

Phase transitional behavior and piezoelectric properties of $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--LiNbO}_3$ ceramics

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Lead-free piezoelectric ceramics $(1-x)(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3\text{--}x\text{LiNbO}_3$ $\{[\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}]\text{NbO}_3\}$ ($x=0.04\text{--}0.20$) have been synthesized by an ordinary sintering technique. The materials with perovskite structure is orthorhombic phase at $x\leq 0.05$ and becomes tetragonal phase at $x\geq 0.07$, a phase $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ with tetragonal tungsten bronze structure begins to appear at $x=0.08$ and becomes dominant with increasing the content of LiNbO_3 . A morphotropic phase boundary between orthorhombic and tetragonal phases is found in the composition range $0.05 < x < 0.07$. Analogous to $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$, the piezoelectric and electromechanical properties are enhanced for compositions near the morphotropic phase boundary. Piezoelectric constant d_{33} values reach 200–235 pC/N. Electromechanical coefficients of the planar mode and the thickness mode reach 38%–44% and 44%–48%, respectively. The Curie temperatures (T_C) of $[\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}]\text{NbO}_3$ ($x=0.04\text{--}0.20$) are in the range of 452–510 °C, at least 100 °C higher than that of conventional $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$. Our results show that $[\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}]\text{NbO}_3$ is a good lead-free high-temperature piezoelectric ceramic. © 2004 American Institute of Physics. [DOI: 10.1063/1.1813636]

Very high piezoelectric and electromechanical properties have been achieved in a series of lead-based ferroelectric solid solution single crystals, such as $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$, $\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3\text{--PbTiO}_3$ (PZNT), and $\text{BiScO}_3\text{--PbTiO}_3$ (BSPT).^{1–3} It is believed that in these systems the high piezoelectric response is related to the morphotropic phase boundary (MPB) between rhombohedral, tetragonal, or monoclinic phases. The existence of these thermodynamically equivalent phases permits almost continuous rotation of the polarization vector under the external electric field, exhibiting enhanced dielectric, piezoelectric, and electromechanical response.^{4,5} However, the toxicity of lead oxide and its high vapor pressure during processing has led to a demand for alternative lead-free piezoelectric materials. The search for alternative piezoelectric materials is now focused on alkali niobates, modified bismuth titanates, and systems in which a MPB occurs.^{6–9} Among them, $(\text{Na}_{0.5}\text{K}_{0.5})\text{NbO}_3$ (NKN) has been considered a good candidate for lead-free piezoelectric ceramics because of its strong piezoelectricity and ferroelectricity. The hot pressed NKN ceramics ($\sim 99\%$ of the theoretical density) have been reported to possess a high Curie temperature ($T_C \sim 420$ °C), a large piezoelectric longitudinal response ($d_{33} \sim 160$ pC/N), and a high planar coupling coefficient ($k_p \sim 45\%$).^{10–13} However, NKN ceramics sintered by ordinary sintering show relatively lower electrical properties ($d_{33} \sim 80$ pC/N, $k_p \sim 36\%$) due to difficulty in the processing of dense ceramics by ordinary sintering.^{11,12} Highly dense NKN– SrTiO_3 and NKN– BaTiO_3 ceramics ($\sim 98\%$ of the theoretical density) have been studied for dielectric and piezoelectric applications, and all exhibit a crossover from typical ferroelectric to ferroelectric relaxor behavior at a higher concentration of substitution. Unfortunately, the piezoelectric and electromechanical properties all

decreased.^{14,15} In this work, the structure and electrical properties of NKN– LiNbO_3 ceramics were studied. The results show that by adding an appropriate amount of LiNbO_3 , enhanced piezoelectric and electromechanical properties can be accessed in NKN– LiNbO_3 ceramics due to the formation of a MPB between the orthorhombic and tetragonal phases.

Ceramics with the normal composition $[\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}]\text{NbO}_3$ ($x=0, 0.04, 0.05, 0.06, 0.07, 0.08, 0.10, 0.15$, and 0.20) were synthesized by the mixed oxide

