Materials Research Bulletin 47 (2012) 2863–2866

Contents lists available at SciVerse ScienceDirect

Materials Research Bulletin

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

Piezoelectric and dielectric properties of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_xTi_{(1-x)})O_3$ ceramics

Seung-Hwan Lee [a], Sung-Gap Lee [b], Young-Hie Lee [a,*]

[a] Department of Electronic Materials Engineering, Kwangwoon University, Republic of Korea
[b] Department of Ceramic Engineering, Engineering Research Institute, Gyeongsang National University, Jinju-Si, Republic of Korea

ARTICLE INFO

Article history:
Available online 26 April 2012

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

ABSTRACT

Lead-free $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_xTi_{(1-x)})O_3$ (0.98NKN–0.02BZT) ceramics with Zr contents were fabricated by a conventional mixed-oxide method. The results indicate that the Zr/Ti ratio significantly influences the structural, piezoelectric, dielectric, and ferroelectric properties of 0.98NKN–0.02BZT ceramics. For the 0.98NKN–0.02BZT ($x = 0$) ceramics sintered at 1090 °C, the bulk density increased as the Zr contents decreased and showed a maximum value at $x = 0$. The Curie temperature of the 0.98NKN–0.02BZT ceramics slightly decreased as the Zr contents increased. The dielectric constant, piezoelectric constant, and electromechanical coupling factor of samples were maximized at $x = 0$, which might be due to the increase in density. A high $d_{33} = 194$ pC/N, $k_p = 38\%$ were obtained for the 0.98NKN–0.02BZT ceramics sintered at 1090 °C for 4 h.

1. Introduction

Piezoelectric ceramics are the main factor of various industries, ranging from high piezoelectric constant actuators to the later development of piezoelectric transducers, sensors, and energy-harvesting devices. Among lead oxide-based piezoelectric materials, the lead zirconate titanate (PZT) composition was extensively used for many years for actuators, sensors, transducers, and so on [1–6]. The outstanding ferroelectric and piezoelectric properties of PZT materials are due to the morphotropic phase boundary (MPB). However, the high toxicity of the lead oxide that is present in the PZT materials has caused critical environmental problems [7–13]. As a result, lead-free piezoelectric materials have been widely studied. Additionally, the innovation of compositions is being maintained in the search for new perovskite structure materials that have a MPB.

In the past few years, many studies have reported $BaTiO_3$, $(Bi, Na)TiO_3$, $(Na, K)NbO_3$ has been studied to replace PZT with lead-free materials. Among them, NKN ceramics has been recently considered as promising candidate for a lead-free piezoelectric material because of its high piezoelectric constant of 160 pC/N (hot pressing process). However, difficulties in the sintering process of pure NKN ceramics have lead to a deviation from these excellent properties, for example, relatively low electrical properties ($d_{33} = 80$ pC/N, $k_p = 36\%$). So, many researchers have reported that the effects of dopants for NKN system. Lately, studies have demonstrated that the piezoelectric properties of Ba-, Zr-, and Ti-doped lead-free NKN ceramics are comparable to those of the most intensively used PZT ceramics [14–20]. Specifically, the addition of $BaTiO_3$ considerably enhances the structural and electrical properties of NKN ceramics owing to compensation for volatilization of Na-, K-, Nb-site. Also, it is reported that an increase in the Zr^{4+} content induces a reduction in the average grain size, decrease electrical properties. However, with increasing Zr^{4+} content, BZT exhibit relaxor behavior, which can be widely used in fabrication of multilayer ceramic capacitor, electrostrictive actuators, and electromechanical transducers. These results have clearly stimulated studies about optimizing the compositions of 0.98NKN–0.02BZT ceramics in order to further improve the electrical properties [21–29]. In this work, a $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_xTi_{(1-x)})$ (0.98NKN–0.02BZT) ceramics were fabricated by using conventional ceramics techniques. We studied that 0.98NKN–0.02BZT ceramics show not only effects of the Zr/Ti ratio on the electrical properties but also control the relaxor ferroelectrics behavior.

2. Experiments

Solid solutions of $0.98(Na_{0.5}K_{0.5})NbO_3–0.02Ba(Zr_xTi_{(1-x)})$ (0.98NKN–0.02BZT) ceramics were produced using the conventional mixed-oxide process. The starting materials used in this study were Na_2CO_3, K_2CO_3, Nb_2O_5, $BaCO_3$, ZrO_2, and TiO_2 of 99.9% purity. They were ball-milled in alcohol with zirconia balls for 12 h and dried at 110 °C for 12 h, followed by calcining at 850 °C for 3 h

---

* Corresponding author. Tel.: +82 2 940 5164; fax: +82 2 915 8084.
E-mail address: yhlee@kw.ac.kr (Y.-H. Lee).

0025-5408/$ – see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.materresbull.2012.04.095

in air. After calcination, the resulting powders were pressed into disk samples with a diameter Ø = 12.8. The disk samples were finally sintered at 1090 °C for 4 h in air. After the sintered samples were polished to a thickness of 1.0 mm, silver electrodes were fired on the top and bottom surfaces. The crystalline structure of the sintered samples was examined using X-ray diffraction (XRD), and scanning electron microscopy (SEM) was used to observe their microstructures. The room temperature dielectric properties were measured using an LCR meter (Z9216, PROTEK) at 1 kHz. A conventional Sawyer–Tower circuit was used to measure the polarization–electric field (P–E) hysteresis loop. To measure the relevant electrical properties, the specimens were immersed in silicon oil and poled at 4 kV/mm for 20 min and then cooled to room temperature in the electric field. The piezoelectric constant (d_{33}) was measured using a piezo-d_{33} meter (Channel Product DT-3300). The electromechanical coupling factor (k_p) was calculated by the resonance method according to Institute of Electrical and Electronics Engineers (IEEE) standards using an impedance analyzer (4294A, Agilent).

