan\delta$ is lower than 0.05 and almost keeps constant through a wide temperature range from 25 to 200 °C.

Fig. 5 shows the tendency of the dielectric constant, $\varepsilon_{33}^T/\varepsilon_0$, and the dissipation factor, $\tan\delta$, of the poled KNN–BNT–LS100*x* ceramics with the content of $LiSbO_3$. It is found that the $\tan\delta$ of all the poled ceramics varies between 0.03 and 0.09. The $\tan\delta$ decreases rapidly while the $\varepsilon_{33}^T/\varepsilon_0$ increases gradually with the

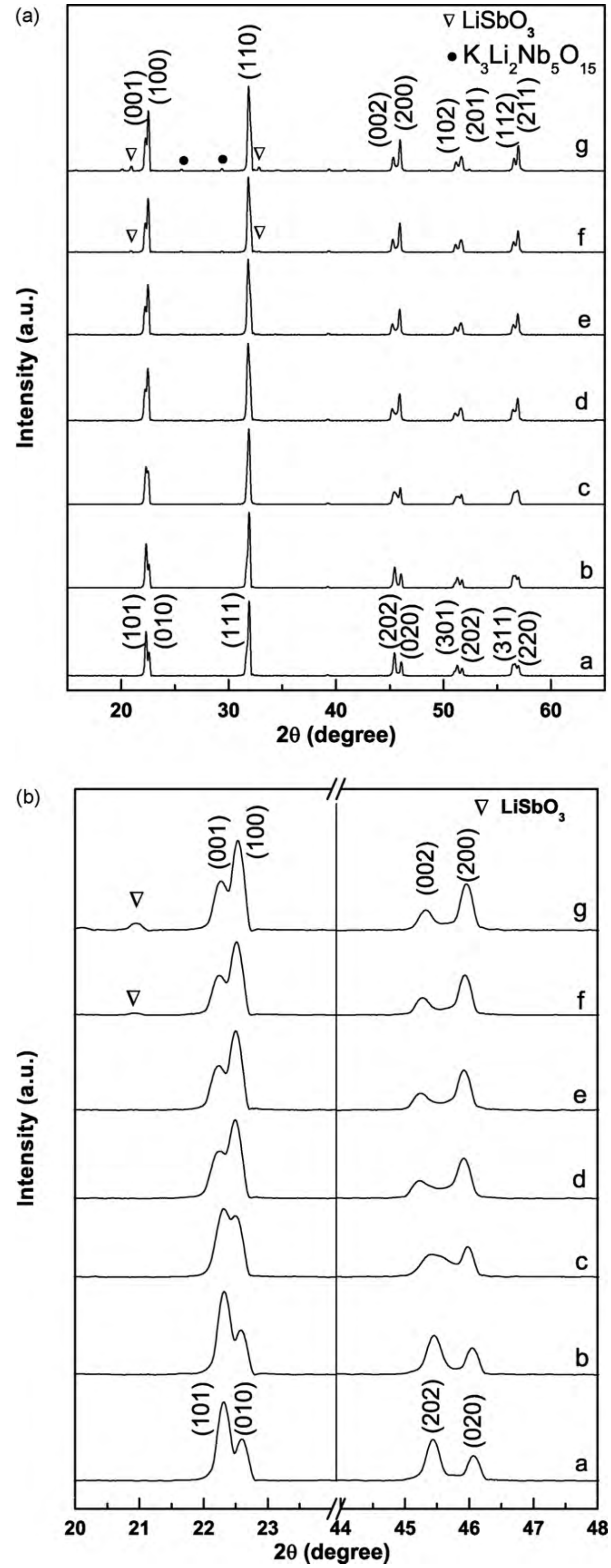

Fig. 1. XRD patterns of KNN–BNT–LS100*x* ceramics of (a) KNN–BNT, (b) KNN–BNT–LS1, (c) KNN–BNT–LS3, (d) KNN–BNT–LS4, (e) KNN–BNT–LS5, (f) KNN–BNT–LS6, (g) KNN–BNT–LS8. (a) Wide range and (b) selected portions.

