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Ferroelectric Phase Transition of Lead Free $(1-x)(Na_{0.5}K_{0.5})NbO_3$- $xLiNbO_3$ Ceramics

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Lead-free $(1-x)(Na_{0.5}K_{0.5})NbO_3$-$xLiNbO_3$, i.e., NKN-LN$x$ (x =0.0, 0.1, 0.2, 0.3, 0.4 mol) was prepared using the conventional solid state reaction method. The effects of LN mixing on the ferroelectric properties of NKN-LNx ceramics were studied using a dielectric constant and *P-E* (Polarization-electric field) measurements. Ferroelectricity was observed in the composition for x approximately varying between 0.0 and 0.4. Minimum remanent polarization $2P_r$=5 C/cm^2 was achieved in the composition for x = 0.2. The ferroelectric phase transition temperature T_C increased with increasing LN content. The ferroelectric phase transition of NKN-LNx ($x \geq 0.1$) is a second-order phase transition, and that of NKN-LNx ($x \leq 0.2$) is a first-order phase transition. These results indicate that the ferroelectric phase transition temperature of NKN-LNx change from that of second-order to weak first-order phase transition according to the LN content.

Keywords: Lead-free, Oxides, Impedance spectroscopy, Dielectric, Phase transition

1. INTRODUCTION

In the field of piezoelectric ceramics, sodium potassium niobate ceramics with lead-free piezoelectric material have been investigated as alternative material for PZT-based ceramics [1-13]. Lead-free ferroelectric materials with perovskite structure have a general formula of ABO_3. In this structure, cations based on their valence states and coordination numbers occupy the A- or B-sites. $Na_{1-y}K_yNbO_3$, NKN is a material with perovskite structure, and it exhibits high piezoelectric properties because its structure permits spontaneous polarization to rotate along three orientations. Sodium potassium niobate (NKN) is a solid solution of potassium niobate (KN) a ferroelectric and sodium niobate (NN), with an Na/K ratio of ~50/50. The piezoelectric applications of $Na_{0.5}K_{0.5}NbO_3$ (NKN), ceramics produced by hot-pressing, are better than those produced by sintering in air atmosphere. Hot-pressed NKN ceramics have been reported to have a high phase transition temperature (T_c ~ 420℃), good piezoelectric properties (d_{33} ~ 160 pC/N), and a high planar coupling coefficient (κ_p~45%) [1-4].

However, NKN ceramics are difficult to obtain using the conventional sintering method because their phase stability is limited to 1,140℃ and they are exposed to moisture. Therefore, attempts have been made to improve the sinterability and piezoelectric properties of KNN through the addition and/or substitution of several cationic elements in the A- or B-sites [10-13]

It is known that $(1-x)(Na_{0.5}K_{0.5})NbO_3$-$xLiNbO_3$, NKN- LN$x$ ceramics are good, lead-free piezoelectric and ferroelectric ceramics. A morphotropic phase boundary between the orthorhombic phase and the tetragonal phase of NKN-LNx was present when x was approximately 0.05 ~ 0.07 mol of LN [8]. Guo *et. al.*, observed that the Curie temperatures (T_C) of NKN- LNx ceramics were in the range of 452 ~ 510℃, according to their LN content, which is at least 100℃ higher than that of Pb(Zr, Ti)O_3. For $(Na_{0.5}K_{0.5})NbO_3$,

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Tc values were observed at 420℃ and 200℃, which correspond to the cubic-orthorhombic and orthorhombic-tetragonal phase transitions, respectively. Two phase transitions were present at x = 0.04, 0.06 mol, similar to the case for NKN, except that the phase transition temperatures were shifted [9]. Many research efforts thus far have been based on the conditions for which a small amount of LN was added to the NKN composition.

In this study, (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x = 0.0, 0.1, 0.2, 0.3, 0.4mol), was synthesized using the conventional solid state method. The purpose of this study is to investigate the phase transition and electrical properties of ($Na_{0.5}K_{0.5}$)NbO_3 in terms of its $LiNbO_3$ content.

