Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 39 (2013) S125–S128

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Effects of $CaTiO_3$ addition on microstructures and electrical properties of $Na_{0.52}K_{0.48}NbO_3$ lead-free piezoelectric ceramics

Cheng-Sao Chen[a], Chen-Chia Chou[b,*], Yung-Shun Lin[b], Pin-Yi Chen[c], Haydn Chen[d]

[a]*Department of Mechanical Engineering, Hwa-Hsia Institute of Technology, New Taipei 235, Taiwan, ROC*
[b]*Department of Mechanical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan, ROC*
[c]*Department of Mechanical Engineering, Ming-Chi University of Technology, New Taipei 243, Taiwan, ROC*
[d]*Department of physics, Tunghai University, Taichung 407, Taiwan, ROC*

Abstract

In this article, various amounts of $CaTiO_3$ (CT) were added into $(Na_{0.52}K_{0.48})NbO_3$ (NKN) ceramics using conventional oxide-mixing method for improving NKN's properties. The experimental results show that the $(1-x)(Na_{0.52}K_{0.48})NbO_3$–$xCaTiO_3$ ($x=0\sim0.07$) solid solution system can be successfully synthesized. Addition of $CaTiO_3$ not only effectively prevents materials from deliquescence, but also improves the density and the electrical properties of the ceramics. The dielectric constant–temperature (ε_r-T) curves exhibit that the temperatures of the Curie point (T_c) and the phase transition from tetragonal to orthorhombic (T_{O-T}) are decreasing monotonously as the amount of CT addition is increased. A morphotropic phase boundary (MPB) can be found in the $(1-x)$NKN$-x$CT solid solution system as the doping amount of $x=0.03$, and the 0.97NKN–0.03CT ceramics, with a high bulk density, 98% theoretical density, and an appropriate grain size of about $1\sim2\ \mu m$, present a superior domain switching ability and the optimum properties: $d_{33}=117$ pC/N, $k_p=0.39$, $P_r=21\ \mu C/cm^2$, and $T_c=333\ ^\circ C$.

Keywords: A. Sintering; B. Microstructure-final; C. Piezoelectric properties; D. Niobates

---

1. Introduction

Piezoelectric ceramics based on lead zirconate titanate (PZT) are widely used in actuators and sensors as well as microelectronic devices due to their outstanding piezoelectric and electrical properties [1,2]. However, the use of lead-based ceramics has caused serious environmental problems because of the high toxicity of lead oxide and its high vapor pressure during sintering. Owing to the environmental protection and human health, numerous investigators have been developing alternative materials to replace PZT ceramics. Recently, considerable attention has been paid to lead-free $(K_yNa_{1-y})NbO_3$ (KNN) ceramics because of their relatively good piezoelectric properties and high Curie temperature of 420 °C, especially near a polymorphic phase boundary at $y=0.5$ where separating orthorhombic and tetragonal phases [3,4]. However, it is well known that the KNN ceramics are difficult to densify by common sintering method and they decompose when exposed to humidity [5]. To improve the sinterability and deliquescence of KNN ceramics, different additions have been added into KNN to form solid solution, such as KNN–$Li(Nb,Ta)O_3$ [3], KNN–$(Li,Sb)NbO_3$ [4], and KNN–$(Bi_{0.5}Na_{0.5})TiO_3$ [6]. These KNN-based ceramics show relatively superior piezoelectric properties because of the formation of so-called morphotropic phase boundary (MPB) [6]. Furthermore, it was reported that the doping of alkaline-earth titanates can promote the densification of KNN ceramics by creating A-site vacancies in case of KNN crystals to enhance the sintering mechanism, and hence improve their properties [7–12]. In the present work, $CaTiO_3$ (CT) has been added into $Na_{0.52}K_{0.48}NbO_3$ (NKN) ceramics in order to investigate systematically the effects of $CaTiO_3$ addition on the microstructures, phase transition behavior, and electrical properties of $Na_{0.52}K_{0.48}NbO_3$ ceramics.

