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Effect of Li addition on phase formation behavior and electrical properties of $(K_{0.5}Na_{0.5})NbO_3$ lead free ceramics

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Abstract

In this work, Li-modified KNN ceramic compositions $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ with $x = 0.03, 0.04, 0.05, 0.06, 0.65$ and 0.07 were prepared by a conventional solid-state mixed-oxide method. The structural phase formation and microstructure were characterized by X-ray diffraction technique (XRD) and scanning electron microscopy (SEM). It has been found that a morphotropic phase boundary (MPB) between orthorhombic phase and tetragonal phases should exist between compositions with Li contents of 6–6.5%. The Curie temperature (T_c) of the ceramics shifted to higher temperature with increasing Li content. The room temperature dielectric constant was also seen to be higher than the pure KNN ceramics. In addition, the ferroelectric properties were found to enhance at near MPB compositions. This study clearly showed that the addition of Li could improve the dielectric and ferroelectric properties in $(K_{0.5}Na_{0.5})NbO_3$ ceramics.

Keywords: C. Dielectric properties; C. Ferroelectric properties; Li-modified KNN

1. Introduction

The $Pb(Zr,Ti)O_3$ or PZT ceramics have been widely used as sensors, actuators and transducers because of their excellent electrical properties [1,2]. However, the PZT contains lead oxide, which pollutes the environment and is harmful to human body. In the last decades, a large number of researches have been carried out on lead-free piezoelectric ceramics to substitute for the widely used PZT for high performance applications [3–5]. Besides the developed potassium sodium niobate ($(K,Na)NbO_3$ abbreviated as KNN) based ceramics with properties comparable to those of unmodified PZT ceramics were reported by Saito et al. [6]. KNN has been considered a good candidate for lead-free piezoelectric ceramics because of its high Curie temperature ($T_c \sim 400\ ^\circ C$) and high piezoelectric properties in compositions close to morphotropic phase boundary (MPB) at around 50% K and 50% Na separating two orthorhombic phases as for PZT [7,8]. However, the KNN has many problems arise, especially during the synthesis. Alkaline based starting powders are moisture sensitive leading often to disintegration of the samples after sintering. Another drawback is the poor densification during sintering samples prepared by the conventional mixed oxide. A good densification of the samples was achieved by other techniques such as hot-pressing and Spark Plasma Sintering (SPS); however, these techniques are quite expensive and not suitable for industrial mass-production [9,10]. $LiTaO_3$ and $LiSbO_3$-modified KNN were recently reported to exhibit properties comparable to those of PZT [11–13]. Since both contain Li, it is thus believed that Li should play a key role in improving properties of KNN ceramics. Therefore, Li-modified KNN ceramics were chosen for this study for more details. These modified compositions promise to be a new generation of environmentally safer piezoelectric materials. In this work, high quality Li-modified KNN ceramics were produced ceramics by the conventional solid-state mixed-oxide technique. The influences of Li modification have been investigated in terms of the phase formation behavior and resulting electrical properties.

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2. Experimental procedure

The powders of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ($x = 0.03$, 0.04, 0.05, 0.06, 0.65 and 0.07, abbreviated as KNNL) were synthesized by a conventional mixed-oxide method. Potassium carbonate (K_2CO_3, 99.9% purity), sodium carbonate (Na_2CO_3, 99.9% purity), lithium carbonate (Li_2CO_3, 99.9% purity) and niobium oxide (Nb_2O_5, 99.9% purity) were used as starting powders. Mixed powder was milled for 24 h with the ZrO_2 balls in isopropanal. Two calcinations at temperature 800 °C for 4 h were then performed to obtain the single phase formation. Pellets were pressed into 10 mm diameter with 1% PVA. The pressed pellets were sintered with the soaking time of 2 h in a double crucible configuration at optimum temperature 1070 °C. To prevent the evaporation of K_2O above 840 °C, the pellets were buried in protective powders [14].