2. EXPERIMENTS

Lead-free (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 mol), was prepared by mixing the oxides, K_2CO_3 (99% purity), Na_2CO_3 (99% purity), $LiNbO_3$ (99% purity) and Nb_2O_5 (99% purity) in a molar ratio used in the conventional solid state reaction method. Before being weighed, the K_2CO_3 and Na_2CO_3 powders were first dried in an oven at 200℃ for 10 h to minimize the effect of moisture. These powders were then milled with ZrO_2 balls for 20 h using ethyl alcohol as a medium and dried. The dried powders were calcined at 850℃ for 2 h. After calcination, the powders were ball-milled again for 20 h and, dried, after which PVA(4 wt%) was added as a binder. They were then pressed into disks with diameter of under 13 mm. After burning off the PVA, the pellets were sintered at 1,070℃ for 2 h. The crystal structures were determined by X-ray power diffraction analysis using CuKα radiation (Philips X' Pert - MPD system). The remnant polarization P_r and coercive field E_c were determined from the P-E (Polarization - Electric field) hysteresis loops, as measured by a Radiant Precision Workstation. To examine their dielectric properties, the ceramics were polished and painted with silver paste on both surfaces, and fired at 800℃ for 30 min. The real and imaginary dielectric constants were measured using an SI1260 impedance analyzer at temperature ranging from room temperature to ~ 600℃ with heating and cooling rates of 0.2℃/min in the frequency range of 1 Hz to 1 MHz.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of the (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x = 0.0, 0.1, 0.2, 0.3, 0.4 mol) ceramics. Studies have reported that a phase of $K_3Li_2Nb_5O_{15}$ (KLN) with a tetragonal tungsten bronze structure starts to appear at x ≥ 0.08 [9]. In this study, it appeared at x ≤ 0.2 but for x ≥ 0.3, the KLN phase and $LiNbO_3$ phase coexisted. This implies that the structures of the NKN-LNx ceramics were transformed, again increasing their $LiNbO_3$ content.

P-E hysteresis loops of (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x= 0.0, 0.1, 0.2, 0.3, 0.4 mol) ceramics measured at room temperature under a driven electric field are plotted in Figs. 2(a)-(f). Generally, the presence of P-E hysteresis loops is considered to be evidence that a material is ferroelectric.

The capacitor is characterized by P-E hysteresis curves. However, the shapes of the P-E loops changed slightly with increasing LN contents. As shown in Fig. 2(f), the value of 2P_r decreases with an increasing LN content below a certain critical level. 2P_r has a minimum value of 5 C/cm^2 near x = 0.2, and it first increases and then decreases after reaching this value. The coercive field 2E_c increases for an increase in the amount of LN in the range between x = 0.0 and x = 0.1 mol., and a further increase in the amount of LN above x = 0.2 mol causes an increase in 2E_c.

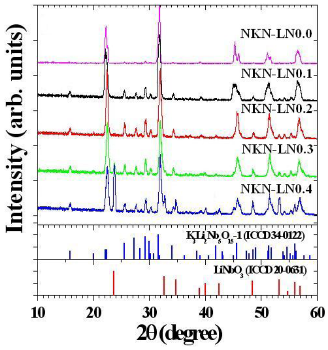

Fig. 1. X-ray diffraction patterns of the (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, NKN-LN$x$ ceramics.

