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Dielectric properties of $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ ceramics fabricated by mechanical alloying

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ABSTRACT

A/B-site complex perovskite $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ (also can be written: $(1-2x)Na_{0.5}Bi_{0.5}TiO_3$–$xK_{0.5}Bi_{0.5}TiO_3$–$xNaNbO_3$) ($x$ = 0–0.08) lead-free piezoelectric ceramics were fabricated by mechanical alloying technique from their oxide/carbonate mixture. Phase evolvements of the mixture and the influence of x value on crystal structure and microstructure were investigated. The perovskite $Na_{0.5}Bi_{0.5}TiO_3$ phase was progressively formed with passing through the intermediate $Bi_4Ti_3O_{12}$ phases with increasing degree of mechanical activation. The Curie–Weiss law and a modified empirical expression were employed to describe the ferroelectric phase transition of $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ ceramics. The results showed that $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ ceramics became more relaxor ferroelectric characteristic with the increase in value of x. The enhancement of relaxor characteristic may arise from structural disorder and compositional fluctuation in the crystal structure.

1. Introduction

There is an increasing demand for the environment friendly materials like lead-free ceramics for different piezoelectric application fields. Sodium bismuth titanate, $Bi_{0.5}Na_{0.5}TiO_3$ (BNT), is a kind of perovskite (ABO_3-type) ferroelectric discovered by Smlenskii et al. [1]. The dielectric constant of BNT shows a flat, frequency-dependent hump assigned to ferroelectric– anti-ferroelectric phase transition at ~230 °C; as well as the symmetry of BNT changes to cubic symmetry at ~520 °C [2]. Therefore, BNT is considered as an excellent candidate of lead-free piezoelectric ceramics because it is ferroelectric with a relatively large remanent polarization, P_r = 38 μC/cm^2, and a relatively large coercive field, E_c = 7.3 kV/mm [1].

Very recently, a novel mechanical alloying technique has been successfully devised to synthesize a variety of lead-based functional ceramics [3–5]. The intrinsic advantage of mechanical alloying lies in its ability to effect a solid state reaction through mechanical activation, instead of by the calcination at a high enough temperature. It can also lead to an improvement in the reactivity of starting materials and therefore the desired ceramic phase is formed at a lowered calcination temperature. Therefore, mechanical alloying technique may minimize or avoid volatilization of alkaline oxides at high temperatures

Potassium bismuth titanate, $Bi_{0.5}K_{0.5}TiO_3$ (BKT), first discovered by Smolenskii [6], also has a perovskite-type ferroelectric structure belonging to tetragonal crystal system at room temperature. It undergoes a phase transition around 380 °C (Curie point). Ivanova et al. [7] reported the lattice parameters of BKT as a = 3.913 Å and c = 3.990 Å at room temperature. Much work has been done to modify and improve the piezoelectric properties of BNT ceramics by cation substitution [8–16], such as $Bi_{0.5}Na_{0.5}TiO_3$–$SrTiO_3$–$Bi_{0.5}Li_{0.5}TiO_3$ [8], $Bi_{0.5}Na_{0.5}TiO_3$–$SrTiO_3$ [9] and $Bi_{0.5}Na_{0.5}TiO_3$–$BaTiO_3$ [12]. Meanwhile, BNT–BKT solid solutions have been reported to be superior piezoelectric in high-frequency ultrasonic applications with a low dielectric constant and a high electromechanical coupling factor along with a high mechanical strength [17–20]. Niobium doped BNT–BKT is A/B-site complex perovskite compound. Therefore, the structure evolvement and relaxor characteristic of BNT–BKT–niobate solid solutions are very interesting.

In this study, A/B-site complex perovskite ferroelectric, $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ solid solutions were prepared by mechanical alloying technique from their oxide/carbonate mixture. The purpose of this work is to illustrate the phase evolvement of the mixture and the effects of ion substitution on crystal structure evolvement in BNT, as well as to understand the relaxor characteristic of the ternary system.