The phase formation behavior of the sintered ceramics was analyzed by X-ray diffraction (XRD), using CuK_α radiation to determine the phases formed and optimum firing temperatures for the formation of desired phase. The densities of all compositions were determined by a method based of the Archimedes principle. The microstructure was examined by scanning electron microscopy (SEM, JEOL Model JSM 840A). For the evaluation of electrical properties, gold electrodes were sputtered on both sides of the samples. The samples were applied with a 50 kV/cm field at temperature of 50 °C for 15 min, and the samples were cooled to room temperature in the electric field. The dielectric properties were measured with an LCR meter (HP-4284A, Hewlett-Packard, Santa Clara, CA) in conjunction with an environmental chamber (9023, Delta Design, Poway, CA). A heating rate of 2 °C/min and frequency of 1 kHz were used during measurement. The piezoelectric coefficient was measured with a Berlincourt-type at a frequency of 100 Hz. Ferroelectric hysteresis loops were evaluated at room temperatures (~25 °C) with a standardized ferroelectric test system (RT-66A, Radiant Technologies, Albuquerque, NM). A peak electric field of 50 kV/cm was applied.

3. Results and discussion

The XRD patterns of the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics with various Li contents are shown in Fig. 1(a). It can be seen that a complete crystalline solution of perovskite structure is formed throughout the whole composition without unwanted phases. This indicates that the Li^+ ions have diffused completely into the KNN lattices to form a new solid solution [15]. Fig. 1(b) is the magnification of XRD patterns in the range of 2θ from 43° to 48°. The ceramics with $x \leq 0.05$, the XRD patterns show only (2 0 2)/(0 2 0) peak splitting, confirming the orthorhombic symmetry. On the other hand, for ceramic compositions with $x \geq 0.065$ the XRD patterns show only (0 0 2)/(2 0 0) peak splitting, confirming the tetragonal symmetry. More interestingly, the composition with $x = 0.06$ exhibited broadening peaks with almost equal intensity, indicating the coexistent of orthorhombic and tetragonal phases. It seems that the structure of the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics is gradually changing from orthorhombic to

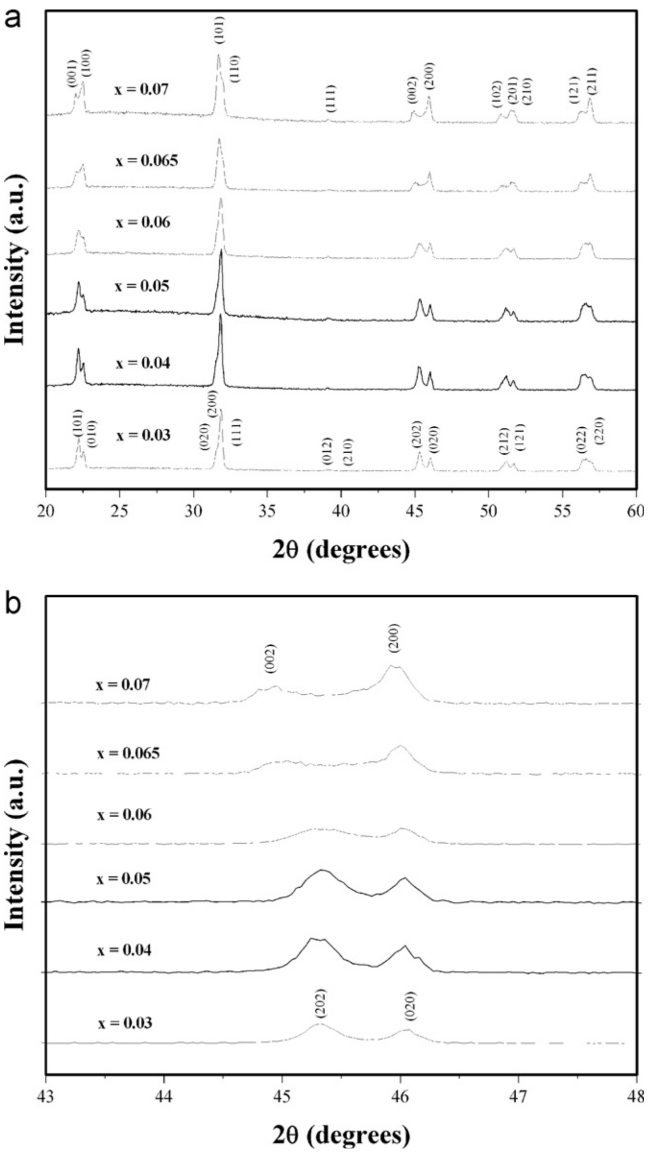

Fig. 1. (a) XRD patterns of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics; (b) selected region of the diffraction patterns.