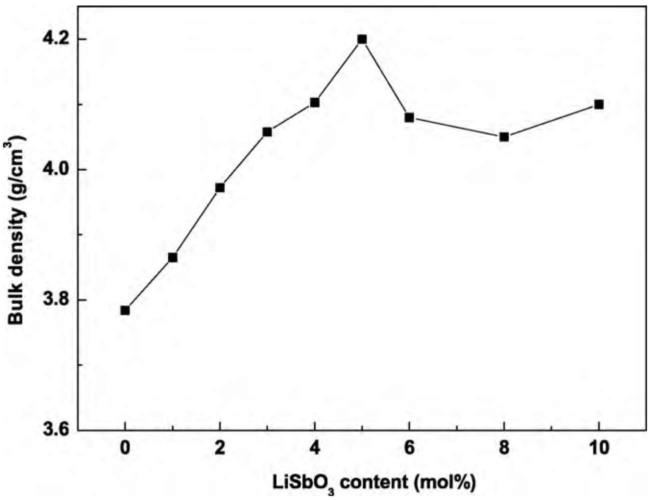

Fig. 2. Bulk densities of the KNN–BNT–LS100*x* ceramics as a function of LiSbO$_3$ content.

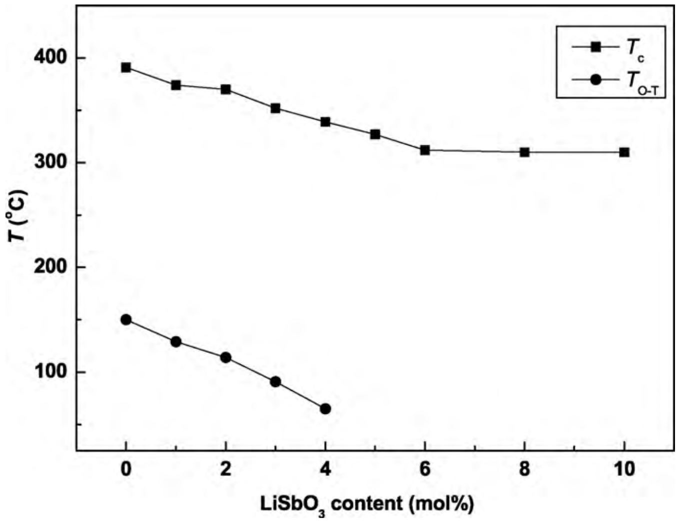

Fig. 4. T_c and T_{O-T} versus the LiSbO$_3$ content for the KNN–BNT–LS100*x* ceramics.

increase of LiSbO$_3$ when $x \leq 4$ mol%. As LiSbO$_3$ content is >5 mol%, the tan δ increases while the $\varepsilon_{33}^T/\varepsilon_0$ remains almost unchanged with increasing LiSbO$_3$. The lowest tan δ value of 0.031 is obtained when LiSbO$_3$ content is 4 mol%, where the value of $\varepsilon_{33}^T/\varepsilon_0$ is 640. It is well known that the dielectric properties of KNN ceramics are related to the density and grain-size distribution [23,24]. According to the results shown in Fig. 2, the density of the KNN–BNT–LS100*x* ceramics is improved by the addition of LiSbO$_3$. Therefore, it may be attributed to an increase in density of KNN–BNT–LS100*x* ceramics that the $\varepsilon_{33}^T/\varepsilon_0$ increases with increasing LiSbO$_3$ when $x \leq 5$ mol%. The maximum $\varepsilon_{33}^T/\varepsilon_0$ value of 803 is obtained when $x = 5$ mol%. This is consistent with the bulk density trend of the ceramics, which reaches the maximum value of 4.2 g/cm^3 when $x = 5$ mol%. However, when the LiSbO$_3$ content is $\geq$5 mol%, the electrical conductivity of the ceramics increases with increasing LiSbO$_3$, resulting in high leakage current [14]. As a result, the dissipation factor of KNN–BNT–LS100*x* ceramics increases obviously with increasing LiSbO$_3$ when $x \geq 5$ mol%.

