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Ceramics International 38S (2012) S347–S350

CERAMICS INTERNATIONAL

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Effects of K/Na ratio on the phase structure and electrical properties of $0.98(K_xNa_{1-x})NbO_3$–$0.02BiScO_3$ lead-free ceramics

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Available online 4 May 2011

Abstract

Lead-free piezoelectric ceramics $0.98(K_xNa_{1-x})NbO_3$–$0.02BiScO_3$ (0.98 $K_xN_{1-x}N$–0.02BS) (x = 0.30–0.60) doped with 0.8 mol% Mn were prepared by conventional solid-state sintering. The effects of K/Na ratio on the phase structure and electrical properties of the Mn doped 0.98 $K_xN_{1-x}N$–0.02BS (0.98 $K_xN_{1-x}N$–0.02BS–Mn) were mainly studied. It is experimentally demonstrated that the electrical properties strongly depend on K/Na ratio in the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics and when $x = 0.45$ the ceramics exhibit optimum electrical properties: $d_{33} \sim 308$ pC/N, $k_p \sim 0.495$, $\varepsilon_r \sim 1577$, tan $\delta \sim 0.028$. These results show that the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramic with $x = 0.45$ is a promising lead-free piezoelectric material.

Keywords: C. Electrical properties; K/Na ratio; Lead-free ceramics; Phase structure

1. Introduction

Lead-based piezoelectric materials, represented by $Pb(Zr,Ti)O_3$ (PZT) and PZT-based ternary-component ferroelectrics, have become the most versatile and the most widely used piezoelectrics since most of them were discovered in 1950s and 1960s [1]. However, the growing environmental concerns have made the high lead content PZT-based ceramics disaffiliated from many commercial applications and materials [2–16]. Currently, more and more attention has been paid to lead-free ceramics to decrease the use of lead oxide with high toxicity.

Among all the lead-free ceramics, $(K_xNa_{1-x})NbO_3$ (KNN) based ceramics have drawn much attention since Saito et al. [4] reported that high piezoelectric constant d_{33} (416 pC/N) can be obtained in textured KNN based ceramics. Recently, a number of studies have been carried out to improve the electrical properties of KNN based ceramics by forming solid solutions with other perovskite or perovskite-like ABO_3 compounds, such as $LiNbO_3$ [5], $LiTaO_3$ [6–8], $LiSbO_3$ [9,10], $BaTiO_3$ [11], $BiScO_3$ [12–14], or a combination of multiple additives [11,15,16]. Among them, $BiScO_3$ is an attractive compound, which could effectively increase the piezoelectric coefficient d_{33} [12]. In addition, one of the most important factors affecting the electrical properties of the KNN-based ceramics is the polymorphic orthorhombic-tetragonal phase transition temperature [10,12]. It has been reported that the molar ratio of K/Na has a significant effect on shifting the polymorphic phase transition to near room temperature [7–9].

According to our previous work [14], 0.8 mol% $MnCO_3$ doped $0.98(K_{0.5}Na_{0.5})NbO_3$–$0.02BiScO_3$ ceramics showed good electrical properties. In this work, $0.98(K_xNa_{1-x})NbO_3$–$0.02BiScO_3$ doped with 0.8 mol% $MnCO_3$ (0.98 $K_xN_{1-x}N$–0.02BS–Mn) was chosen as the research system, and the effects of K/Na ratio on the dielectric, piezoelectric, and ferroelectric properties of the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics were mainly investigated.

