Materials Research Bulletin 44 (2009) 1188–1190

Contents lists available at ScienceDirect

Materials Research Bulletin

journal homepage: www.elsevier.com/locate/matresbu

Short communication

Lead-free ceramics based on alkaline niobate tantalate antimonate with excellent dielectric and piezoelectric properties

Jian Fu, Ruzhong Zuo *, Xusheng Fang, Kun Liu

Institute of Electro Ceramics & Devices, School of Materials Science and Engineering, Hefei University of Technology, Hefei 230009, PR China

ARTICLE INFO

Article history:
Received 10 September 2008
Received in revised form 29 October 2008
Accepted 4 November 2008
Available online 19 November 2008

Keywords:
A. Ceramics
D. Dielectric properties
D. Ferroelectricity
D. Piezoelectricity

ABSTRACT

This paper reports lead-free $(Na_{0.52}K_{0.48-x})(Nb_{0.94-x}Sb_{0.06})O_3$–$x$$LiTaO_3$ compositions with significantly enhanced piezoelectric properties. The 6% Sb substituted $Na_{0.52}K_{0.48}NbO_3$ was modified by a small amount of $LiTaO_3$, leading to the formation of a morphotropic phase boundary between orthorhombic and tetragonal phases in the range of x = 0.035–0.04 where the materials show a strong compositional dependence of various electrical properties. Excellent properties of d_{33} = 335 pC/N, k_p = 53%, $\varepsilon_{33}^T = 2063$, Q_m = 41 and T_c = 291 °C were obtained in the composition with x = 0.04, indicating that the ceramics studied are promising as a lead-free piezoelectric candidate.

1. Introduction

Extensive attempts have recently been focused on making $(Na_{0.5}K_{0.5})NbO_3$ (NKN) based lead-free piezoelectric ceramics, based on their good dielectric, piezoelectric and electromechanical properties, and relatively high Curie temperatures. Particularly, the (Li, Ta, Sb) substituted NKN ceramics exhibit significantly improved sinterability and various electrical properties such that they have been expected as a typical candidate to replace conventional lead-based piezoelectric ceramics [1–8]. However, the reported electrical properties of these materials so far seriously diverge in a quite broad range, significantly depending on processing conditions, microstructure, compositional design, and so on [9]. The NKN-based materials with recognized good piezoelectric properties usually have a relatively low Curie temperature [1,2], which probably limits their working temperature ranges in device applications. Moreover, the currently reported piezoelectric properties (~300 pC/N) of this system are still not enough to compete with those of lead-based piezoelectric ceramics [1]. Therefore, it is crucial how to prepare a lead-free piezoelectric ceramic with significantly enhanced overall properties. In (Li, Ta, Sb) substituted NKN compositions, the enhancement of piezoelectric properties can be realized through forming a two-phase coexistence zone by shifting a polymorphic phase boundary close to room temperature, however, is usually accompanied with a rapid drop of the Curie temperature [2,5]. It was recognized that Sb in the compositions plays a key role in the change of dielectric constants and Curie temperatures [10]. The more covalent Sb may make better contribution to the dielectric and piezoelectric properties than Ta and Nb.

In this study, a specially designed lead-free composition, $(Na_{0.52}K_{0.48-x})(Nb_{0.94-x}Sb_{0.06})O_3$–$x$$LiTaO_3$ (NKNS–xLT) (x = 0.025–0.05), in which the amount of Sb is prescribed, was manufactured by ordinary sintering and the compositional dependence of various electrical properties was investigated in details.

2. Experimental

Sodium carbonate (Na_2CO_3, 99.8%), potassium carbonate (K_2CO_3, 99.0%), lithium carbonate (Li_2CO_3, 99.9%), niobium oxide (Nb_2O_5, 99.5%), tantalum oxide (Ta_2O_5, 99.9%) and antimony oxide (Sb_2O_3, 99.9%) were used as raw materials. These powders were weighed according to the above chemical formula and then ball mixed in nylon jars with ZrO_2 balls for 8 h using ethanol as the medium. The slurry was dried and calcined twice at 850 °C for 5 h. After calcination, the powders were ball-milled again for 24 h. The dried powders were then compacted into disk samples with desired aspect ratios, followed by a sintering procedure in air at 1060–1120 °C for 3 h. Silver paste was fired on both sides of the disk samples at 550 °C for 30 min as the electrodes for dielectric and piezoelectric measurements. The samples were poled at 110 °C in a silicone oil bath by applying a dc field of ~2.0 kV/mm for 15 min.

