Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 38S (2012) S301–S304

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Enhanced piezoelectric properties of $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ ceramics by Ta substitution

Y.S. Sung [a], J.H. Lee [a], S.W. Kim [a], T.H. Lee [a], J.M. Kim [a],
J.H. Cho [a], T.K. Song [a], M.H. Kim [a,*], T.G. Park [b]

[a] School of Nano & Advanced Materials Engineering, Changwon National University, Gyeongnam 641-773, Republic of Korea
[b] Department of Electrical Engineering, Changwon National University, Gyeongnam 641-773, Republic of Korea

Abstract

The effects of Ta substitution for B-site Nb in $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ (NKNT) ceramics were investigated in the range of $x = 0$–0.6. It was found that polymorphic phase transitions (PPT) were significantly influenced by Ta substitution. Transitions among orthorhombic, tetragonal, and cubic phases in sequence with temperature, $T_{O\text{-}T}$ and T_C, respectively, decreased linearly with x. At $x = 0.45$, $T_{O\text{-}T}$ was reduced to room temperature from 182 °C at $x = 0$, and subsequently piezoelectric coefficient (d_{33}) at room temperature was enhanced up to 284 pC/N from 120 pC/N at $x = 0$ due to the coexistence of ferroelectric orthorhombic and tetragonal NKNT phases. With x further increasing beyond $x = 0.45$, d_{33} decreased due to there being no orthorhombic but only a tetragonal NKNT phase at room temperature with $T_{O\text{-}T}$ below room temperature.

Keywords: C. Dielectric properties; C. Piezoelectric properties; NKNT; Polymorphic phase transition

1. Introduction

Due to the high piezoelectric coefficient (d_{33}), 416 pC/N, obtained in $(Na,K,Li)(Nb,Ta,Sb)O_3$ ceramics [1], $(Na,K)NbO_3$ (NKN) ceramics [2–6] of an ABO_3 perovskite structure has been re-investigated as a potential base for substituting $Pb(Zr,Ti)O_3$ (PZT)-based ceramics. In addition, various NKN based solid solutions with complex compositions have been tried for even higher d_{33} values. Not much progress has been made in reproducing high piezoelectric properties. It is thus necessary to have a systematic approach designed for more effective study, rather than just pursuing high d_{33} in NKN-based ceramics.

As in the case of other piezoelectric ceramics such as PZT and Bi-based titanate solid solutions, NKN has a morphotropic phase boundary (MPB) between two orthorhombic phases [5,6]. It is determined mainly by an A-site ratio between Na and K, which is 0.52–0.53 mol of Na. Piezoelectric properties of NKN in general increased at MPB as in other piezoelectric ceramics [6,7]. However, unlike other piezoelectric ceramics, MPB between orthorhombic phases is not the only cause for the high d_{33} values in NKN-based ceramics. In addition to MPB, there is polymorphic phase transition (PPT) between orthorhombic and tetragonal phases in NKN-based ceramics, which affects piezoelectric properties significantly [8].

There have been various elements such as Li, Ba, Bi, Sb, Ta, etc., and solid solutions such as $LiNbO_3$ and $LiTaO_3$ [9–16] used for substituting A- and/or B-site of NKN to raise d_{33} in NKN-based ceramics. In most cases of simultaneous substitution on both A- and B-site, the individual effects of either A-site or B-site substitution on PPT become difficult to distinguish from one other. Knowing that MPB is intrinsically determined by A-site Na/K [2–6,8], whereas PPT can be extrinsically controlled by Li on A-site and/or Ta on B-site [10,15,17] in NKN-based ceramics, in this study, only Ta was chosen to form $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ (NKNT) ceramics while keeping the A-site ratio between Na and K to an MPB composition in order to clarify the effects of B-site Ta.

2. Experimental

NKNT ceramics with various x in the range of 0–0.6 were prepared by a conventional solid state reaction method using

---

* Corresponding author. Tel.: +82 55 2133711; fax: +82 55 2626486.
E-mail address: mhkim@changwon.ac.kr (M.H. Kim).

