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Ceramics International 38S (2012) S315–S318

CERAMICS INTERNATIONAL

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Temperature stability and phase transition of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ ceramics

Jeong-Ho Cho *, Yoo-Jung Choi, Young-Jin Lee, Young-Hun Jeong, Myoung-Pyo Chun, Joong-Hee Nam, Byung-Ik Kim

Electronic Components Center, Korea Institute of Ceramic Engineering and Technology, Seoul 153-023, Republic of Korea

Available online 4 May 2011

Abstract

$Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3(x = 0.35–0.55)$ ceramics were prepared using the conventional solid state sintering method. The thermal behaviors of Li-modified $(K_xNa_{1-x})NbO_3$ ceramics were investigated from −30 to 150 °C, and the effect of Na/K ratio in $(K_xNa_{1-x})NbO_3$ ceramics on thermal behavior and electrical properties was also studied. In the case of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ ceramics with 0.5 wt.% ZnO, the transition temperature was sharply decreased because of a phase transition as the composition range of x was 0.425–0.475. From the results of the temperature dependence of piezoelectric properties, it is assumed that the Na-rich phase is less stable than the K-rich phase for temperature change.

Keywords: C. Piezoelectric properties; C. Thermal properties; D. Perovskites; $(K_{0.5}Na_{0.5})NbO_3$

1. Introduction

$(K_xNa_{1-x})NbO_3$ (abbreviated as KNN) a compound of the morphotropic phase boundary (MPB) composition in the $xKNbO_3$–$(1 - x)NaNbO_3$ solid solution, is recognized as one of the promising host materials for preparing lead-free piezoelectrics. Due to the sensitivity to the properties of nonstoichiometry and a complex densification process, however, special handling of K_2O powder is required to manufacture KNN ceramics. Various strategies such as hot pressing, hot forging and SPS (spark plasma sintering) have been used to overcome this problem [1]. Hot-pressed KNN ceramics showed good piezoelectric properties (d_{33} = 160 pC/N and k_p = 45%) along with a high Curie temperature ($T_c \sim 420$ °C) [1–3].

Recently, it has been reported that KNN ceramics obtained by replacing the A and/or B site show high piezoelectric properties. In particular, solid solutions of KNN with different end members containing Li, such as $LiSbO_3$ [4–6], $LiNbO_3$ [7,8], $LiTaO_3$ [9], and so on [10], have been reported to exhibit a thickness coupling coefficient $k_t > 50\%$ and the converse piezoelectric coefficient d_{33} around 200 pm/V for the Li substituted ceramics, and a $k_t > 50\%$ and d_{33} over 300 pm/V for the Li and Ta-modified composition [11]. A d_{33} over 400 pm/V has been reported in textured (K,Na,Li)(Nb,Ta)O_3 ceramics [12]. In doped materials, the maximum properties were reported in compositions containing about 6 mol% Li and this maximum has been attributed to the presence of an MPB between an orthorhombic and a tetragonal phase. On the other hand, the thermally induced phase transition between these phases for this composition occurs at close to room temperature [11,12].

Temperature stability is one of the important characteristics for the application of piezoelectric ceramics. In particular, for application to automotives the piezoelectric properties, such as electromechanical coupling factor, d_{33}, g_{33} and dielectric constant, must be stable in the temperature range of −40 °C and 125 °C. However, the thermally induced phase transitions have influence on temperature stability of piezoelectric properties. The domain configuration changes on crossing the orthorhombic–tetragonal phase transition temperature during temperature cycling lead to partial depoling of the samples [13]. Although Hollenstein et al. [13] have reported the temperature stability of piezoelectric properties of Li-modified KNN ceramics in the temperature range of 20–140 °C, few results are available on the temperature range of −40 °C to 150 °C. Likewise, nothing

* Corresponding author. Tel.: +82 2 3282 2424; fax: +82 2 3282 2410.
E-mail address: goedc@kicet.re.kr (J.-H. Cho).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.109

is known about the effect of the K/Na ratio in KNN ceramics on temperature stability.