3. Results and discussion

Fig. 1 shows the room temperature XRD patterns of the 0.98NKN–0.02BZT ceramics sintered at 1090 °C with various compositional conditions. XRD analyses were conducted to observe the microstructure and degree of crystallization. It is evident that all compositions showed a typical perovskite structure with an orthorhombic symmetry and no secondary peaks could be observed. Fig. 2 shows the enlarged XRD patterns of the 0.98NKN–0.02BZT ceramics sintered at 1090 °C. The splitting of the peaks from 43° to 48° at $x = 0$–0.2 in the compositional conditions shows the crystallinity and variation of interplanar distance. The 2θ peak positions of (0 0 2) and (0 2 0) were shifted slightly to a lower angle with the increase of Zr^{4+} contents. It can be inferred that Ti^{4+} exists in relatively smaller amounts in the B-site than Zr^{4+}. The radius of Zr^{4+} (0.079 nm) is bigger than that of Ti^{4+} (0.068 nm) and this causes the shift to a lower angle as calculated by the Bragg's law equation of $n\lambda = 2d\sin\theta$. Furthermore, 0.98NKN–0.02BZT ceramics at $x = 0$ have strong orthorhombic properties. The patterns of the 0.98NKN–0.02BZT ceramics remain in an orthorhombic structure, but change into a weak orthorhombic peak as the content of Zr^{4+} increases. Moon et al. [11] reported electrical properties of NKN–LT ceramics were influenced by degree of crystallization. Therefore, it can be inferred that structural stability leads to superior electrical properties. Fig. 3 shows the cross-sectional morphology of modified 0.98NKN–0.02BZT ceramics with different compositional conditions. It is clear that a porous microstructure with relatively big and homogeneous grains was seen in the sample of 0.98NKN–0.02BZT at $x = 0$. The grain size decreased and became heterogeneous with the increase of Zr contents. It seems to be connected with the lower degree of grain growth caused by slow substitution of the Zr^{4+}. Ions that have a smaller radius create fast diffusion and grain growth. The temperature dependence of the dielectric constant of 0.98NKN–0.02BZT ceramics with various compositional conditions is shown in Fig. 4. The maximum Curie temperature (T_c) is significantly shifted towards a lower temperature with the increase of Zr contents. Also, the 0.98NKN–0.02BZT ceramics exhibited inferior dielectric constant. However it shows the typical relaxor-like behavior with the increase of Zr contents. The highest T_c, dielectric constant were obtained 427 °C, 7211 respectively in the sample at $x = 0$ and then with Zr content increasing, T_c, dielectric constant decrease. It can be inferred that the peak value of the dielectric constant was significantly influenced by the compositional conditions of the 0.98NKN–0.02BZT ceramics.

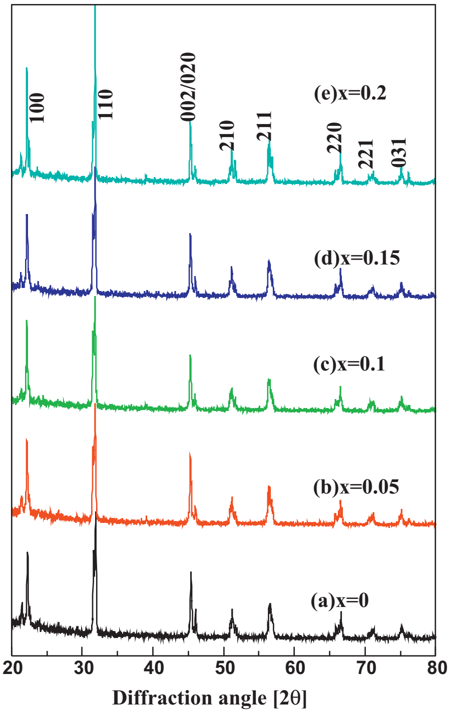

Fig. 1. (a–e) XRD patterns of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_xTi_{(1-x)})O_3$ ceramics.

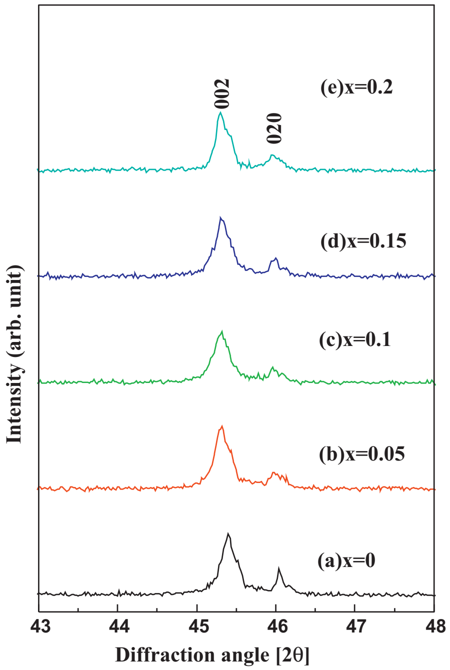

Fig. 2. (a–e) XRD patterns of $0.98(Na_{0.5}K_{0.5})NbO_3$–$0.02Ba(Zr_xTi_{(1-x)})O_3$ ceramics near the (0 0 2) and (0 2 0) planes.

Fig. 5 shows the relative density d_{33} and k_p of 0.98NKN–0.02BZT ceramics as a function of the Zr contents. All results show the average values which was obtained by measuring 5 times of each 5 samples. All samples have a good relative density in the range of 88.1–96%. It is well known that the relative density affects the piezoelectric properties of 0.98NKN–0.02BZT ceramics. As the Zr