Fig. 6 shows the piezoelectric constant, d_{33}, and the mechanical quality factor, Q_m, of the ceramics as a function of LiSbO$_3$ content. It is found that the d_{33} enhances with the increase of LiSbO$_3$ content when $x \leq 4$ mol% and then decreases rapidly. The maximum d_{33} value of 250 pC/N is obtained when LiSbO$_3$ content is 4 mol%. According to the XRD analysis shown in Fig. 1, the ceramic with 4 mol% LiSbO$_3$ possesses the tetragonal symmetry, indicating that the highest piezoelectric coefficient d_{33} can be obtained for the tetragonal compositions close to the MPB. The outstanding piezoelectric properties near the MPB are considered to be attributed to the increase amount of spontaneous polarization vectors [25–27].

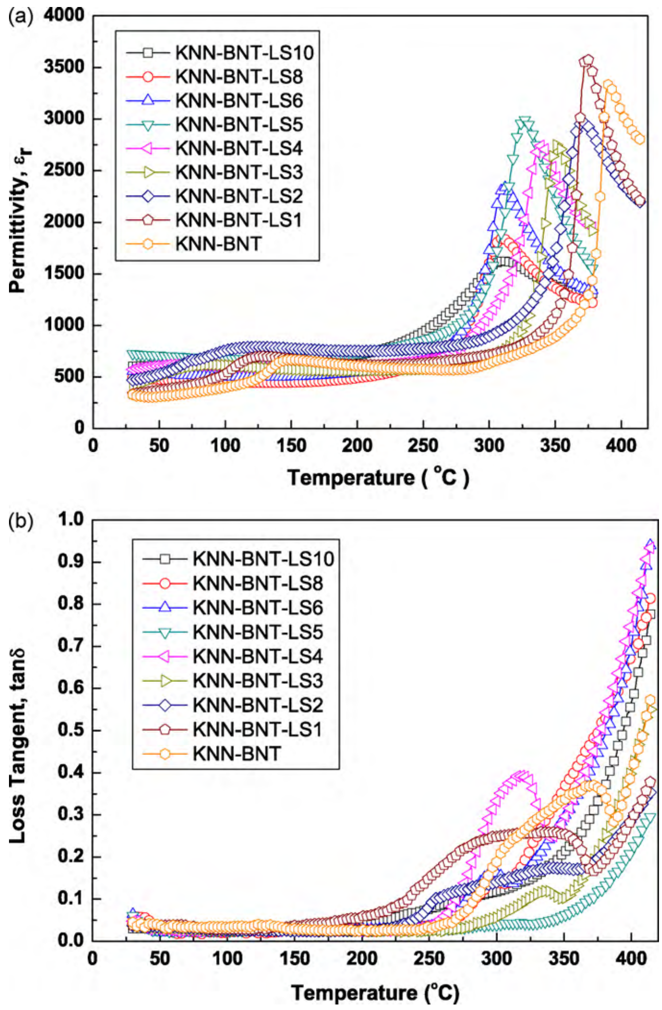

Fig. 3. Temperature dependence of (a) permittivity and (b) loss tangent of the ceramics with different LiSbO$_3$ content at 10 kHz.