Therefore, we have investigated the thermal behavior of Li-modified KNN ceramics in the temperature range of −30 °C to 150 °C, and the effect of K/Na ratio in KNN ceramics on thermal behavior and electrical properties was also studied.

2. Experimental

$Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO (x = 0.35, 0.375, 0.40, 0.425, 0.45, 0.475, 0.50, 0.525, and 0.55) ceramics were prepared using a solid state reaction method. The starting materials used in this study were K_2CO_3, Na_2CO_3, Nb_2O_5, Li_2CO_3 above 99% purity. The powders were mixed in a high density polyethylene (HDPE) bottle for 24 h using a ZrO_2 ball in ethyl alcohol and then they were calcined at 850 °C for 5 h in air. These powders, milled with 5 wt.% polyvinyl alcohol (PVA) aqueous solution, were uni-axially pressed into disks of 10 mm diameter at a pressure of 100 MPa and were subsequently sintered at 1030–1070 °C for 5 h in air. The samples were poled by applying a dc field of 40 kV/cm at 120 °C for 30 min.The density of prepared samples was measured by the Archimedes principle and the crystal structures were determined by X-ray powder diffraction using Cu Kα radiation (XRD, D/MAX-2500V, RIGAKU, Japan). The microstructure evolution was observed using a scanning electron microscopy (SEM, JSM-6700F, JEOL, USA). To investigate the piezoelectric properties, the resonant and anti-resonant frequencies were measured by a network analyzer (HP5100A, Agilent, USA) according to IEEE standards, and then the electromechanical coupling factor (k_p) was calculated. These dielectric and piezoelectric measurements were carried out in the temperature range of −30 °C to 300 °C. To minimize aging effects, the resonance measurements were prepared at least 24 h after the poling.

3. Results and discussion

As previously mentioned, it is difficult to obtain dense KNN ceramics by using a conventional sintering technique. In order to obtain higher densities and better electrical performance of Li-modified KNN ceramics, ZnO was added to them as sintering aids. Among several additives, ZnO gave rise to pronounced improvement in KNN sintering [14]. The composition of 2 mol% Li and 0.5 wt.% ZnO was selected to give a transition temperature from orthorhombic phase to tetragonal phase (T_{O-T}) above 150 °C and high density. The XRD patterns and densities of $Li_{0.02}(K_yNa_{1-y})_{0.98}NbO_3$ with 0.5 wt.% ZnO sintered at 1050 °C for 5 h are shown in Figs. 1 and 2. @@Single phase with perovskite structure and no secondary phase were confirmed through the entire range of compositions. For all samples, orthorhombic symmetry was ascertained through the peaks corresponding to the (2 0 2)/(0 2 0) plane in a narrow scanned XRD pattern, which does not reveal a seismic change. All samples with the K/Na ratio (x = 0.35, ~0.55) had a high density of 95–96% in spite of using a conventional sintering technique.

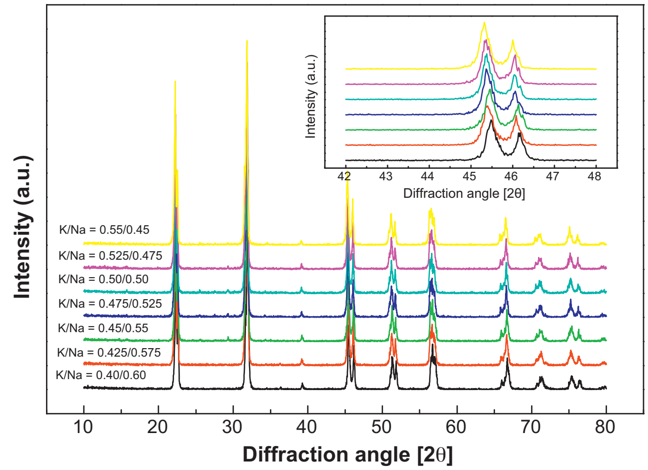

Fig. 1. XRD patterns of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics sintered for 5 h at 1050 °C.