2. Experimental

Lead-free ceramics $0.98(K_xNa_{1-x})NbO_3$–$0.02BiScO_3$ + 0.8 mol% $MnCO_3$ (x = 0.30, 0.35, 0.40, 0.45, 0.50, 0.55, 0.60) were prepared using a conventional solid-state reaction process, as reported previously [16]. X-ray diffraction (XRD) character-

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0272-8842/$36.00
doi:10.1016/j.ceramint.2011.04.117

ization of the ceramics was performed using Cu Kα radiation (λ = 1.54178 Å) in the mode of θ–2θ scan (DX1000, Dandong, China). The temperature dependence of the dielectric constant of the samples was measured using an impedance analyzer (Agilent E4980A). The samples were poled in silicone oil at 5 kV/mm for 15 min at 80 °C. The piezoelectric constant (d_{33}) was measured using a piezo-d_{33} meter (ZJ-3A, China) after aging for 24 h. The electromechanical coupling factors (k_p and k_t) were measured and calculated by the resonance–antiresonance method using an impedance analyzer (Agilent 4294A). The polarization versus electric field (P–E) hysteresis loops of the ceramics was observed using a Radiant Precision Workstation (USA) at 10 Hz.

3. Results and discussion

Fig. 1 shows the XRD patterns of the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x (i.e., K content). It is clear that all the ceramics possess a pure perovskite structure and no secondary phase is observed. Ceramics with different K/Na ratios should contain both the orthorhombic and tetragonal phases at room temperature. Hence, no significant difference is observed in their room-temperature XRD patterns.

The temperature dependences of ε_r measured at 10 kHz for the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics are shown in Fig. 2(a), It can be seen that all the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics exhibit two phase transitions, i.e., a paraelectric cubic–ferroelectric tetragonal phase transition at T_C and a polymorphic orthorhombic–tetragonal phase transition at $T_{o\text{-}t}$. Fig. 2(b) shows T_C and $T_{o\text{-}t}$ of the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x. As shown in Fig. 2(b), T_C increases slightly at $0.35 \leq x \leq 0.45$, and then drops with further increase of x. Unlike T_C, the observed $T_{o\text{-}t}$ decreases from 107 °C to 72 °C as x increases from 0.35 to 0.45 and then remains almost unchanged at the larger x. Although the $T_{o\text{-}t}$ (≥72 °C) of the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics is higher than room temperature, the transition from tetragonal to orthorhombic phase is gradual and hence the ceramics should contain a certain amount of the tetragonal phase as well as the orthorhombic phase at room temperature, which is consistent with the results of XRD patterns (Fig. 1).

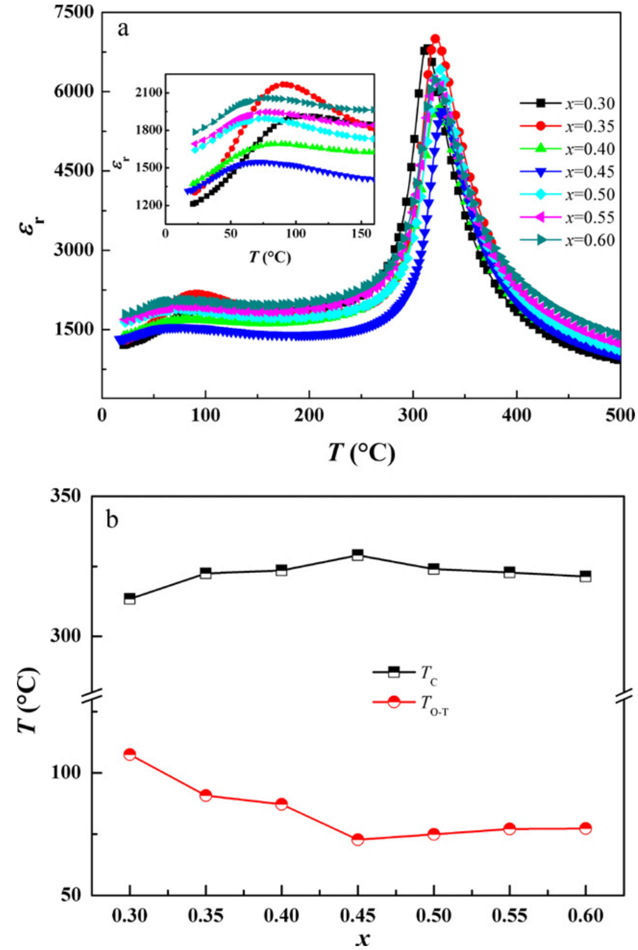

Fig. 2. (a) Dielectric constant of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of temperature, and (b) T_C and $T_{o\text{-}t}$ of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x.