2. Experimental procedures

Polycrystalline ceramic samples of $(1-x)$ $(Na_{0.52}K_{0.48})NbO_3$–$xCaTiO_3$ ($x=0-0.07$) were prepared using solid-state

---

[*] Corresponding author. Tel.: +886 2 27376493; fax: +886 2 27376460.
E-mail address: ccchou@mail.ntust.edu.tw (C.-C. Chou).

0272-8842/$ - see front matter © 2012 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2012.10.047

reaction. Stoichiometric amount of Na_2CO_3, K_2CO_3, Nb_2O_5, $CaCO_3$, and TiO_2 powders ($\geq 99.5\%$ purity) were mixed and ball-milled in ethanol with zirconia mill media for 24 h and then dried. The dried mixture was calcined at 950 °C for 5 h. The calcined powders were uniaxially pressed into pellets under 50 MPa and then sintered at 1100–1140 °C for 2 h in air. In order to prevent the loss of K^+ and Na^+, the pellets were buried in a plenty amount of protective powder with the same composition during sintering. The density of the sintered pellets is determined by Archimedes' method. The structure of the bulks was analyzed using a Rigaku D/max-B x-ray diffractometer (XRD) with monochromatic Cu K_α radiation. The electrical properties of the ceramic samples were measured using silver electrodes. The polarization versus electric field (*P–E*) behavior was characterized at room temperature and 60 Hz using a modified Sawyer–Tower circuit. The temperature dependence of dielectric constant ($\varepsilon_r - T$) under weak electric field was measured at 100 kHz with an impedance analyzer (HP-4194, Hewlett-Packard) in conjugation with a tube furnace during heating at a rate of 5 °C/min. The piezoelectric constant d_{33} was measured using a ZJ-2 type quasi-static meter (Channeal CADT-3300) at 100 Hz. Microstructural observations were performed using a Hitachi S-4700 scanning electron microscope (SEM) and a Philips Tecnai-20 transmission electron microscope (TEM) operating at 15 kV and 200 kV, respectively.

3. Results and discussion

The pure NKN ceramics can be densified, having a relative density of ~94% T.D. (theoretical density of NKN is 4.51 g/cm^3) after sintering. Adding CT to NKN can effectively promote densification. The relative density increases significantly with increasing CT content of up to a 3 mol% CT addition, in which the density reaches up to 98%T.D, and then the density of the samples decreases slightly with increasing CT content, around 96–97%T.D., for 5 mol% and 7 mol% CT-doped ones. Besides, it is noteworthy that the doped samples are able to avoid effectively the deliquescence of NKN ceramics.

Fig. 1 shows the XRD patterns of the $(1-x)$NKN–xCT ceramics with $x=0$–0.07 in the 2θ range of 20°–60° at room temperature. All the samples showed a pure perovskite phase and no secondary phase was detected by XRD. It can be seen that pure NKN ceramics ($x=0$) have an orthorhombic structure. The crystal structure, however, started to change from orthorhombic to tetragonal when $x \geq 0.03$ and the variation was completed at $x=0.07$. The results imply that the MPB, in which both the orthorhombic to tetragonal phases coexist, corresponds to the composition of $0.03 \leq x \leq 0.05$.

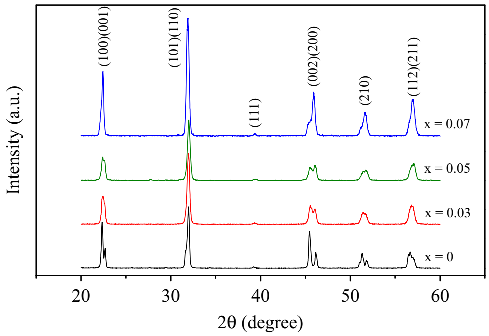

Fig. 1. X-ray diffraction patterns of the $(1-x)$NKN–xCT ceramics in the range of 2θ from 20° to 60°.