Fig. 3 shows the microstructures obtained for $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics sintered at 1050 °C. Facet interfaces and abnormal grain growth are commonly observed, which are typical characteristics of KNN ceramics. With the increase of potassium concentration, the size of fine grains with irregular-shaped decreased but grain size of the cubes increased.

The morphotropic phase boundary (MPB) of the materials is an important factor affecting the electrical properties. The high piezoelectric response was generally considered to be obtained from the MPB between different ferroelectric phases. In the perovskite solid solution xNbO$_3$–$(1-x)$NaNbO$_3$ system, enhanced piezoelectric properties have been reported in proximity to a MPB at $x \approx 0.5$, separating two orthorhombic phases [15,16]. However, the addition of Li into KNN ceramics gives rise to a shift of polymorphic phase boundary composition, which can be confirmed by electrical properties of KNN ceramics with changing K/Na ratio.

Fig. 4(a) shows the dielectric permittivity of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO (x = 0.35–0.55) ceramics as a function of temperature. As shown in Fig. 4(b), a

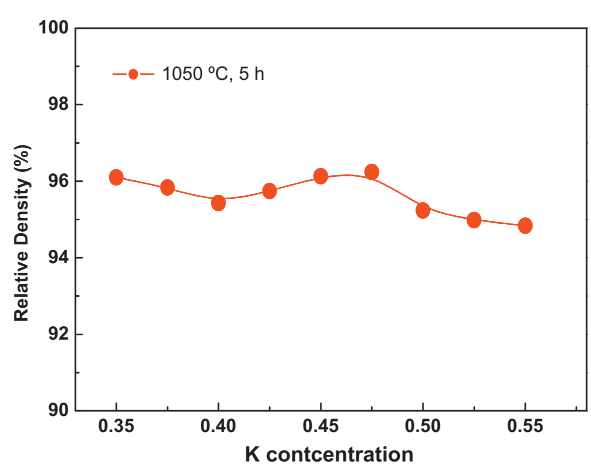

Fig. 2. Relative density of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics as a function of $KNbO_3$ content.

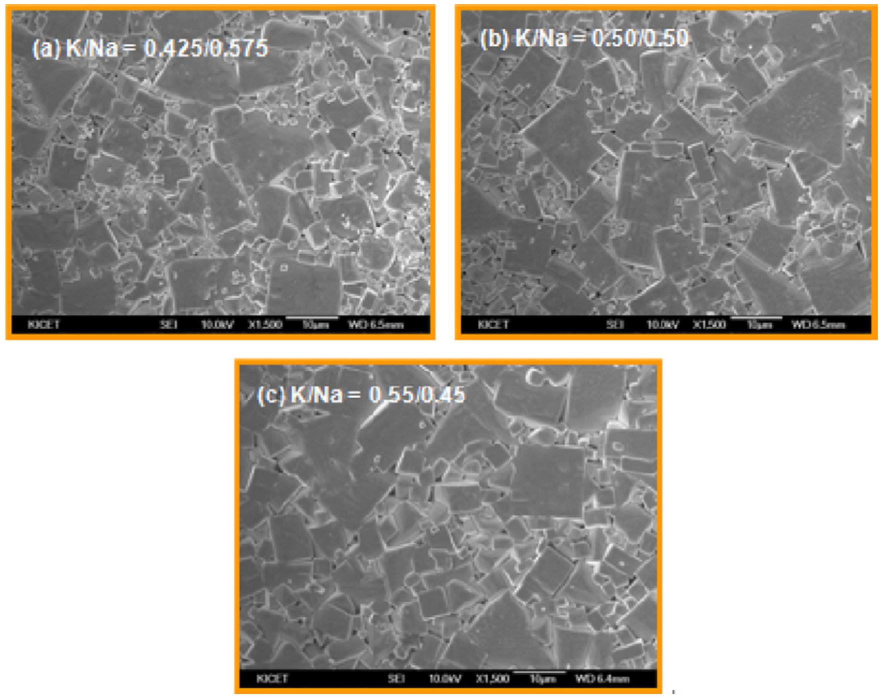

Fig. 3. Microstructures of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics sintered for 5 h at 1050 °C.