0272-8842/$36.00 © 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2011.04.106

raw powders of Na_2CO_3 (99.95%), K_2CO_3 (99.995%), Nb_2O_5 (99.9%), and Ta_2O_5 (99.9%). Hygroscopic Na_2CO_3 and K_2CO_3 were fully dried at 200 °C for at least 12 h to remove moisture absorbed from their surroundings, and then weighed in a glove box. The raw powders were milled with yttria-stabilized zirconia balls in anhydrous alcohol for 2 h. After being dried at 90 °C in a dry oven, the powders were calcined at 700 °C, then 850 °C for 5 h in air twice with intermediate ball milling and drying. The calcined powders were re-milled, dried, and mixed with 0.5 wt.% polyvinyl alcohol for pelletizing. The powders were pressed into pellets of 10 mm in diameter and ∼1 mm in thickness at a uniaxial pressure of 150 MPa. The pellets placed in an Al_2O_3 crucible with a lid were covered with the powders of the same compositions to keep the pellets from losing volatile components during sintering at 1080–1250 °C based on differential thermal analysis (DTA, TA5000/SDT2960, TA Instruments, USA) for 4 h in air.

X-ray diffraction (XRD, X'pert MPD 3040, Philips, The Netherlands) patterns were analyzed to identify phases and distinguish lattices. 5 N Si (Alfa Aesar, USA) powder was used as an internal standard to calibrate XRD patterns obtained using an X-ray diffractometer of Cu Kα lines. For dielectric and piezoelectric properties measurement, both surfaces of pellets polished down to 0.5 mm in thickness were painted with Ag paste and cured at 650 °C for 0.5 h in air. Pellets were poled at a dc electric field of 40 kV/cm in silicone oil at 120 °C for 0.5 h, then field-cooled to room temperature. The temperature dependence of dielectric constant (ε) and loss tangent ($\tan\delta$) was measured by an impedance analyzer (HP 4192A, Agilent, USA) in the temperature range from room temperature to 650 °C upon heating and cooling at various frequencies. Room temperature d_{33} was measured using a piezo-d_{33} meter (IACAS, ZJ-6B, China) at 0.25 N and 110 Hz.

3. Results and discussion

From DTA experiments, it was found that, with increasing Ta substitution for Nb, the melting temperatures of NKNT ceramics were linearly increased. Thus, the sintering temperatures for the samples were adjusted to be higher at higher Ta substitution, instead of using the same sintering temperature for all samples. Otherwise, the samples were either poorly sintered or partially melted. Nevertheless, the apparent densities of the sintered ceramics relative to the theoretical density were around 92–94%, which indicates poor sintering characteristics of NKNT ceramics in ordinary sintering in air [3,4,12–14].

Fig. 1 shows the XRD patterns of NKNT ceramics at $x = 0$–0.6 sintered at 1080–1250 °C. No impurity peak other than NKNT perovskite peaks was observed. With x increasing, two structural transitions occurred as indicated, one from orthorhombic to tetragonal phases, then the other from tetragonal to cubic phases. The presence of either a tetragonal or a cubic phase in XRD patterns implies that PPT temperatures from low to high temperature in NKNT ceramics, $T_{O\text{-}T}$ and $T_{T\text{-}C}$ (Curie temperature, T_C) among orthorhombic, tetragonal, and cubic phases, respectively, were lowered with Ta substitution for Nb in B-site of NKNT ceramics.

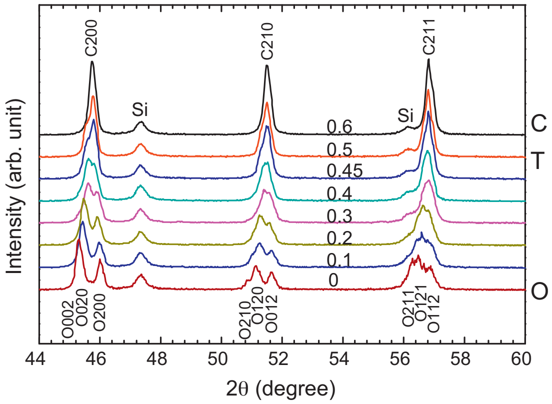

Fig. 1. XRD patterns of $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ ceramics with various x sintered at 1080–1250 °C for 4 h in air. O: orthorhombic, T: tetragonal, C: cubic.

Complementary to the XRD results, the sintered samples were examined by SEM as shown in Fig. 2. There was no impurity phase other than NKNT grains. At all compositions, grains in general were of rather square shapes, with not much difference in size associated with different sintering temperatures. This similarity in morphology supports the idea that the effective sintering temperatures were not much different for all samples, despite the nominal sintering temperatures being different from sample to sample, depending on Ta compositions.