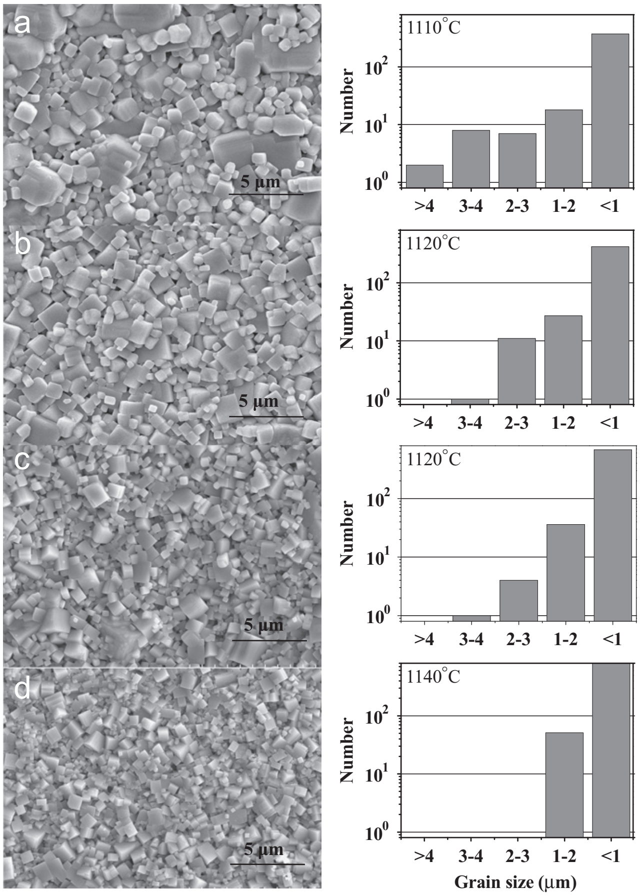

Fig. 2. SEM micrographs and grain size distributions of the $(1-x)$NKN–xCT ceramics: (a) $x=0$, sintered at 1110 °C for 2 h; (b) $x=0.03$, sintered at 1120 °C for 2 h; (c) $x=0.05$, sintered at 1120 °C for 4 h; and (d) $x=0.07$, sintered at 1140 °C for 2 h.

Incorporation of the CT additives not only alters the crystal structure of the NKN ceramics, but also modifies significantly their microstructures. The typical SEM micrographs and the corresponding grain size distributions shown in Fig. 2 for the $(1-x)$NKN–xCT ceramics indicate that the grain size becomes smaller gradually with the increase of the CT content, and the doped ceramics have more uniform size distribution and are denser than that of the pure NKN.

The temperature dependence of the dielectric constant (ε_r) of the $(1-x)$NKN–xCT ceramics is shown in Fig. 3(a), which shows that pure NKN ceramics ($x=0$) have two phase transition peaks at 391 and 189 °C, corresponding to the cubic-tetragonal (T_c) and tetragonal-orthorhombic (T_{O-T}) transitions, respectively. For the samples with $x=0.03$, the two phase transition peaks are observed, similar to those of pure NKN. However, the addition of a small amount of CT