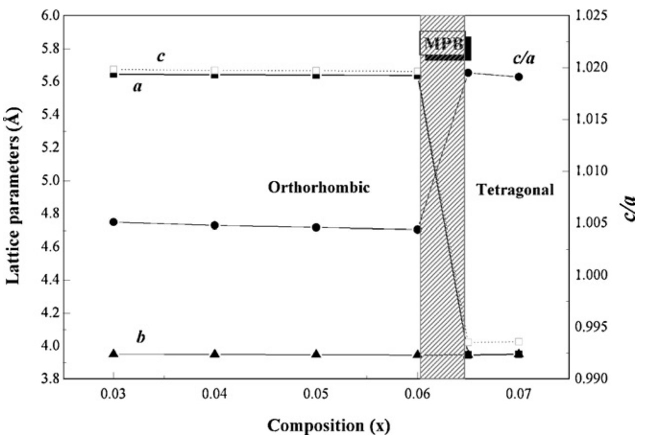

Fig. 2. Lattice parameters and tetragonality of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics. Shaded area indicates expected MPB region.

tetragonal with increasing x contents [11,12,16]. This observation is obviously associated with lattice parameters, as shown in Fig. 2. The parameters *a* and *c* decrease initially and then increase with Li contents. Thus, distortion and deformation of the structure took place when K^+ and Na^+ ions were substituted into the site with Li^+ ions, because the ionic radius of Li^+ (0.90 Å) is smaller than the ionic radii of K^+ and Na^+ (1.33 and 0.97 Å, respectively). The calculated *c*/*a* ratio decreases slightly from $x = 0.03$ to $x = 0.05$ and then increases sharply at $x = 0.065$. The result further confirms that the phase transition from orthorhombic to tetragonal is found near the compositions of $x = 0.06$ and 0.065. To a first approximation, it could be said that the composition around $x = 0.06$–0.065 is close to the morphotropic phase boundary (MPB) of the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics, where the structure of the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics is gradually changing from orthorhombic to tetragonal [11,12,16].

Fig. 3 shows microstructure of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics sintered at their optimum sintering temperature. The microstructure of the ceramics shows square- or rectangular-shaped grains and some large abnormal grains. The compositions with $x = 0.03$ up to $x = 0.06$ show uniform grain growth, whereas the compositions with $x = 0.065$ and $x = 0.07$ exhibit non-uniform grain growth patterns. The average grain size was