After confirming crystal structure and phase purity of samples, piezoelectric properties were measured and compared. Fig. 3 shows the variation in room temperature d_{33} with Ta substitution for Nb in which d_{33} increased from 120 pC/N at $x = 0$ up to 284 pC/N, showing a peak value at $x = 0.45$, then decreased with further Ta substitution. Considering that the compositions of samples were all at MPB, this result clearly indicates that something other than MPB is responsible for the variation in d_{33} in NKNT ceramics, namely PPT.

The temperature dependence of the dielectric properties of NKNT ceramics was measured to examine the effects on Ta substitution for Nb on phase transitions. As shown in Fig. 4, two distinct transitions occurred in the dielectric properties of NKNT ceramics. One is T_C and the other is $T_{O\text{-}T}$. It is this PPT of interest in addition to MPB that is responsible for high piezoelectric properties in NKNT-based ceramics unlike other piezoelectric ceramics. $T_{O\text{-}T}$ in particular is the one that is responsible for d_{33} around room temperature. A phase diagram shown in Fig. 5, which is similar to one of the $KNbO_3$–$KTaO_3$ [17], was constructed with $T_{O\text{-}T}$ and T_C, separating cubic, tetragonal, and orthorhombic phase regions. $T_{O\text{-}T}$ is clearly around room temperature at $x = 0.45$, while it is below room temperature beyond $x = 0.45$, which explains the variation in d_{33}.

In the case of MPB at which two piezoelectric phases coexist, higher piezoelectric properties are resulted from better poling, with more poling directions available with the coexistence of two ferroelectric phases than with either of the two [6]. Similarly, two ferroelectric orthorhombic and tetragonal phases that coexist at $T_{O\text{-}T}$ can improve piezoelectric

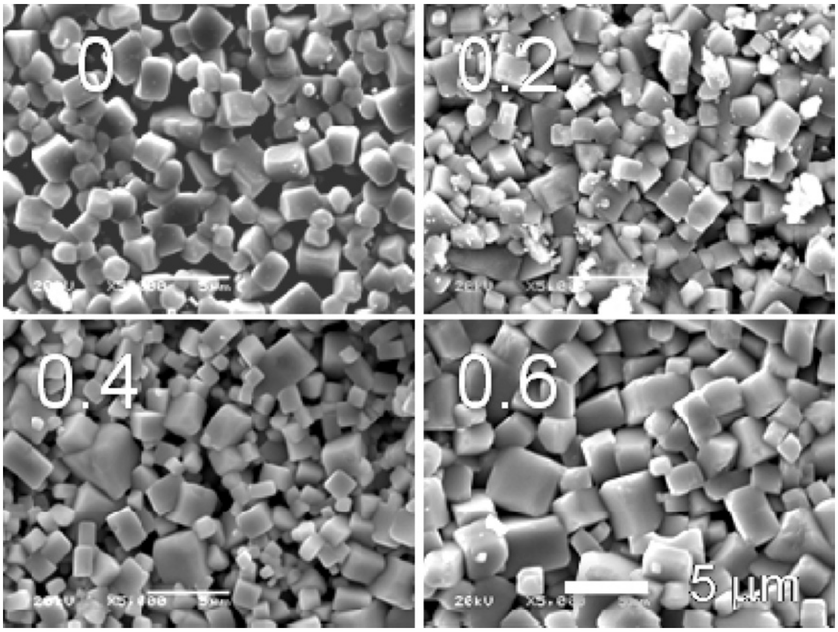

Fig. 2. SEM images of $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ ceramics with $x = 0$ (1080 °C), 0.2 (1150 °C), 0.4 (1200 °C), and 0.6 (1250 °C) sintered for 4 h in air, respectively.

properties in NKNT ceramics. Normally, because d_{33} is measured at room temperature, higher d_{33} would be measured if $T_{O\text{-}T}$ happens to be around room temperature. Both T_C and $T_{O\text{-}T}$ were lowered with increasing Ta substitution for Nb in Fig. 5. At $x = 0.45$, $T_{O\text{-}T}$ is around room temperature, which is responsible for high d_{33}. Note that in Fig. 5 $T_{O\text{-}T}$ is lowered below room temperature and only T_C was seen at $x = 0.5$ and 0.6, indicating the presence of only a tetragonal phase beyond $x = 0.5$ at which d_{33} was lowered.