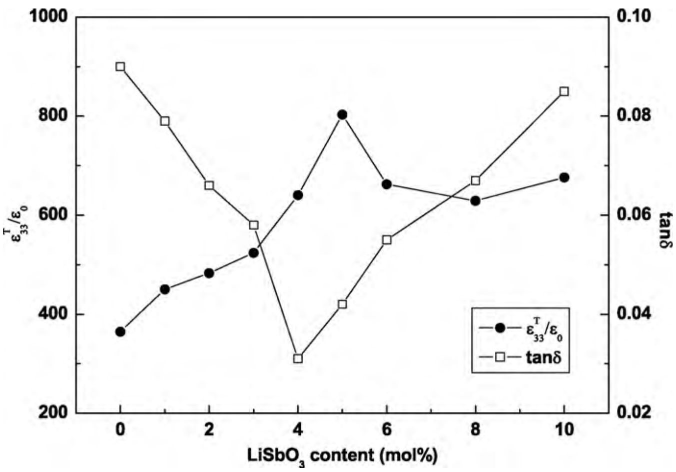

Fig. 5. Dielectric constant, $\varepsilon_{33}^T/\varepsilon_0$, and the dissipation factor, tan δ, versus the content of LiSbO$_3$ for the KNN–BNT–LS100*x* ceramics.

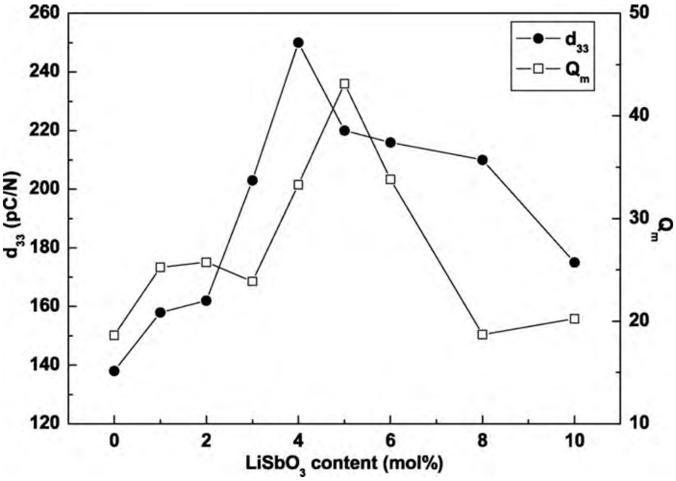

Fig. 6. Piezoelectric constant, d_{33}, and mechanical quality factor, Q_m, versus the content of $LiSbO_3$ for the KNN–BNT–LS100*x* ceramics.

In addition, according to the analysis shown in Fig. 3, the transition from orthorhombic to tetragonal of KNN–BNT–LS4 ceramic takes place in a wide temperature range from room temperature to 65 °C. Therefore, the piezoelectric properties could be improved by shifting the orthorhombic to tetragonal phase transition to near or below room temperature [28]. The decay of piezoelectric properties when $LiSbO_3$ content is ≥6 mol% may be due to the formation of the phases of $LiSbO_3$ and $K_3Li_2Nb_5O_{15}$.

All the ceramics have relatively low Q_m value in the range of 18–43. When $LiSbO_3$ content is ≤5 mol%, the Q_m value increases with increasing $LiSbO_3$. When the content of $LiSbO_3$ is higher than 5 mol%, the Q_m decreases with the increase of $LiSbO_3$. The highest Q_m value of 43 is obtained when $LiSbO_3$ content is 5 mol%.

Fig. 7 shows the electromechanical coupling factors, k_p, k_t and k_{33} of the ceramics with different content of $LiSbO_3$. The planar electromechanical coupling factor, k_p, of the ceramics with 0–10 mol% $LiSbO_3$ varies between 0.25 and 0.32, with a trend to increase with increasing $LiSbO_3$ when $x \leq 5$ mol% and then decrease. The thickness electromechanical coupling factor, k_t, of the ceramics varies between 0.25 and 0.35. The highest k_t values of 0.35 is obtained when $LiSbO_3$ content is 4 mol%. The longitudinal electromechanical coupling factor, k_{33}, of the ceramics varies between 0.36 and 0.45, and the maximum k_{33} values of 0.447 is obtained when $LiSbO_3$ content is 4 mol%. The frequency dependences of impedance, *Z*, and phase angle, *θ*, of the ceramic with 4 mol% $LiSbO_3$ at the planar-mode resonance are shown in Fig. 8. The maximum value of phase angle *θ* is 12.9°.