morphotropic phase boundary (MPB) was found, which shows phase transition temperature from a low symmetry phases (Pm and Bmm2) to tetragonal with potassium content. The transition temperature decreases abruptly in the composition range of 0.425–0.475 of potassium content. Below 0.42, the orthorhombic is stable, and this phase transforms into a tetragonal phase of C4mb at high temperatures. Ahtee et al. [17,18] reported that the crystal structure of $NaNbO_3$ rich composition in the range of 30–48 mol% $KNbO_3$ is monoclinic of Pm, however, it is difficult to distinguish sharply between orthorhombic and monoclinic phases for KNN ceramics from XRD patterns. Above 48%, an orthorhombic phase of Bmm2 [17,18] is stable, and this phase transforms into a tetragonal phase of P4mm at high temperatures. Thus, there is an abrupt discontinuity of phase transition temperature. It is assumed that two orthorhombic phases coexist in the composition range of 0.425–0.475 of potassium content.

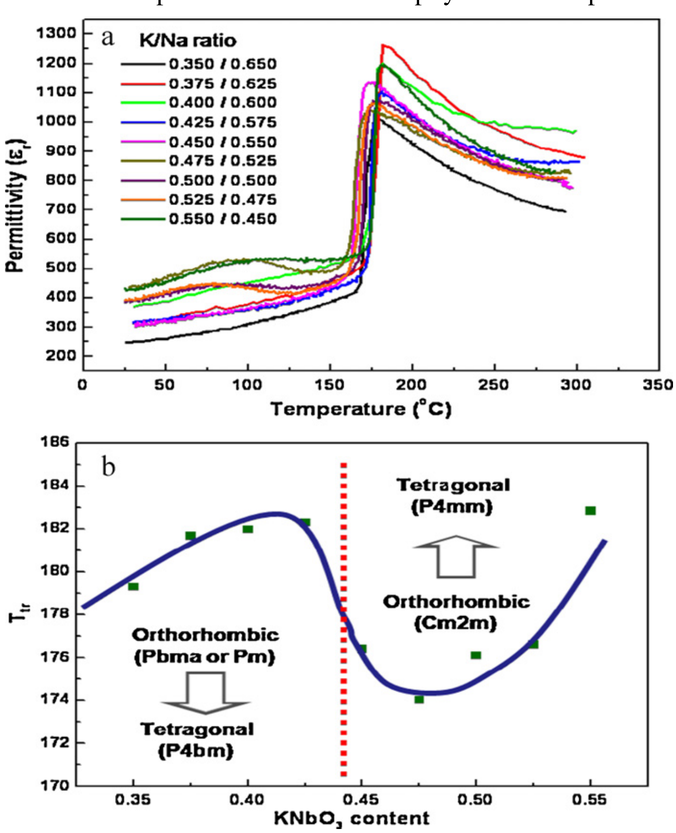

Fig. 4. (a) Temperature dependence of permittivity and (b) phase transition temperature (T_{O-T}) of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics ($x = 0.35$–0.55).