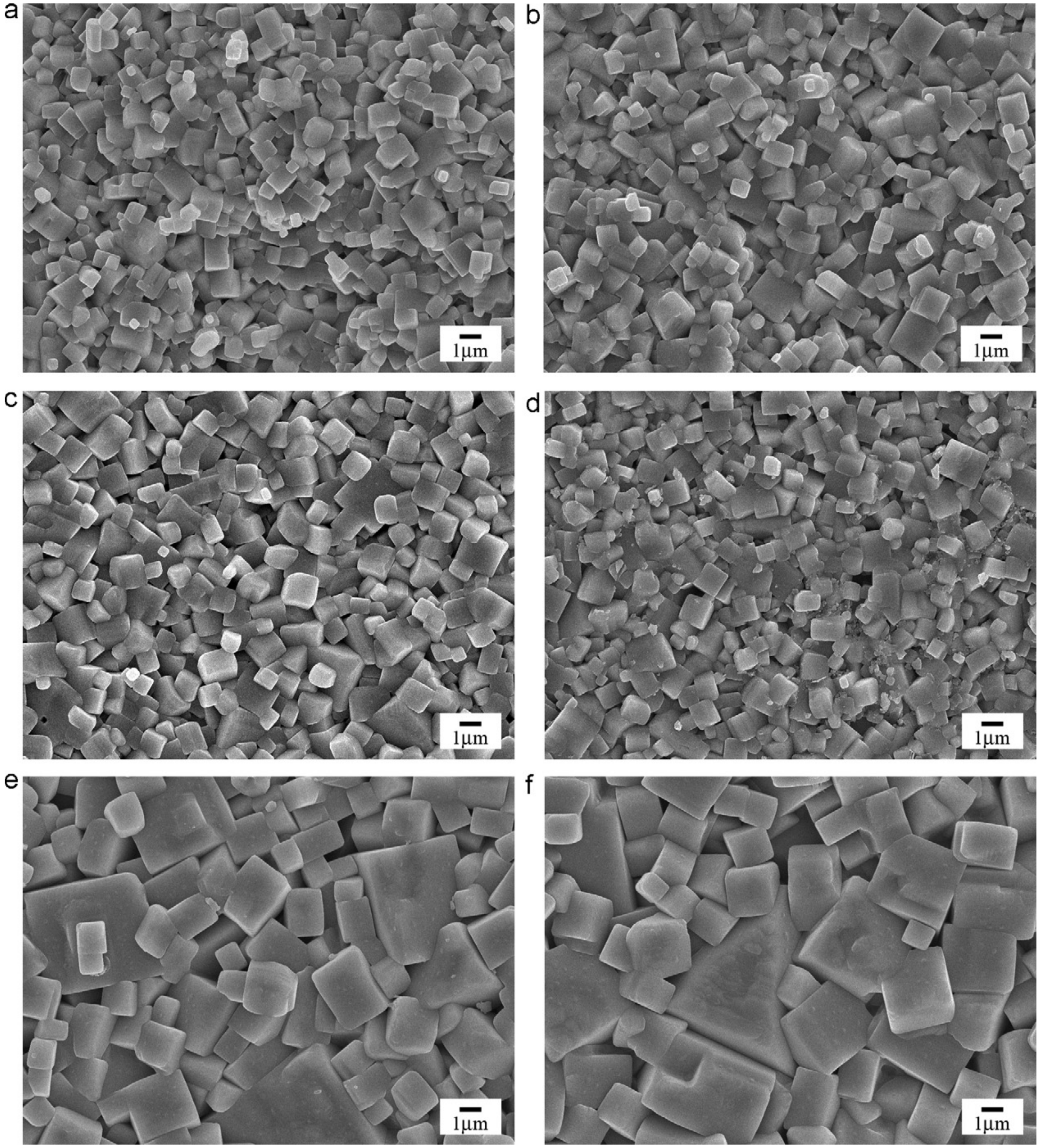

Fig. 3. SEM micrographs of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ with various compositions: (a) $x = 0.03$, (b) $x = 0.04$, (c) $x = 0.05$, (d) $x = 0.06$, (e) $x = 0.065$ and (f) $x = 0.07$.

Table 1
Physical and electrical properties of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics.

Composition (x)	Density (g/cm^3)	Average grain size (μm)	T_c (°C)	ε_r (at 25 °C, 1 kHz)	tan δ (at 25 °C, 1 kHz)	d_{33} (pC/N)
0.00[a]	4.34	–	420	500	0.15	–
0.03	4.15 ± 0.02	1.00 ± 0.06	443	407	0.027	100
0.04	4.25 ± 0.05	1.07 ± 0.14	445	611	0.070	158
0.05	4.13 ± 0.03	1.11 ± 0.12	452	572	0.128	140
0.06	4.17 ± 0.03	1.17 ± 0.09	455	719	0.032	163
0.065	4.11 ± 0.09	2.02 ± 0.33	465	744	0.030	165
0.07	4.20 ± 0.01	2.08 ± 0.51	471	736	0.038	188
Pz24[b]	7.7	–	330	400	0.002	–

[a] Ref. [11].
[b] Ref. [20].

determined with the linear intercept method and is summarized in Table 1. The grains have different size and size distributions from <0.2 to 5 μm, depending on the Li content. It is evident that the average grain size increases with increasing Li content, indicating that Li addition promotes grain growth [17]. The micrographs show abnormal grain growth behavior, especially the compositions $x = 0.065$ and $x = 0.07$, indicating that the population of abnormal grain increases with Li addition. It can be explained in term of a reduction of the critical driving force for rapid grain growth by addition of Li. The critical driving force for rapid grain growth decreases by adding Li [18].