Fig. 3(a) shows the piezoelectric constant d_{33}, electromechanical coupling coefficients k_p and k_t for the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x. It can be found from

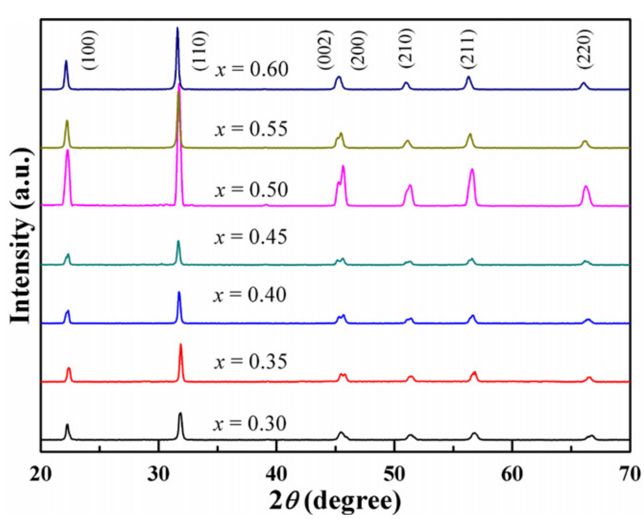

Fig. 1. XRD patterns of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x.

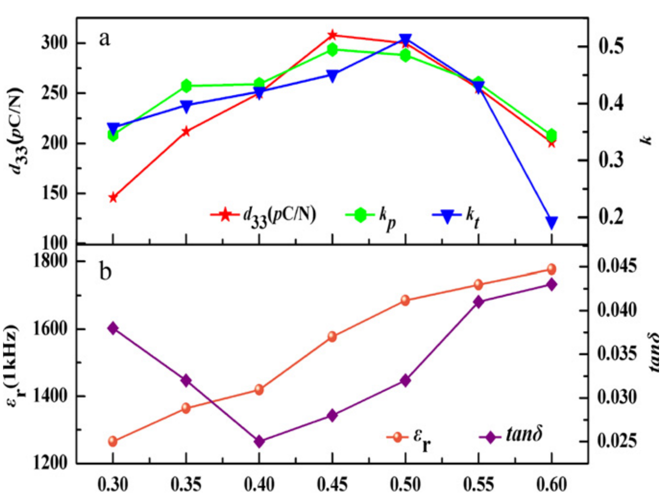

Fig. 3. (a) d_{33}, k_p and k_t of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x, and (b) ε_r and tan δ of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of x.

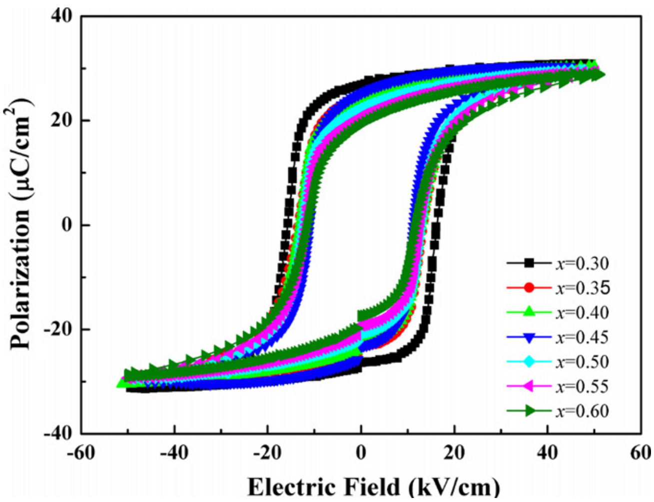

Fig. 4. *P–E* hysteresis loops of 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of *x*.