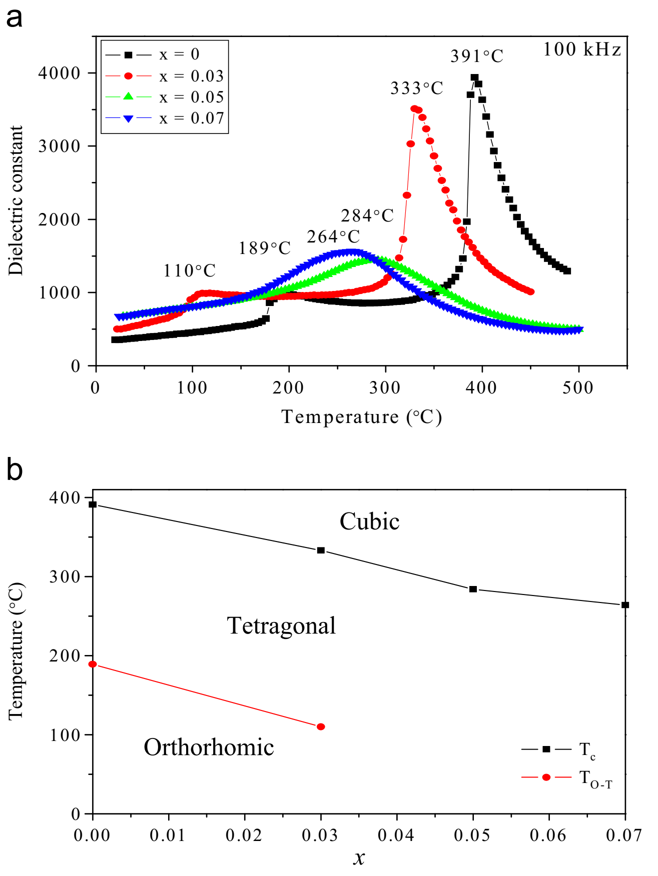

Fig. 3. (a) Temperature dependence of the dielectric constant measured at 100 kHz; (b) variations of the phase transition temperature T_c and T_{O-T} with x for the $(1-x)$NKN–xCT ceramics.

additive causes the two transition peaks to shift to lower temperatures and the maximum value of dielectric constant at these temperatures also decrease. As the CT content is greater than 0.03, only a cubic-tetragonal transition peak can be observed. Besides, it should be noticed that the peak becomes broader appreciably, which exhibits a relaxor-like ferroelectric transition behavior, for the samples with $x=0.05$ and 0.07. It is suggested that the dispersion in phase transition is due to the microscopic composition fluctuation or the cation disorder in perovskite lattice since non-ferroelectric materials, such as $CaTiO_3$ in this case, are added [7,11].

The variations of the phase transition temperature T_c and T_{O-T} with x for the $(1-x)$NKN–xCT ceramics are shown in Fig. 3(b), which indicates that the T_c and T_{O-T} are decreasing monotonously as the amount of CT addition is increased. Furthermore, the T_{O-T} is reduced below room temperature for $x \geq 0.05$, indicating that the CT addition stabilizes the tetragonal phase. A MPB between ferroelectric orthorhombic and tetragonal phases in the $(1-x)$NKN–xCT solid solution should exist approximately at the doping amount of $x=0.03$, which is coincident with the XRD results in Fig. 1.

Fig. 4 shows the piezoelectric constant d_{33} and the electromechanical coupling factor k_p of the $(1-x)$NKN–xCT ceramics as a function of x. The k_p shows the same tendency with d_{33}. The best properties of these samples exist at the MPB compositions with $x=0.03$. For the pure NKN ($x=0$), it has d_{33} of 81 pC/N and k_p of 27.7%. The addition of a small amount of CT increases the piezoelectric performances significantly until they reach the highest values at $x=0.03$. The MPB compositions show the properties of d_{33}, 117 pC/N, and k_p, 39%. Beyond this doping amount, the properties deteriorate very rapidly with increasing CT content. So it is clear that the MPB plays an important role in improving the piezoelectric properties of $(1-x)$NKN–xCT ceramics, even though only 3 mol% CT was added.

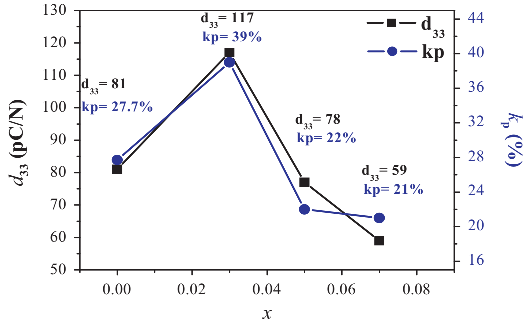

Fig. 4. Variations of d_{33} and k_p with x for the $(1-x)$ NKN–xCT ceramics.