The improvement in piezoelectric properties in NKN by MPB was about 100% up from ∼80 pC/N [2] at off-MPB composition, $x = 0.5$, to ∼160 pC/N at MPB composition, $x = 0.52$ [8]. By comparison, the improvement by PPT in NKNT ceramics at MPB in this study was more than 100% up from ∼120 pC/N to ∼280 pC/N. This reveals that PPT between orthorhombic and tetragonal phases is more effective than MPB.

One drawback of PPT that should be mentioned is its temperature dependence, in contrast with temperature insensitive MPB. So become piezoelectric properties including d_{33} due to PPT in NKNT ceramics. This temperature dependence of d_{33} restricts NKNT-based ceramics to applications within a narrow range of operating temperatures. They are still, however, good candidates for replacing PZT for the applications under a constant operating temperature. They can be tailor-made for a specific temperature range via controlling composition with Ta substitution for Nb.

There are other issues to be clarified for a better understanding of how and why Ta depresses PPT temperatures. Comparing Ta with Nb, they are different in atomic weight but the same in 5+ valence and ionic radius [18]. Nevertheless, orthorhombic and tetragonal lattice distortions appeared to be reduced with Ta in Fig. 1. Lattice distortion affecting

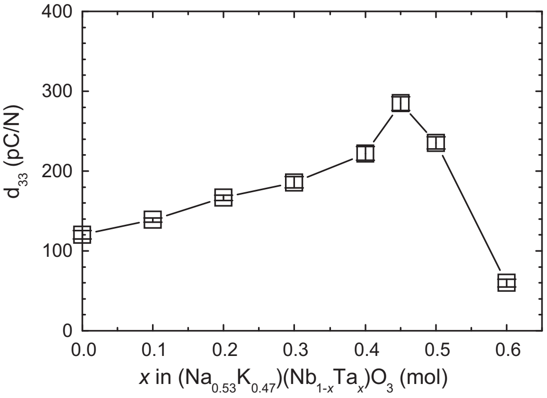

Fig. 3. Room temperature piezoelectric coefficient (d_{33}) of $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ ceramics with various x sintered at 1080–1250 °C for 4 h in air. A quasi-static d_{33} meter was used to measure d_{33} at 0.25 N and 110 Hz.

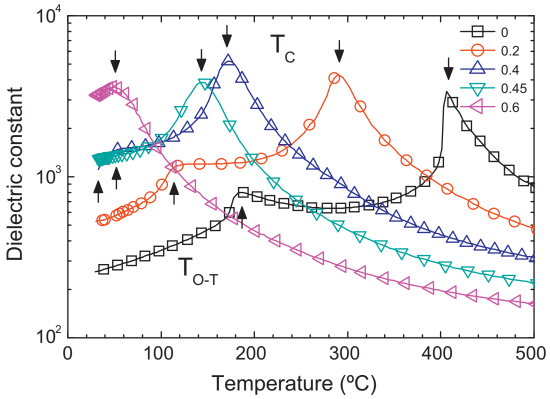

Fig. 4. Temperature dependent dielectric constant (ε) of $(Na_{0.53}K_{0.47})(Nb_{1-x}Ta_x)O_3$ ceramics with various x at 100 kHz showing the variation in T_C and $T_{O\text{-}T}$ arrow-marked by Ta substitution for Nb.

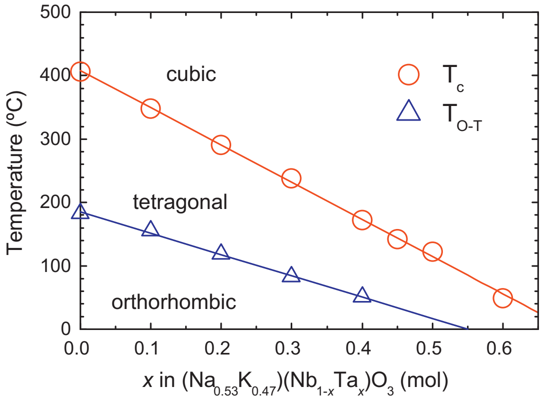

Fig. 5. A temperature–composition phase diagram constructed based on XRD and dielectric results representing phase regions and polymorphic phase transition (PPT) temperatures. Regions of cubic, tetragonal, and orthorhombic phases were divided by T_C and $T_{O\text{-}T}$.

piezoelectric properties [19] is also an important issue that should be addressed, considering that PPT may not be the only cause of the gradual change in d_{33} with Ta in Fig. 3, because PPT itself is not gradual but abrupt in temperature.