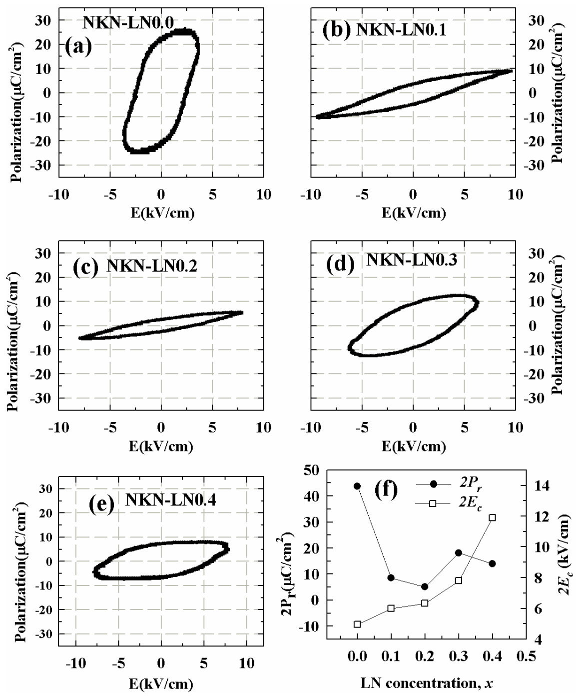

Fig. 2. Ferroelelctric hysteresis loops of the (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, NKN-LN$x$ ceramics for (a) x =0.0, x =0.1, (c) x =0.2, (d) x =0.3, and (e) x =0.4 mol, (f) remanent polarization and coercive field of NKN-LNx ceramics as a function of the LN contents x.

The tendency of varying 2P_r is similar to that of 2E_c when the range of x is approximately above x = 0.2 mol.

Du *et al.* [8] reported the dielectric properties of NKN-LNx ceramics for the case that the amount of LN is below x = 0.2 mol; when the amount LN is x = 0.06 mol, E_c achieves its minimum value of 13.4 kV/cm and P_r reaches its minimum value of 20 C/cm^2. They proposed that NKN-LN0.06 ceramics are a promising candidate for lead-free high-temperature piezoelectric ceramics.

Figures 3(a) and (e) show the real (ε') dielectric constant at 1 MHz as a function of temperature for of (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x=0.0, 0.1, 0.2, 0.3, 0.4 mol) ceramics. In the case of NKN-LN0.0 ceramics, the values of ε' increase with decreasing temperature. At T_C (the temperature at which ε' is maximized) = 409℃, ε' beings to decrease, forming a large λ-type peak in the dielectric constant *vs*. temperature curve upon heating and cooling.

As the temperature decreases, if we assume that the phase

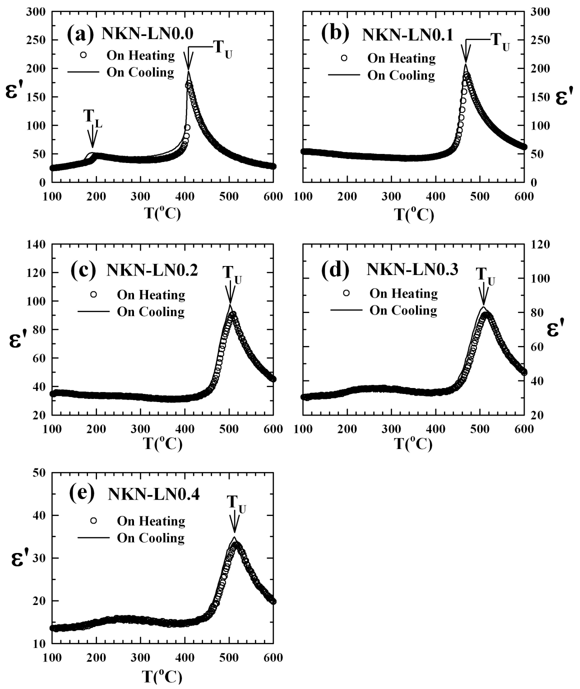

Fig. 3. The temperature dependence of the real dielectric constant ε' in(1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, NKN-LN$x$ ceramics at 1 MHz on heating (symbol) and cooling (solid line), (a) x=0.0, (b) x =0.1, (c) x =0.2, (d) x =0.3, and (e) x =0.4 mol.

transition temperature is the mid-point of the steepest curve of ε', then the lower transition occurs at $T_{OT,C}$ (low temperature phase transition point) = 176℃ upon cooling and at $T_{OT,H}$=195℃ upon heating with a thermal hysteresis of 19℃ This result is similar to that reported by Guo *et al.* [9].

In the case of NKN-LN0.1, a low temperature anomaly was not observed at T_{OT} upon heating or cooling.