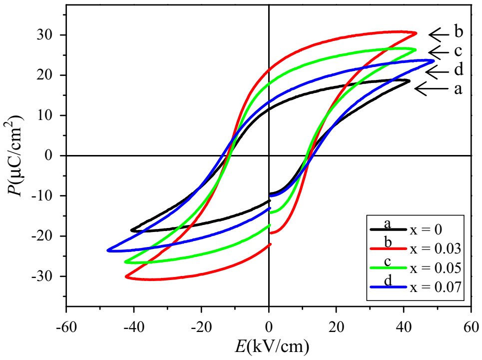

Fig. 5. P–E hysteresis loops of the $(1-x)$NKN–xCT ceramics.

The P–E hysteresis loops shown in Fig. 5 for the $(1-x)$NKN–xCT ceramics reveal that all the P–E loops of the ceramics are typical ferroelectric hysteresis. It can be seen that the 0.97NKN–0.03CT ceramics possess a larger remanent polarization P_r, 21 μC/cm^2, than pure NKN and other ceramics with different CT content. With further increasing the doping content of CT, however, the values of P_r decrease, while the coercive field E_c does not change significantly with CT content. The results can be not only ascribed to the formation of MPB NKN, which stemmed from incorporation of 3 mol% CT additives, but also due to the increase of the bulk density that diminishes the leakage current enhancing the polarization in process [12]. It should be noted that both the incorporation of CT species and the increase in bulk density will result in the increase in the P_r value. However, the CT addition in NKN ceramics will pronouncedly modify the crystal structure and enhance the density at the same time. That is, a proper amount of CT doping is the dominant influence on the ferroelectric activities for the $(1-x)$NKN–xCT ceramics.

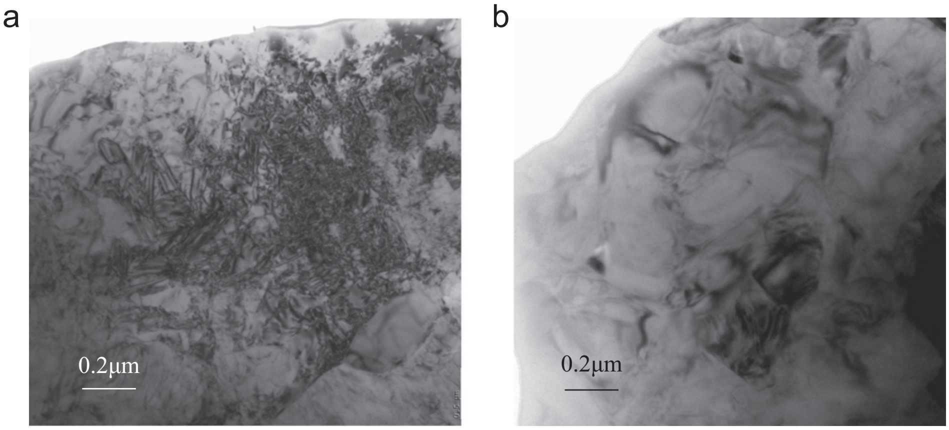

Fig. 6. TEM images of (a) the pure NKN ($x=0$) ceramics; (b) the 0.97NKN–0.03CT ($x=0.03$) ceramics

It is known that the MPB, between orthorhombic and tetragonal phases for the $(1-x)$NKN–xCT ceramics, where the polarization vector of domains can rotate almost continuously under the external electric field. However, the ferroelectric domain structure and electrical properties of ferroelectric ceramics are grain size dependent [13]. To clarify the influence of microstructure on their properties for the $(1-x)$NKN–xCT ceramics, the microstructural characteristics of these materials are observed further using TEM. A typical TEM image of the pure NKN ceramics is shown in Fig. 6(a), that presents a more complicated domain configuration within a single grain, whereas the 0.97NKN–0.03CT ceramics (shown in Fig. 6(b)) not only show fine-grained microstructure with an appropriate grain size of about 1–2 μm, but also appear simpler domain arrangements, and hence exhibit a superior domain switching ability and the optimum electrical properties.