The temperature dependence of the dielectric constant in $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics measured at 1 kHz is shown in Fig. 4. All samples show typical temperature dependence of the dielectric constant curves. It is also evident that two phase transitions, corresponding to the orthorhombic to tetragonal (T_{ot}) and ferroelectric tetragonal to paraelectric cubic (T_c) phase transition, respectively, are clearly observed. For $x \leq 0.05$, the broadened peak at T_{ot} shifted toward the lower temperature regions with increasing Li content. On the other hand, compositions with $x \geq 0.06$ show no peak corresponding to T_{ot}, which means that the tetragonal phase was stabilized at room temperature [16]. The room temperature dielectric constant (ε_r), dielectric loss (tan δ) and Curie temperature (T_c) of the ceramics are listed in Table 1. It is seen that Curie temperature generally increases from 443 to 471 °C with increasing Li content. The maximum dielectric constant also follows the same trend. Clearly, this observation can be expected because $LiNbO_3$ has a large crystal anisotropy and high Curie temperature of 1200 °C [16]. The temperature dependence of the dielectric loss for $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics measured at 1 kHz is shown in Fig. 4. It can be seen that the dielectric loss is lower than 10% from room temperature up to 300 °C and reaches a peak at the Curie temperature, after which it increases rapidly, as a result of conductive losses.

Also listed in Table 1 for direct comparison are physical and electrical properties of pure KNN [11] and PZT-based ceramic (Pz24) [20]. The density between 4.11 and 4.25 g/cm^3 were achieved for the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics prepared by the conventional solid-state mix oxide, which is slightly lower than that of pure KNN ceramics [11]. The dielectric constant of the prepared ceramic compositions with Li content between 6 and 7% was found to be 407–736, which is higher than that that of pure KNN and Pz27 ceramics. Therefore, the enhancement of the dielectric properties in Li-substituted KNN ceramics as compared to KNN pure ceramic confirms that the addition of Li improves the dielectric properties of KNN ceramics, particularly in the near MPB compositions.

The polarization-field (P–E) hysteresis loops of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics are plotted in Fig. 5. The well-developed and fairly symmetric hysteresis loops with the

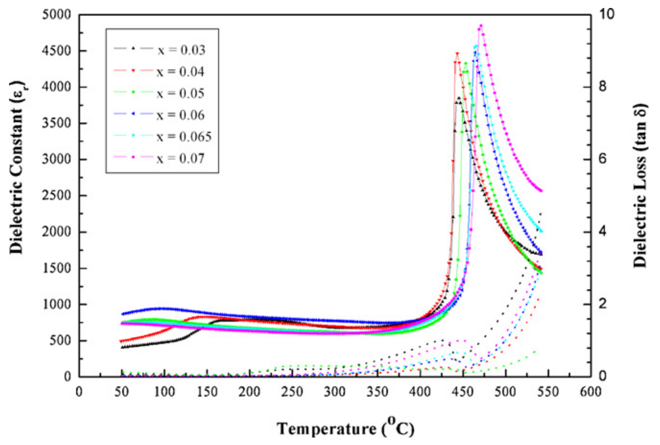

Fig. 4. Temperature-dependent dielectric properties of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics (measured at 1 kHz).

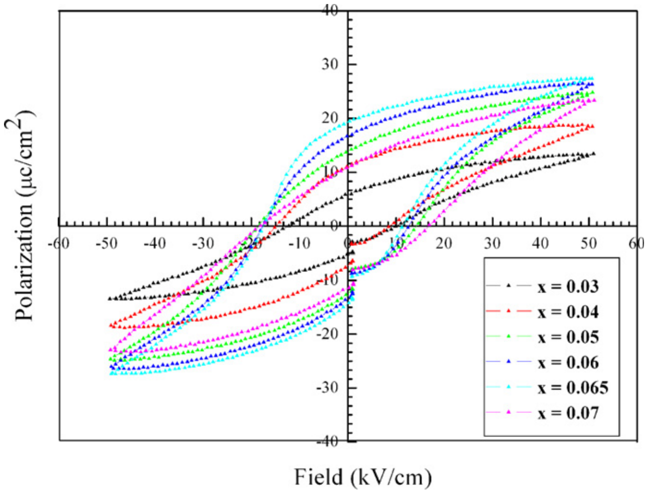

Fig. 5. Hysteresis loops of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics measured at room temperature.