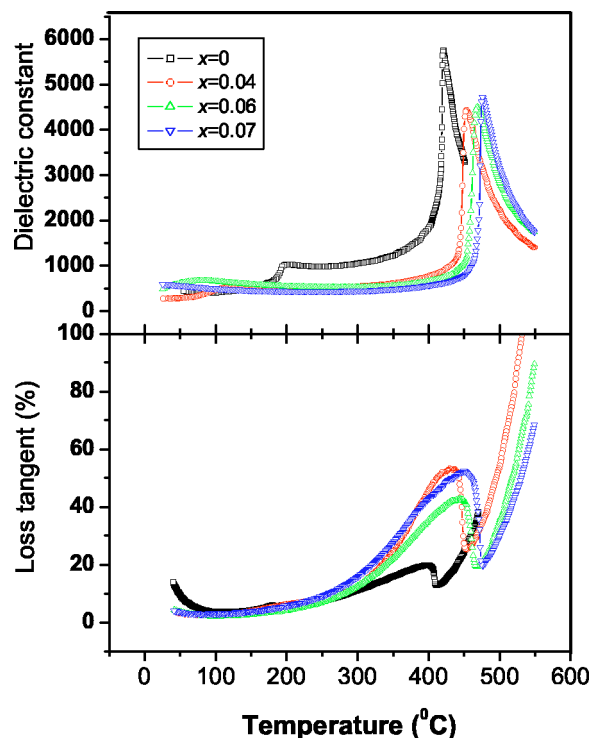


FIG. 1. (Color online) Temperature dependence of dielectric constant and loss of the $(1-x)\text{NKN}\text{--}x\text{LiNbO}_3$ ceramics with $x=0, 0.04, 0.06$, and 0.07 at 10 kHz.

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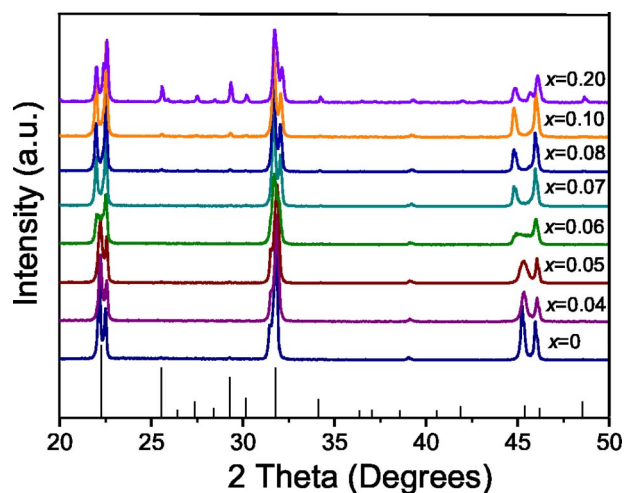


FIG. 2. (Color online) X-ray diffraction patterns of the $(1-x)\text{NKN}-x\text{LiNbO}_3$ ceramics. The vertical lines in the bottom are ICDD data of $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ with tetragonal tungsten bronze structure.

method. The starting materials used in this study were K_2CO_3 , Na_2CO_3 , and Nb_2O_5 of 99.9% purity, and Li_2CO_3 of 98% purity. They were milled in polyethylene with ZrO_2 balls for 24 h using ethanol as a medium. After calcination at 850°C for 10 h, the calcined powders were ball milled again for 24 h, dried, and then poly(vinylalcohol) was added as a binder. The granulated powders were subsequently granulated and pressed into disks of 12 mm diameter under 98 MPa, followed by a cold-isostatic pressing under 200 MPa. These powder compacts were fired in air at selected temperatures, depending on their x , in the range between 1100°C and 1040°C . The bulk densities were obtained by Archimedes method. Their crystal structures were determined by x-ray powder diffraction analysis obtained using a $\text{Cu K}\alpha$ filter through Ni foil (Rigaku; RAD-B system).

For electrical characterization, samples were polished and painted with silver paste on the sample surfaces. Their dielectric properties were measured using an Agilent 4294A precision impedance analyzer in the temperature range from 30 to 550°C . For piezoelectric and electromechanical measurements, the samples were immersed in silicon oil and poled in a 30 kV/cm field. The electric field was applied at a temperature of 150°C for 30 min, and the specimens were

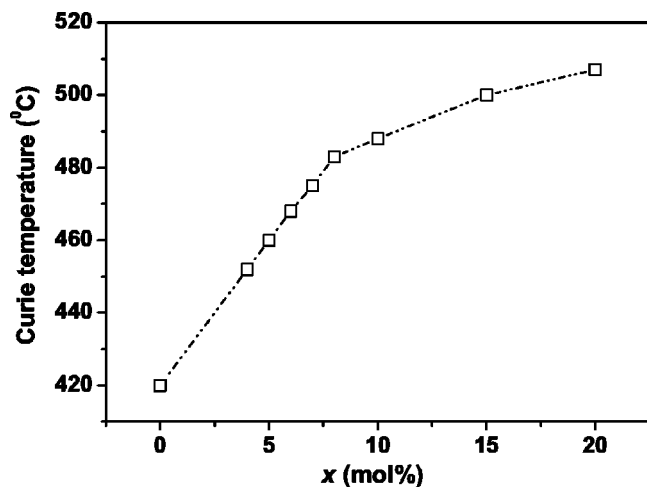


FIG. 3. Concentration dependence of the Curie temperature (T_C) for $(1-x)\text{NKN}-x\text{LiNbO}_3$ ceramics.