Fig. 3(a) that d_{33} increases and then decreases with increasing *x*, giving a maximum value of 308 pC/N at $x = 0.45$. The observed k_p exhibits a similar dependence on *x* as d_{33}, and reaches a maximum value of 0.495 at $x = 0.45$. As Chang et al. [7] and Wu et al. [9] reported, the polymorphic phase transition (PPT) at $T_{o\text{-}t}$ is shifted to near room temperature and K_xNN-based ceramics exhibit excellent electrical properties when K/Na ratio is between 0.66 and 1. Though the $T_{o\text{-}t}$ for specimen we obtained when $x = 0.45$ is a little higher than room temperature, the PPT is gradual and so we get both the tetragonal phase and the orthorhombic phase at room temperature as shown in Fig. 2. These may lead to the optimum electrical properties in the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics at $x = 0.45$. Fig. 3(b) reveals the dielectric constant ε_r and dielectric loss tan δ for the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics as a function of *x*. The ε_r value increases with increasing *x*. The tan δ value of the ceramics shows almost no change with increasing *x*. All these results clearly show that the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramic at $x = 0.45$ possesses enhanced dielectric and piezoelectric properties at room temperature: $d_{33} = 308$ pC/N, $k_p = 0.495$, $k_t = 0.451$, $\varepsilon_r = 1577$, and tan $\delta = 0.028$. Therefore, it is found that the K/Na ratio in the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics plays a very important role in improving the dielectric and piezoelectric properties.

All the 0.98 $K_xN_{1-x}N$–0.02BS–Mn ceramics exhibit a well-saturated and square-like *P–E* loop under an electric field of 5 kV/mm. Fig. 4 shows the room temperature *P–E* loops of the ceramics measured at 10 Hz. It can be seen that the ferroelectric properties are composition dependent, and *P–E* hysteresis loops became slimmer with increasing K/Na ratio. For the ceramic with $x = 0.45$, the remnant polarization (P_r) and the coercive electric field (E_C) are 25.5 $\mu C/cm^2$ and 11.3 kV/cm, respectively.

4. Conclusions

0.98 $K_xN_{1-x}N$–0.02BS–Mn ($x = 0.30$–0.60) lead-free piezoelectric ceramics were prepared by conventional solid-state sintering technique. The effects of K/Na ratio on phase structure, dielectric, piezoelectric, and ferroelectric properties of 0.98 $K_xN_{1-x}N$–0.02BS–Mn lead-free piezoelectric ceramics were investigated. The XRD results show that the ceramics possess a pure perovskite structure. For the ceramic with $x = 0.45$, the piezoelectric properties become optimum, giving $d_{33} = 308$ pC/N, $k_p = 0.495$, $k_t = 0.451$, $\varepsilon_r = 1577$, and tan $\delta = 0.028$. Our results indicate that the coexistence of the tetragonal phase and the orthorhombic phase at room temperature caused by the gradual PPT leads to the excellent properties. As a consequence, the nearly equal K/Na ratio may not be necessary to obtain excellent electrical properties at least in some KNN based ceramics and the K content about 45 mol% may be instructive for further design and development of new KNN based piezoelectric systems.

Acknowledgements

This work was supported by National Science Foundation of China (NSFC Nos. 11075110 and 50972095) and Foundation of Doctor Training Program in University and College in China (Nos. 20030610035, and 20080610020).