At high temperatures, the complex dielectric response of NKN-LN0.1 was found to be similar to that of NKN-LN0.0. The sharp peaks around T_C for the NKN-LN0.0 and NKN-LN0.1 samples show a second-order phase transition without thermal hysteresis.

In the case of NKN-LNx ($x \geq 0.2$), the ferroelectric phase transition temperature T_C shifted to a higher value with an increase in the LN content, whereas the dielectric peak broadened. The temperature anomaly of the real dielectric constant appeared at T_C in all the samples upon heating and cooling with a small thermal hysteresis, which corresponded to at weak first-order phase transition. A low-temperature dielectric anomaly was not observed upon heating and cooling. In NKN-LNx samples with $0 \leq x \leq 0.07$, Guo et al. [9] reported that the phase transition of NKN-LN0.0 was observed at 420℃ and 200℃, which corresponds to the cubic-orthorhombic (at T_C) and orthorhombic-tetragonal (at T_{OT}) phase transitions. Also, $LiNbO_3$ has lithium niobate structure, which can be described as a heavily distorted perovskite or an ordered phase derived from the corundum structure with space group R_{3C} (C_{3V}^6). So, it is evident that two effects on the structure of NKN ceramics have been observed in NKN-$LiNbO_3$ ceramics. At lower $LiNbO_3$ concentrations, Li mainly replaces Na and K in the *A* sites of ABO_3 perovskite structure (i.e. form a solid solution), leading to a linear shift of the Curie point (T_C) to higher temperature [9]. However, the structure of solid solution transforms from orthorhombic to tetragonal symmetry due to the large distortion caused by Li^+ [9].

The phase transition temperatures also shifted increasing the LN content. T_C shifted to a higher value, and T_{OT}, to a lower value [11]. Thus, we expect that a low-temperature phase transition of this sample should appear at room temperature because these phase transition temperatures decrease with an increase in LN contents.

Table 1. Phase transition temperature (T_{OT}, T_C) of NKN-LNx ceramics on heating and cooling. unit: ℃

Samples	On Heating		On Cooling		ΔT_{OT}	ΔT_C
	$T_{OT,H}$	$T_{OT,C}$	$T_{C,H}$	$T_{C,C}$		
NKN-LN0.0	195	176	409	409	19	0
NKN-LN0.1			469	469		0
NKN-LN0.2			509	502		7
NKN-LN0.3			517	508		9
NKN-LN0.4			521	514		7

The values of T_{OT}, T_C, and ΔT obtained for all the samples are presented in Table 1. Here, ΔT indicates the degree of the first- and second-order phase transition of NKN-LNx. These results indicate that the phase transition of NKN-LNx ceramics occurs when T_C changes from a second-order to weak first-order phase transition with increasing LN contents. Our results also show the possibility that the concentration of x = 0.2 may be the critical concentration for a first- to second-order-ferroelectric phase transition.

4. CONCLUSIONS

In conclusion, (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$, i.e., NKN-LN$x$ (x=0.0, 0.1, 0.2, 0.3, 0.4mol) ceramics, were synthesized using the solid state reaction method. The effects of LN mixing on the ferroelectric properties of these two ceramics were studied through dielectric and P-E measurements. The value of P_r increased with increasing Nb content. (1-x)($Na_{0.5}K_{0.5}$)NbO_3-$x$$LiNbO_3$ ceramics exhibited a minimum remanent polarization of $2P_r$=5 μC/cm^2 at an LN content of x ~ 0.2. These results indicate that LN doping can change the ferroelectric properties of NKN-LNx ceramics. The phase transition temperature, T_C, increased with increasing LN contents. The ferroelectric phase transition of NKN-LNx ($x \leq 0.1$), is a second-order transition without thermal hysteresis, and NKN-LNx ($x \geq 0.2$) is a weak first-order transition with small thermal hysteresis. Thus, our results demonstrate the possibility that the concentration of x ~ 0.2 may be the critical concentration for a first-to-second-order-ferroelectric phase transition.

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