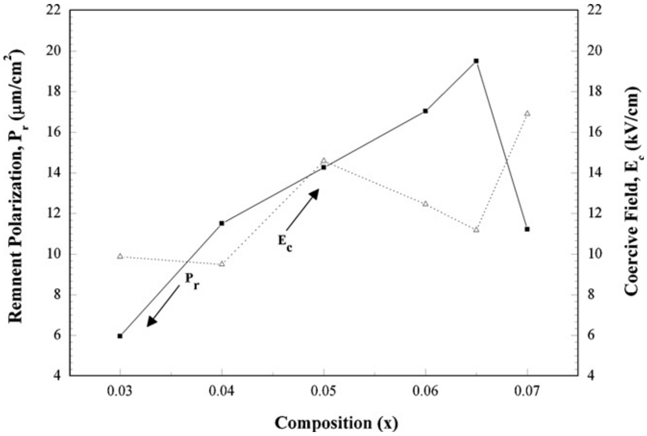

Fig. 6. Hysteresis parameters of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics at room temperature.

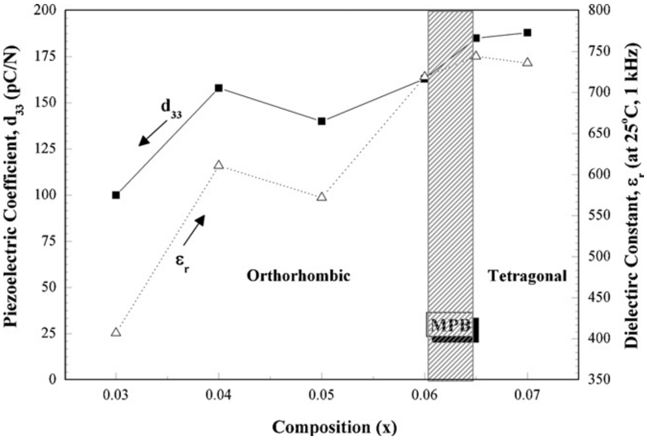

Fig. 7. Piezoelectric coefficient and dielectric constant of $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics at room temperature. Shaded area indicates expected MPB region.

field are observed for all compositions. To further assess ferroelectric characteristics in $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ ceramics, the ferroelectric parameters, remnant polarization (P_r) and the coercive field (E_c) were considered. Both of the remnant polarization (P_r) and the coercive field (E_c) exhibited a clear dependency on Li content. It can be seen that the remnant polarization (P_r) increases with increasing Li content. With an addition of 6.5% of Li, the remnant polarization (P_r) achieves its maximum value of 19.5 $\mu C/cm^2$ and further increase in Li content causes the decrease the remnant polarization (P_r). Furthermore, the coercive field (E_c) increases with increasing Li content. Nevertheless, the coercive field (E_c) shows a noticeable decrease at compositions with Li content of 6 and 6.5%. This observation further supports that the MPB should exist near the two compositions, where easier domain wall movement results in lower coercive field [19]. In Fig. 6, the ferroelectric parameters are displayed as a function of Li content. It is seen that the addition of Li improves the ferroelectric characteristic of KNN ceramics, especially in the composition with 6.5% Li addition which shows the maximum remnant polarization (P_r). In addition, the piezoelectric coefficients (d_{33}) were showed in Table 1 and Fig. 7. The d_{33} values exhibited a clear dependency on Li content and the densities. The ceramics show peak values of $d_{33} = 185$ and 188 pC/N near the composition with $x = 0.065$ and $x = 0.07$. The MPB compositions are well known to possess enhanced properties, with the most important example being $Pb(Zr,Ti)O_3$ ceramics [7]. Combining this observation with earlier discussion on XRD results leads to the conclusion that the MPB between orthorhombic and tetragonal phases of this ceramic system should lie near the compositions with 6–6.5% Li content, as indicated by shaded area in Figs. 2 and 7.

4. Conclusions

In this study, ceramics in the $((K_{0.5}Na_{0.5})_{1-x}Li_x)NbO_3$ system (when $x = 0.03$, 0.04, 0.05, 0.06, 0.065 and 0.07) were successfully prepared by the conventional mixed-oxide technique. The ceramics were identified by XRD as a single-phase perovskite structure with a gradual change from orthorhombic to tetragonal symmetry, and a possible morphotropic phase boundary (MPB) between two phases near compositions between $x = 0.06$ and $x = 0.065$. The Curie temperature (T_c) of the ceramics was shifted to higher temperature with increasing Li content. The room temperature dielectric constant in Li-modified KNN was higher than that of the pure KNN ceramic. In addition, the ferroelectric properties were found to enhance at compositions with 6–6.5% Li content, further support the existence of MPB near the two compositions. This study clearly shows that the addition of Li could improve the dielectric and ferroelectric properties in $(K_{0.5}Na_{0.5})NbO_3$ ceramics.