Chemical composition and crystal structure have influence on the temperature stability of piezoelectric properties. Fig. 5(a) shows the temperature dependence of k_p for $Li_{0.02}(K_{0.5}Na_{0.5})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics, which undergoes phase transition above 150 °C. Thermal treatment gives rise to no phase transition and no degradation of k_p in the temperature range of −30 to 150 °C. However, in the case of heat treatment above the transition temperature, k_p decreases significantly as shown in Fig. 5(b), in which the blue line indicates a Na-rich phase (K/Na = 0.375/0.625) and red circles indicate a K-rich phase (K/Na = 0.55/0.45). With increasing temperature, k_p increases up to phase transition temperature and then decreases. Temperature coefficients of k_p are 328 ppm/°C in Na-rich phase and 217 ppm/°C in K-rich phase, which are evaluated in the range from room temperature to transition temperature. After the heating and cooling cycle, k_p are reduced to 73.9% and 78.7% of the initial values in the Na-rich phase and K-rich phase, respectively. $NaNbO_3$ reveals complicated phase transitions in its phase diagram, implying the thermal instability of the $NaNbO_3$ crystal structure. Therefore, it is

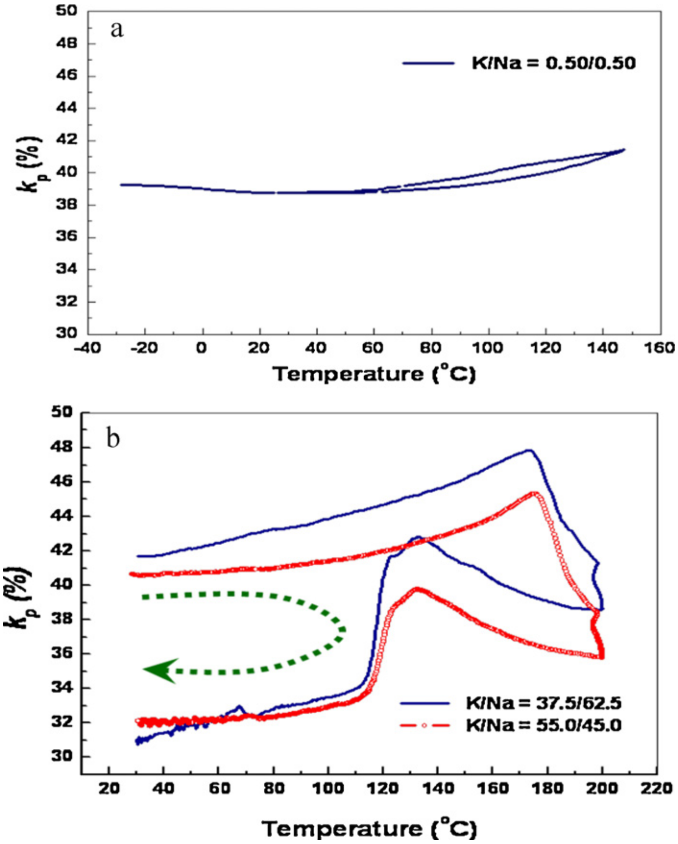

Fig. 5. Temperature dependence of k_p in $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics with different chemical compositions and heat treatment conditions.

assumed that the Na-rich phase is less stable than the K-rich phase against temperature change.

4. Conclusions

The thermal behavior of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics in the temperature range of −30 °C to 150 °C has been investigated. The effect of Na/K ratio in KNN ceramics on thermal behavior and electrical properties was also studied. In the case of $Li_{0.02}(K_xNa_{1-x})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics, in the compositions of 2 mol% Li leads to a T_{O-T} higher than 150 °C. Moreover, the transition temperature decreases abruptly in the composition range of $x = 0.425$–0.475, which implies that two phases coexist. The electromechanical coupling factor (k_p) of $Li_{0.02}(K_yNa_{1-y})_{0.98}NbO_3$ with 0.5 wt.% ZnO ceramics is much higher than that of its end members, $K_{0.02}Na_{0.98}NbO_3$ and $KNbO_3$. However, the drastic increase of k_p due to two phases coexisting as PZT was not observed. From the temperature dependence of piezoelectric properties, it is assumed that the Na-rich phase is less stable than the K-rich phase as a function of temperature change.

Acknowledgements

This work was financially supported by the Fundamental R&D Program for Core Technology of Materials funded by the Ministry of Knowledge Economy, Republic of Korea.

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