The relative densities were evaluated by the Archimedes method. The crystal structure was examined by an X-ray diffractometer (D/Mzx-rB, Rigaku, Japan) using a Cu Kα radiation.

* Corresponding author. Tel.: +86 551 2905285; fax: +86 551 2905285.
E-mail address: piezolab@hfut.edu.cn (R. Zuo).

0025-5408/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.materresbull.2008.11.009

The microstructure was observed by means of a scanning electron microscope (SEM, SSX-550, Shimadzu, Japan). Dielectric properties were measured as a function of temperature by a LCR meter (Agilent E4980A, USA). The piezoelectric strain constant d_{33} was measured by a Belincourt-meter (YE2730A, Sinocera, Yangzhou, China). The planar electromechanical coupling factor k_p and the mechanical quality factor Q_m were determined by a resonance–antiresonance method with an impedance analyzer (PV70A, Beijing Band ERA Co., Ltd., China).

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of NKNS–*x*LT ceramics synthesized at 1090 °C for 3 h. All compositions show a pure perovskite structure, indicating that Li^{+} and Ta^{5+} have completely diffused into the NKNS lattice to form solid solutions within the studied composition range. Similar to pure NKN ceramics [11], the NKNS–*x*LT ceramics at room temperature have an orthorhombic symmetry when $x \leq 0.035$. With further increasing *x*, the phase structure changes to a single tetragonal symmetry ($x > 0.04$). Therefore, a phase transformation between the orthorhombic and the tetragonal phases can be identified in the composition range of $0.035 < x < 0.04$, during which two kinds of ferroelectric phases with different symmetries may coexist. Moreover, in the tetragonal zone, it can be seen that the tetragonality gradually increases with the increase of *x*, which implies that the Curie temperature may probably increase with adding more LT.

The SEM image of NKNS-0.04LT ceramics sintered at 1090 °C for 3 h is shown in Fig. 2. The morphology of other compositions appears the same. It is obvious that most of grains are faceted and the addition of LT does not have any significant effect on the average grain size. However, the grains show a bimodal grain size distribution. This kind of grain morphology is typical for alkaline niobate systems [12]. In addition, it can be seen that all samples have been well densified with little porosity (>96% theoretical densities), showing a significantly improved sinterability compared to pure NKN compositions.

The variation of dielectric constants at 10 kHz with changing temperature for unpoled samples is shown in Fig. 3. Like pure NKN ceramics, the NKNS–*x*LT ceramics ($x \leq 0.035$) exhibit two-phase transitions above room temperature: the tetragonal–cubic ferroelectric phase transition (T_c) and the orthorhombic–tetragonal (T_{o-t}) polymorphic phase transition. The sample with $x = 0$ was reported to have a T_{o-t} of ~124 °C and a T_c of ~320 °C, respectively [10]. Owing to the addition of LT, T_{o-t} shifts to lower temperatures,

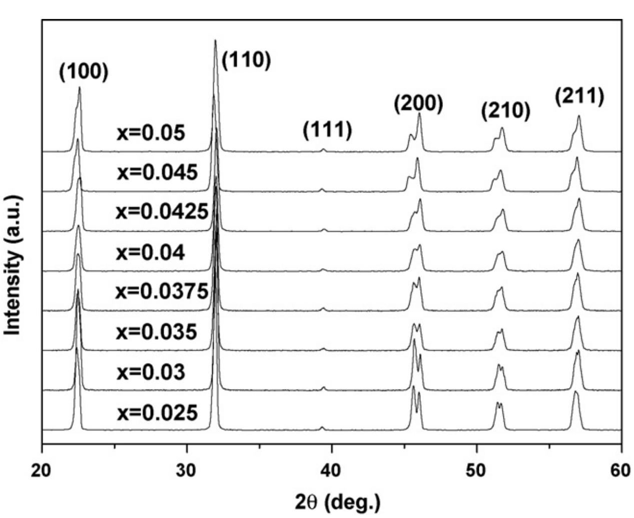

Fig. 1. X-ray diffraction patterns of NKNS–*x*LT ceramics with different *x* as indicated.