4. Summary

It was confirmed that a solid solution between Nb and Ta in NKNT ceramics formed with no impurity phase. Ta affected PPT temperatures significantly in NKNT ceramics depressing both T_C and $T_{O\text{-}T}$, subsequently causing the variation in d_{33}. With Ta, room temperature d_{33} gradually increased from 120 pC/N to 284 pC/N, which was attributed to the coexistence of orthorhombic and tetragonal phases by the gradual decrease of $T_{O\text{-}T}$ to room temperature from $x = 0$ to $x = 0.45$. The decrease in d_{33} beyond $x = 0.45$ was due to $T_{O\text{-}T}$ decreased below room temperature causing only a tetragonal phase around room temperature. A temperature–composition phase diagram was constructed to describe phase regions and PPT temperatures for NKNT ceramics.

Acknowledgements

This work was supported by the National Research Foundation of Korea Grant funded by the Korean Government (2009-0088570) and the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0025055). This work was also supported by the Gyeongnam, Changwon Science Research Park Project of the Korean Ministry of Education, Science and Technology.

References

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature 432 (2004) 84–86.
[2] L. Egerton, D.M. Dillon, Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate, Journal of the American Ceramic Society 42 (1959) 438–442.
[3] R.E. Jaeger, L. Egerton, Hot pressing of potassium–sodium niobates, Journal of the American Ceramic Society 45 (1962) 209–213.
[4] G.H. Haertling, Properties of hot-pressed ferroelectric alkali niobate ceramics, Journal of the American Ceramic Society 50 (1967) 329–330.
[5] V.J. Tennery, K.W. Hang, Thermal and X-ray diffraction studies of the $NaNbO_3$–$KNbO_3$ system, Journal of Applied Physics 39 (1968) 4749–4753.
[6] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic Press, New York, 1971.
[7] B. Jaffe, R.S. Roth, S. Marzullo, Piezoelectric properties of lead zirconate-lead titanate solid-solution ceramics, Journal of Applied Physics 25 (1954) 809–810.
[8] Y.J. Dai, X.W. Zhang, K.P. Chen, Morphotropic phase boundary and electrical properties of $K_{1-x}Na_xNbO_3$ lead-free ceramics, Applied Physics Letters 94 (2009) 042905.
[9] D. Tanaka, T. Tsukada, M. Furukawa, S. Wada, Y. Kuroiwa, Thermal reliability of alkaline niobate-based lead-free piezoelectric ceramics, Japanese Journal of Applied Physics 48 (2009) 09KD08.
[10] Y.G. Lv, C.L. Wang, J.L. Zhang, L. Wu, M.L. Zhao, J.P. Xu, Tantalum influence on physical properties of $(K_{0.5}Na_{0.5})(Nb_{1-x}Ta_x)O_3$ ceramics, Materials Research Bulletin 44 (2008) 284–287.
[11] P. Zhao, R. Tu, T. Goto, B.P. Zhang, S. Yang, Effect of Ta content on phase structure and electrical properties of piezoelectric lead-free $[(Na_{0.535}K_{0.480})_{0.942}Li_{0.058}](Nb_{1-x}Ta_x)O_3$ ceramics, Journal of the American Ceramic Society 91 (2008) 3440–3443.
[12] Y. Wang, D. Damjanovic, E. Naama Klein, N. Hollenstein, Setter, Compositional inhomogeneity in Li- and Ta-modified $(K,Na)NbO_3$ ceramics, Journal of the American Ceramic Society 90 (2007) 3485–3489.
[13] 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.
[14] E. Hollenstein, M. Davis, D. Damjanovic, N. Setter, Piezoelectric properties of Li- and Ta-modified $(K_{0.5}Na_{0.5})NbO_3$ ceramics, Applied Physics Letters 87 (2005) 182905.
[15] 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.
[16] 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.
[17] S. Triebwasser, Study of ferroelectric transitions of solid-solution single crystals of $KNbO_3$–$KTaO_3$, Physical Review 114 (1959) 63–71.
[18] R.D. Shannon, Revised effective ionic radii and systematic studies of interatomic distances in halides and chalcogenides, Acta Crystallographica A32 (1976) 751–767.
[19] Y.S. Sung, J.M. Kim, J.H. Cho, T.K. Song, M.H. Kim, T.G. Park, Roles of lattice distortion in $(1-x)(Bi_{0.5}Na_{0.5})TiO_3$–$xBaTiO_3$ ceramics, Applied Physics Letters 96 (2010) 202901.