4. Conclusions

Experimental results show that the $(1-x)(Na_{0.52}K_{0.48})NbO_3$–$x$$CaTiO_3$ ($x \leq 0.07$) solid solution system can be successfully synthesized. The addition of $CaTiO_3$ not only prevents effectively the deliquescence, but also improves the density and the electrical properties of the ceramics. The T_c and T_{O-T} are decreased as the amount of CT addition in NKN is increased. A MPB can be found in the $(1-x)$NKN–xCT ceramics as the doping amount of $x=0.03$. The 0.97NKN–0.03CT ceramics, with a high bulk density and an appropriate grain size of about $1\sim2$ μm, present a superior domain switching ability and the optimum properties: $d_{33}=117$ pC/N, $k_p=0.39$, and $P_r=21$ μC/cm^2.

Acknowledgment

Financial support from the National Science Council of Taiwan, Republic of China through Project nos. 97–2923-M-029-001-MY3 and 99–2221-E-011–043-MY2 is greatly acknowledged by the authors.

References

[1] E. Cross, Materials science: lead-free at last, Nature 432 (2004) 24–25.
[2] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free Piezoceramics, Nature 432 (2004) 84–87.
[3] Y. Guo, K. Kakimoto, H. Ohsato, $(Na_{0.5}K_{0.5})NbO_3$–$LiTaO_3$ lead-free piezoelectric ceramics, Materials Letters 59 (2005) 241–244.
[4] 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, S. Zhang, T.R. Shrout, Perovskite $(Na_{0.5}K_{0.5})NbO_{1-x}(LiSb)_xNb_{1-x}O_3$ lead-free piezoceramics, Applied Physics Letters 88 (2006) 212908–212909.
[5] Y. Guo, K. Kakimoto, H. Ohsato, Phase transitional behavior and piezoelectric properties of $(Na_{0.5}K_{0.5})NbO_3$–$LiNbO_3$ ceramics, Applied Physics Letters 85 (2004) 4121–4123.
[6] R. Zuo, X. Fang, C. Ye, Phase structures and electrical properties of new lead-free $(Na_{0.5}K_{0.5})NbO_3$–$(Bi_{0.5}Na_{0.5})TiO_3$, Applied Physics Letters 90 (2007) 092904–092905.
[7] Y. Guo, K. Kakimoto, H. Ohsato, Dielectric and piezoelectric properties of lead-free $(Na_{0.5}K_{0.5})NbO_3$–$SrTiO_3$ ceramics, Solid State Communications 129 (2004) 279–284.
[8] Y. Chang, Z. Yang, X. Chao, R. Zhang, X. Li, Dielectric and piezoelectric properties of alkaline-earth titanate doped $(K_{0.5}Na_{0.5})NbO_3$ ceramics, Materials Letters 61 (2007) 785–789.
[9] H.Y. Park, K.H. Cho, D.S. Paik, S. Nahm, H.G. Lee, D.H. Kim, Microstructure and piezoelectric properties of lead-free $(1-x)(K_{0.5}Na_{0.5})NbO_3$–$x$$CaTiO_3$ ceramics, Journal of Applied Physics 102 (2007) 124101–124105.
[10] R.C. Chang, S.Y. Chu, Y.F. Lin, C.S. Hong, Y.P. Wong, An investigation of $(Na_{0.5}K_{0.5})NbO_3$–$CaTiO_3$ based lead-free ceramics and surface acoustic wave devices, Journal Of The European Ceramic Society 27 (2007) 4453–4460.
[11] M. Kosec, V. Bobnar, M. Hrovat, J. Bernard, B. Malic, J. Holc, New lead-free relaxors based on the $(K_{0.5}Na_{0.5})NbO_3$–$SrTiO_3$ solid solution, Journal of materials research 19 (2004) 1849–1854.
[12] Y. Guo, K. Kakimoto, H. Ohsato, Structure and electrical properties of lead-free $(K_{0.5}Na_{0.5})NbO_3$–$BaTiO_3$ ceramics, Japanese journal of applied physics 43 (2004) 6662–6666.
[13] G. Arlt, D. Hennings, G. de With, Dielectric properties of fine-grained barium titanate ceramics, Journal of Applied Physics 58 (1985) 1619–1625.