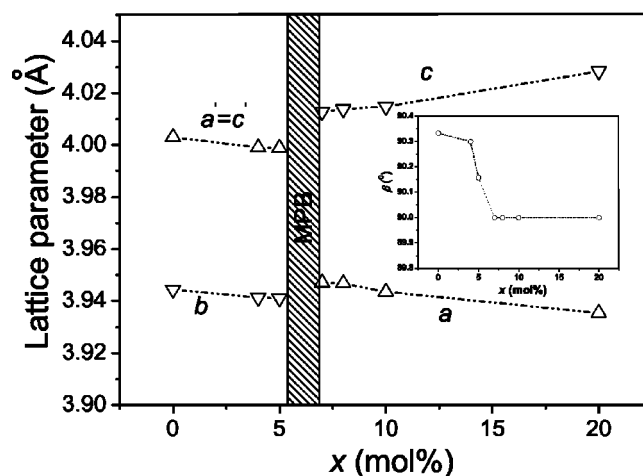


FIG. 4. The variation of the lattices parameters of the $\text{NKN}-\text{LiNbO}_3$ ceramics as a function of LiNbO_3 concentration x .

cooled to room temperature in the electric field. The piezoelectric constant d_{33} was measured using Berlincourt-type quasi-static meter at approximately 55 Hz. The electromechanical coupling coefficients were determined by a resonance and antiresonance method performed on the basis of IEEE standards using an impedance analyzer (Agilent 4294A).

The temperature dependence of the dielectric constant (ϵ_r) and loss at 10 kHz for some unpoled $[\text{Li}_x(\text{Na}_{0.5}\text{K}_{0.5})_{1-x}]\text{NbO}_3$ samples with $0 \leq x \leq 0.07$ is shown in Fig. 1. For pure NKN, phase transitions are observed at 420 and 200°C , corresponding to the phase transitions of cubic-orthorhombic (at T_C) and orthorhombic-tetragonal (at T_{O-T}), respectively. In the samples with $x=0.04$ and 0.06 , similar to that of pure NKN, the two phase transitions are observed, however the phase transition temperatures are

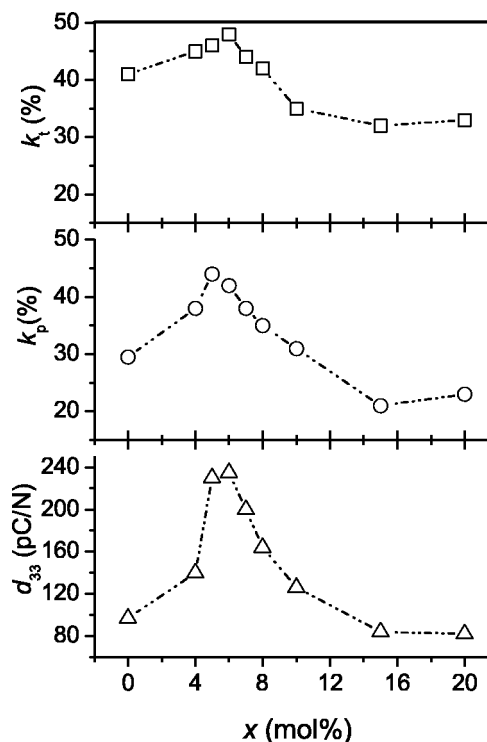


FIG. 5. Electrical properties of $(1-x)\text{NKN}-x\text{LiNbO}_3$ ceramics as a function of the LiNbO_3 content.

TABLE I. The electrical and physical properties of the sintered $(1-x)\text{NKN}-x\text{LiNbO}_3$ ceramics.