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References

[1] A.J. Moulson, J.M. Herbert, Electroceramics: Materials, Properties, Applications, John Wiley & Sons Ltd., Chichester, 2003.
[2] G.H. Haertling, Ferroelectric ceramics: history and technology, J. Am. Ceram. Soc. 82 (4) (1999) 797–818.
[3] M.D. Maeder, D. Damjanovic, N. Setter, Lead free piezoelectric materials, J. Electroceram. 13 (2004) 385–392.
[4] E. Ringgaard, T. Wurlitzer, Lead-free piezoceramics based on alkali niobates, J. Eur. Ceram. Soc. 25 (2005) 2701–2706.
[5] T.R. Shrout, S.J. Zhang, Lead-free piezoelectric ceramics: alternatives for PZT, J. Electroceram. 19 (2007) 113–126.
[6] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoelectrics, Nature 432 (2004) 84–86.
[7] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press Limited, India, 1971.
[8] G.Z. Zang, J.F. Wang, H.C. Chen, W.B. Su, C.M. Wang, P. Qi, B.Q. Ming, J. Du, L.M. Zheng, Perovskite $(Na_{0.5}K_{0.5})_{1-x}(Li,Sb)_xNb_{1-x}O_3$ lead-free piezoceramics, Appl. Phys. Lett. 88 (2006) 212908–212911.

[9] R.E. Jaeger, L. Egerton, Lead-free piezoceramics based on alkali niobates, J. Am. Ceram. Soc. 45 (5) (1962) 209–213.

[10] R. Wang, R. Xie, T. Sekiya, Y. Shimoto, Y. Akimune, N. Hirosaki, M. Itoh, Piezoelectric properties of spark-plasma-sintered $(Na_{0.5}K_{0.5})NbO_3$–$PbTiO_3$ ceramics, Jpn. J. Appl. Phys. 41 (2002) 7119–7122.

[11] Y. Guo, K. Kakimoto, H. Ohsato, Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics, Appl. Phys. Lett. 85 (18) (2004) 4121–4123.

[12] Y. Guo, K. Kakimoto, H. Ohsato, $(Na_{0.5}K_{0.5})NbO_3$–$LiTaO_3$ lead-free piezoelectric ceramics, Mater. Lett. 59 (2–3) (2005) 241–244.

[13] G.Z. Zang, J.F. Wang, H.C. Chen, W.B. Su, C.M. Wang, P. Qi, B.Q. Ming, J. Du, L.M. Zheng, Piezoelectric properties in perovskite $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ lead-free ceramics, J. Appl. Phys. 100 (10) (2006) 104108–104112.

[14] U. Fl?ckiger, H. Arend, H. Oswald, Synthesis of $KNbO_3$ powder, J. Am. Ceram. Soc. 56 (6) (1977) 575–577.

[15] D. Lin, K.W. Kwok, K.H. Lam, H.L.W. Chan, Structure, piezoelectric and ferroelectric properties of Li- and Sb-modified $K_{0.5}Na_{0.5}NbO_3$ lead-free ceramics, J. Phys. D: Appl. Phys. 40 (2007) 3500–3505.

[16] M. Matsubara, T. Yamaguchi, K. Kikuta, S.C. Hirano, Effect of Li substitution on the piezoelectric properties of potassium sodium niobate ceramics, Jpn. J. Appl. Phys. 44 (8) (2005) 6136–6142.

[17] Y. Saito, H. Takao, High performance lead-free piezoelectric ceramics in the $(K,Na)NbO_3$–$LiTaO_3$ solid solution system, Ferroelectrics 338 (2006) 17–32.

[18] M.S. Kim, S.J. Jeong, J.S. Song, Microstructures and piezoelectric properties in the Li_2O-excess $0.95(Na_{0.5}K_{0.5})NbO_3$–$0.05LiTaO_3$ ceramics, J. Am. Ceram. Soc. 90 (10) (2007) 3338–3340.

[19] H. Du, F. Tang, D. Liu, D. Zhu, W. Zhou, S. Qu, The microstructure and ferroelectric properties of $(K_{0.5}Na_{0.5})NbO_3$–$LiNbO_3$ lead-free piezoelectric ceramics, Mater. Sci. Eng. B 136 (2007) 165–169.

[20] http://www.ferroperm-piezo.com/.