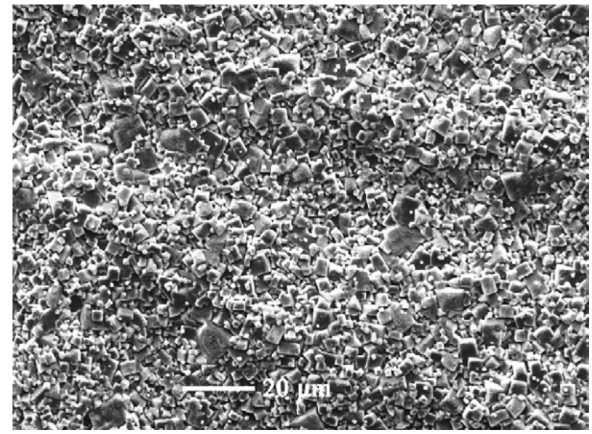

Fig. 2. SEM image on free surfaces of NKNS–*x*LT with *x* = 0.04.

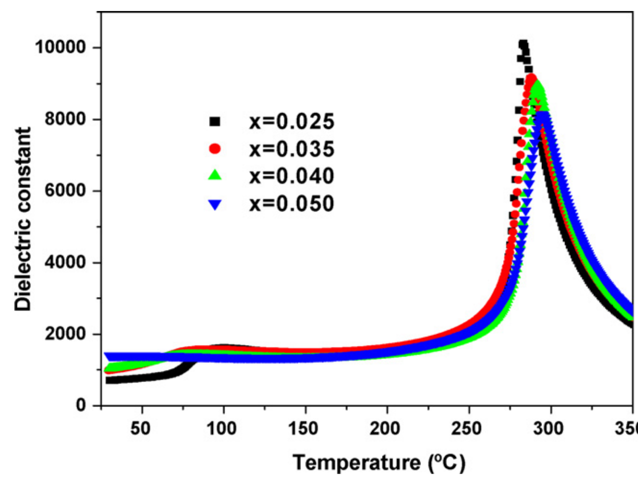

Fig. 3. Dielectric constants versus temperature curves measured at 10 kHz for NKNS–*x*LT ceramics as indicated.

gradually getting close to room temperature. Further increase of *x* ($x > 0.04$) causes T_{o-t} to move below room temperature such that only one dielectric constant peak (T_c) can be detected. Thus, the compositions with $x > 0.04$ should have a single tetragonal symmetry. The phase transition behavior of NKNS–*x*LT ceramics with changing *x* completely agrees with the X-ray diffraction examination. On the other hand, T_c slowly moves to higher temperature with increasing *x*, which is probably ascribed to the enhancement of the tetragonality.

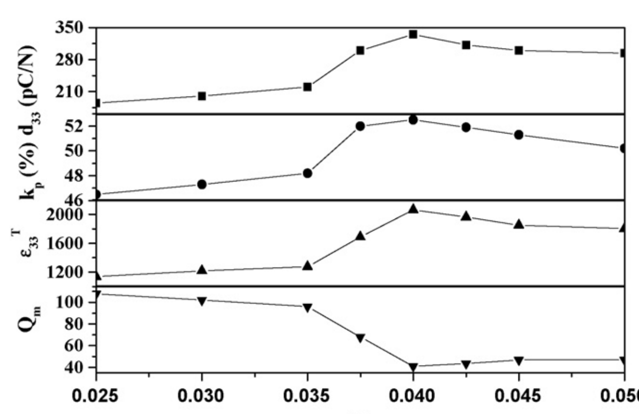

Fig. 4. Various electrical properties of poled NKNS–*x*LT ceramics as a function of the LT content *x*.

Table 1
Comparison of various electric properties for several (Li, Ta, Sb) modified NKN compositions.

Compositions	d_{33} (pC/N)	k_p	T_c (°C)
$(Na_{0.52}K_{0.435}Li_{0.045})(Nb_{0.905}Sb_{0.045}Ta_{0.05})O_3$ [2]	308	0.51	339
$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.76}Ta_{0.2}Sb_{0.04})O_3$ [3]	252	0.42	260
$0.965[K_{0.5}Na_{0.5}(Nb_{0.925}Ta_{0.075})O_3]$–$0.035LiSbO_3$ [4]	244	0.51	354
$(K_{0.44}Na_{0.52}Li_{0.04})(Nb_{0.86}Ta_{0.10}Sb_{0.06})O_3$ [1]	300	–	253
$(Na_{0.52}K_{0.44})(Nb_{0.94}Sb_{0.06})O_3$–$0.04LiTaO_3$ (this study)	335	0.53	291