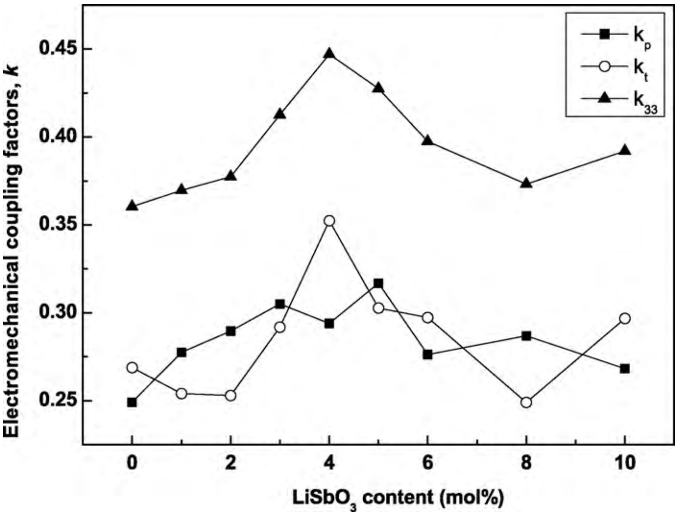

Fig. 7. Electromechanical coupling factors, k_p, k_t and k_{33} versus the content of $LiSbO_3$ for the KNN–BNT–LS100*x* ceramics.

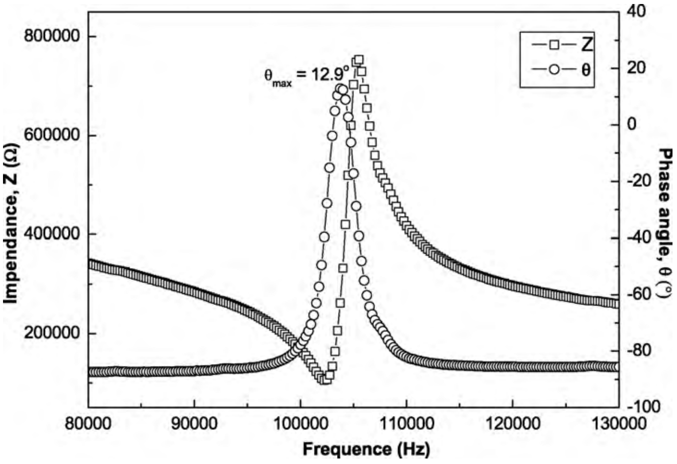

Fig. 8. Frequency dependences of impedance *Z* and phase angle *θ* for the KNN–BNT–LS4 ceramic at the planar-mode resonance.

4. Conclusions

The KNN–BNT–LS100*x* (*x* = 0, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, 0.08, 0.1) ceramics have been synthesized by conventional solid-state reaction technique. The influences of the $LiSbO_3$ on the crystal structure, dielectric, and piezoelectric properties of the ceramics have been studied. XRD analysis revealed that the ceramics formed single-phase solid solutions with perovskite structure when $x < 0.06$. As the content of $LiSbO_3$ was ≥6 mol%, a trace amount of secondary phases $LiSbO_3$ and $K_3Li_2Nb_5O_{15}$ were detected. A MPB between orthorhombic and tetragonal phases was identified in the composition range of $0.01 < x < 0.04$. The Curie temperature, T_c, and the orthorhombic–tetragonal transition temperature, T_{O-T}, of the ceramics decreased as $LiSbO_3$ increased. The dielectric and piezoelectric properties of ceramics were enhanced for the compositions near the MPB. The outstanding electrical properties of d_{33} = 250 pC/N, Q_m = 33, k_p = 0.294, k_t = 0.35, k_{33} = 0.447, T_c = 339 °C, T_{O-T} = 65 °C, $\varepsilon_{33}^T/\varepsilon_0 = 640$ and $\tan\delta = 0.031$ were obtained when $LiSbO_3$ content is 4 mol%.

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