References

[1] B. Jaffe, W.R. Cook, H. Jaffe, Piezoelectric Ceramics, Academic, New York, 1971.
[2] L. Egerton, D.M. Dillom, Piezoelectric and dielectric properties of ceramics in the system potassium–sodium niobate, Journal of the American Ceramics Society 42 (9) (1959) 438–442.
[3] R.E. Jaeger, L. Egerton, Hot pressing of potassium–sodium niobates, Journal of the American Ceramics Society 45 (5) (1962) 209–213.
[4] Y. Saito, H. Takao, T. Tani, T. Nonoyama, K. Takatori, T. Homma, T. Nagaya, M. Nakamura, Lead-free piezoceramics, Nature (London) 432 (2004) 84–87.
[5] K. Wang, J.F. Li, Domain engineering of lead-free Li-modified (K,Na)NbO_3 polycrystals with highly enhanced piezoelectricity, Advanced Functional Materials 20 (2010) 1–6.
[6] R.Z. Zuo, J. Fu, D.Y. Lv, Phase transformation and tunable piezoelectric properties of lead-free $(Na_{0.52}K_{0.48-x}Li_x)(Nb_{1-x-y}Sb_yTa_x)O_3$ system, Journal of the American Ceramics Society 92 (1) (2009) 283–285.
[7] Y.F. Chang, Z.P. Yang, D.F. Ma, Z.H. Liu, Z.L. Wang, Phase coexistence and high electrical properties in $(K_xNa_{0.96-x}Li_{0.04})(Nb_{0.85}Ta_{0.15})O_3$ piezoelectric ceramics, Journal of Applied Physics 105 (2009), pp. 054101–054101-7.
[8] J.G. Wu, D.Q. Xiao, Y.Y. Wang, L. Wu, Y.H. Jiang, J.G. Zhu, K/Na ratio dependence of the electrical properties of $[(K_xNa_{1-x})_{0.95}Li_{0.05}](Nb_{0.95-}](Nb_{0.95}Ta_{0.05})O_3$ lead-free ceramics, Journal of the American Ceramics Society 91 (7) (2008) 2385–2387.
[9] J.G. Wu, D.Q. Xiao, Y.Y. Wang, J.G. Zhu, P. Yu, Effects of K content on the dielectric, piezoelectric, and ferroelectric properties of $0.95(K_xNa_{1-x})NbO_3$–$0.05LiSbO_3$ lead-free ceramics, Journal of Applied Physics 103 (2008), pp. 024102–024102-4.
[10] S.J. Zhang, X. Ru, T.R. Shrout, G.Z. Zang, J.F. Wang, Piezoelectric properties in perovskite $0.948(K_{0.5}Na_{0.5})NbO_3$–$0.052LiSbO_3$ lead-free ceramics, Journal of Applied Physics 100 (2006), pp. 104108–104108-6.
[11] D.M. Lin, K.W. Kwok, H.L.W. Chan, Structure, dielectric, and piezoelectric properties of CuO-doped $K_{0.5}Na_{0.5}NbO_3$–$BaTiO_3$ lead-free ceramics, Journal of Applied Physics 102 (2007) 074113.
[12] H.L. Du, W.C. Zhou, F. Luo, D.M. Zhu, S.B. Qu, Y. Li, Z.B. Pei, Design and electrical properties' investigation of $(K_{0.5}Na_{0.5})NbO_3$–$BiMeO_3$ lead-free piezoelectric ceramics, Journal of Applied Physics 104 (2008) 034104–134104.

[13] X.H. Li, J.L. Zhu, M.S. Wang, Y.S. Luo, W. Shi, L.H. Li, J.G. Zhu, D.Q. Xiao, $BiScO_3$-modified $(K_{0.475}Na_{0.475}Li_{0.05})(Nb_{0.95}Sb_{0.05})O_3$ lead-free piezoelectric ceramics, Journal of Alloys and Compounds 499 (2010) L1–L4.

[14] X.H. Li, M. Jiang, J. Liu, J.L. Zhu, X.H. Zhu, J.G. Zhu, D.Q. Xiao, Enhanced piezoelectrical properties in Mn doped 0.98 $K_{0.5}Na_{0.5}NbO_3$–$0.02BiScO_3$ lead-free ceramics, Journal of the American Ceramics Society 92 (2009) 1625–1628.

[15] D.M. Lin, K.W. Kwok, H.L.W. Chan, Piezoelectric and ferroelectric properties of Cu-doped $K_{0.5}Na_{0.5}NbO_3$ lead-free ceramics, Journal of Physics D: Applied Physics 41 (2008), pp. 045401–045401-6.

[16] D.M. Lin, K.W. Kwok, H.L.W. Chan, Dielectric and piezoelectric properties of $K_{0.5}Na_{0.5}NbO_3$–$AgSbO_3$ lead-free ceramics, Journal of Applied Physics 106 (2009), pp. 034102-034102-5.