Fig. 4 shows various electrical properties of poled NKNS–*x*LT ceramics. It can be seen that there is a strong compositional dependence of the dielectric, piezoelectric and electromechanical properties. These properties reach the maxima in the phase transition zone where a two-phase coexistence can be expected. This would preferably be explained by an increase of possible spontaneous polarization states [13]. By comparison, Q_m shows different tendency with changing x because it has little relation with the amount of spontaneous polarization directions. It seems that the NKNS–*x*LT ceramics with an orthorhombic structure have slightly higher Q_m than those with a tetragonal structure. The excellent electrical properties were obtained in the composition with $x = 0.040$, which exhibits a d_{33} of 335 pC/N, a k_p of 53%, an ε_{33}^T of 2063, a Q_m of 41 and a T_c of 291 °C. These results are compared with those previously reported in Table 1. The results demonstrate that this material system has comparable overall properties to some lead-based piezoelectric ceramics. Particularly, the dielectric constant ε_{33}^T and the piezoelectric constant d_{33} were significantly enhanced compared to previously reported values [1–3]. Noticeably, the Curie temperature is still moderate and even 50 °C higher than that reported by Saito et al. [1]. It can be realized that the addition of more Sb and the special composition design around a two-phase coexistence zone has made main contributions.

4. Conclusions

Lead-free NKNS–*x*LT ($x = 0.025$–0.05) piezoelectric ceramics were fabricated by a solid-state reaction method and their phase transitional behavior and various electrical properties were investigated. Excellent electrical properties of $d_{33} = 335$ pC/N, $k_p = 53\%$, $\varepsilon_{33}^T = 2063$, $Q_m = 41$ and $T_c = 291$ °C were obtained in the composition with $x = 0.04$, which lies in a phase transformation zone between the orthorhombic and the tetragonal phases. The results indicate that not only the addition of Li, Ta and Sb can promote the sinterability of NKN ceramics, but also a suitable increase in the Sb content may significantly improve the dielectric and piezoelectric properties. The results indicate that the materials studied have a potential as a candidate for the application of lead-free piezoelectric ceramics.

Acknowledgements

This work was financially supported by HFUT RenCai Foundation (No. 103-035006) and a special Program for Excellence Selection ‘‘R & D of Novel Lead-Free Piezoelectric Ceramics’’ (No. 103-035034), an open fund of State Key Laboratory of New Ceramics and Fine Processing (Tsinghua University). The project was sponsored by the Scientific Research Foundation for the Returned Overseas Chinese Scholars, State Education Ministry.

References

[1] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Nature 432 (2004) 84.
[2] B.Q. Ming, J.F. Wang, P. Qi, G.Z. Zang, J. Appl. Phys. 101 (2007) 054103.
[3] Z.P. Yang, Y.F. Chang, L.L. Wei, Appl. Phys. Lett. 90 (2007) 042911.
[4] D.M. Lin, K.W. Kwok, H.L.W. Chan, J. Phys. D: Appl. Phys. 40 (2007) 6060.
[5] E.K. Akdogan, K. Kerman, M. Abazari, A. Safari, Appl. Phys. Lett. 92 (2008) 112908.
[6] J.G. Wu, T. Peng, Y.Y. Wang, D.Q. Xiao, J.M. Zhu, Y. Jin, J.G. Zhu, P. Yu, L. Wu, Y.H. Jiang, J. Am. Ceram. Soc. 91 (2008) 319.
[7] Y.F. Chang, Z.P. Yang, L.R. Xiong, Z.H. Liu, Z.L. Wang, J. Am. Ceram. Soc. 91 (2008) 2211.
[8] T. Lee, K.W. Kwok, H.L.W. Chan, J. Phys. D: Appl. Phys. 41 (2008) 155402.
[9] Y.L. Wang, D. Damjanovic, N. Klein, E. Hollenstein, N. Setter, J. Am. Ceram. Soc. 90 (2007) 3485.
[10] D.M. Lin, K.W. Kwok, H.Y. Tian, H.L.W. Chan, J. Am. Ceram. Soc. 90 (2007) 1458.
[11] R.Z. Zuo, J. Rodel, R.Z. Chen, L.T. Li, J. Am. Ceram. Soc. 89 (2006) 2010.
[12] Y. Saito, H. Takao, Ferroelectric 338 (2006) 17.
[13] L. Wu, J.L. Zhang, S.F. Shao, P. Zheng, C.L. Wang, J. Phys. D: Appl. Phys. 41 (2008) 035402.