LiNbO ₃ content (x)	0	0.04	0.05	0.06	0.07	0.08	0.10	0.15	0.20
Density (g/cm ³)	4.34	4.35	4.36	4.35	4.33	4.29	4.28	4.28	4.24
d_{33} (pC/N)	97	140	230	235	200	164	126	84	82
k_p (%)	29	38	44	42	38	35	31	21	23
k_t (%)	41	45	46	48	44	42	35	32	33

shifted: T_C to higher temperatures, and T_{O-T} to lower temperatures. When the LiNbO₃ content is greater than 0.07, only the cubic–tetragonal phase transition is observed. It should be noted that all the samples still show classic ferroelectric behavior after the addition of LiNbO₃. On the other hand, it is found that, for $x \geq 0.07$, ϵ_r is nearly temperature independent in the range from room temperature to 400 °C, indicating thermal stability associated with a high- T_C piezoelectrics. The dielectric loss is lower than 4% in the range of room temperature to 200 °C and reaches a peak at the Curie temperature, after which it increases rapidly owing to conductive losses.

Figure 2 shows the x-ray diffraction patterns of NKN–LiNbO₃ ceramics. For $x \leq 0.07$, only phases with perovskite structure are detected. A phase $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ (ICDD: 52-0157) with a tetragonal tungsten bronze structure begins to appear at $x=0.08$. Although both NKN and LiNbO₃ have octahedral NbO₆ basic structure units, they belong to different structures. NKN has the perovskite structure with space group $\text{Amm}2$ (C_{2v}^{14}). LiNbO₃ however has the 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–LiNbO₃ ceramics. At lower LiNbO₃ concentrations, Li mainly replaces Na and K in the A sites of ABO₃ perovskite structure (i.e. form a solid solution), leading to a linear shift of Curie point (T_C) to higher temperature (Fig. 3). However, the structure of solid solution transforms from orthorhombic to tetragonal symmetry due to the large distortion caused by Li⁺. The variation of lattice parameters as a function of the LiNbO₃ content is shown in Fig. 4. A MPB between orthorhombic and tetragonal phase should exist at $0.05 < x < 0.07$. The c/a ratio of NKN–LiNbO₃ ceramic with $x=0.07$ is 1.024, which is between that of PZNT ($c/a=1.02$) (Ref. 2) and BSPT ($c/a=1.03$).³ At higher LiNbO₃ concentrations, the solubility of Li into A sites of NKN becomes difficult due to the different ways that LiNbO₃ and NKN crystallize. And only small T_C shift are observed (Fig. 3), which indicates a “composite” mixing effect due to the formation of $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$.

The various piezoelectric and electromechanical properties for NKN–LiNbO₃ ceramics are shown in Table I and Fig. 5. The pure NKN samples showed good piezoelectric properties compared with the previous reports.^{11,12} This should attribute to the increasing of the density (theoretical density: 4.51 g/cm³), which has been reported in the recent papers.^{14,16} By increasing the content of LiNbO₃, the density values of the ceramics bodies initially increase, and decrease significantly at a LiNbO₃ content of $x=0.08$. This should ascribe to the formation of $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ with the lower density (theoretical density: 4.376 g/cm³). Similar to Pb(Zr,Ti)O₃, on the other hand, we found that the properties

show a strong compositional dependence near the MPB region. Poled samples show peak values of piezoelectric constant $d_{33}=235$ pC/N, and electromechanical coupling coefficients, $k_p=44\%$ and $k_t=48\%$ for samples with compositions near the orthorhombic side of the orthorhombic–tetragonal phase boundary. So it is evident that the MPB between the orthorhombic and tetragonal phases plays a very important role in the enhancement of piezoelectric properties of NKN–LiNbO₃ ceramics.

In conclusion, NKN–LiNbO₃ ceramics ($x=0.04$ – 0.20) possessing high Curie temperatures >450 °C have been investigated. Phases with perovskite structure are achieved for $x \leq 0.07$. A phase $\text{K}_3\text{Li}_2\text{Nb}_5\text{O}_{15}$ with tetragonal tungsten bronze structure begins to appear after the Li content reaches its solubility limit in the A sites of NKN ceramics ($x=0.08$). A morphotropic phase boundary between orthorhombic and tetragonal phases is found at $0.05 < x < 0.07$. Enhanced piezoelectric and electromechanical responses $d_{33}=200$ – 235 pC/N, $k_p=38\%$ – 44% , and $k_t=44\%$ – 48% are obtained for samples with composition near the MPB. The excellent piezoelectric and electromechanical properties with a high Curie temperature indicate that this system may be a promising lead-free material for a wide range of electromechanical transducer applications. Growth Li-doped NKN films will be also interesting for applications in nonvolatile memory, microwave technique, surface acoustic wave devices, and microsensors.

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