2. Experimental procedures

Mechanical alloying technique was used to prepare $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$, ($x$ = 0, 0.02, 0.04, 0.06, 0.08) solid solutions. Reagent grade oxide or carbonate pow-

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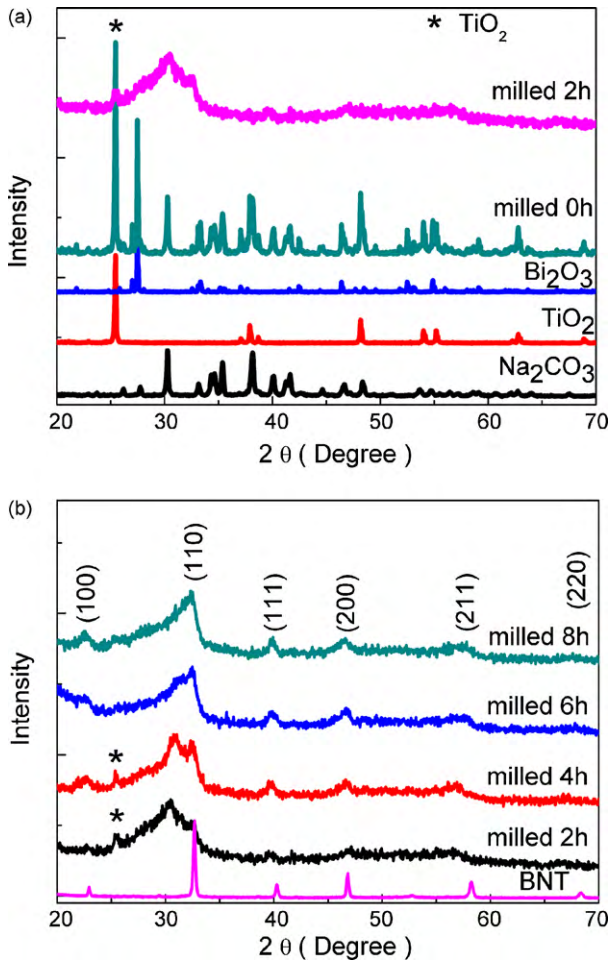

Fig. 1. (a) XRD patterns of Na_2CO_3, K_2CO_3 and TiO_2 and their mixture mechanically activated for 0 h and 2 h; (b) XRD pattern of the mixture mechanically activated for 2–8 h and pure BNT ceramics, indexed based on ICSD-043769.

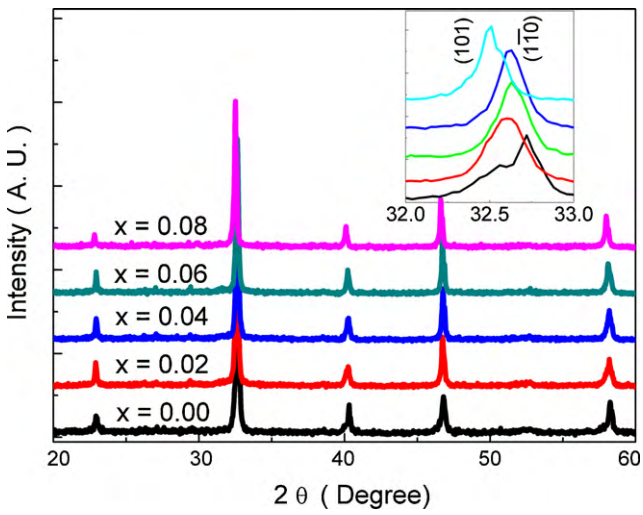

Fig. 2. XRD patterns of $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ ceramics, inset, (1 1 0) peak evolves with the increase in the value of x.

ders of Na_2CO_3, $K_2CO_3 \cdot 1.5H_2O$, Bi_2O_3, TiO_2 and Nb_2O_5 were used as raw materials. The oxides and carbonates were mixed in a planetary mill by ball milling for 0–8 h. After being mixed, the mixture was pressed at 150 MPa into pellets with 20 mm in diameter and about 1.5 mm in thickness. The green compacts were sintered at 1080 °C for 2 h in air atmosphere. Gold had been sputtered on the surfaces of sample as electrodes.

X-ray powder diffraction (XRD) patterns were taken on a PANalytical X'Pert-PRO powder X-ray diffractometer with Cu Kα radiation. Microstructure evolution was studied by scanning electron microscopy (SEM) (JSM-6380LV, JEOL). Relative dielectric constant and loss factor at room temperature and elevated temperature were measured using Agilent 4294A impedance analyzer.

3. Results and discussion

For the sample $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ with $x = 0$, XRD patterns of initial mixture (Na_2CO_3, Bi_2O_3 and TiO_2) and the mixture after milled for 0 h and 2 h are shown in Fig. 1a. After milled

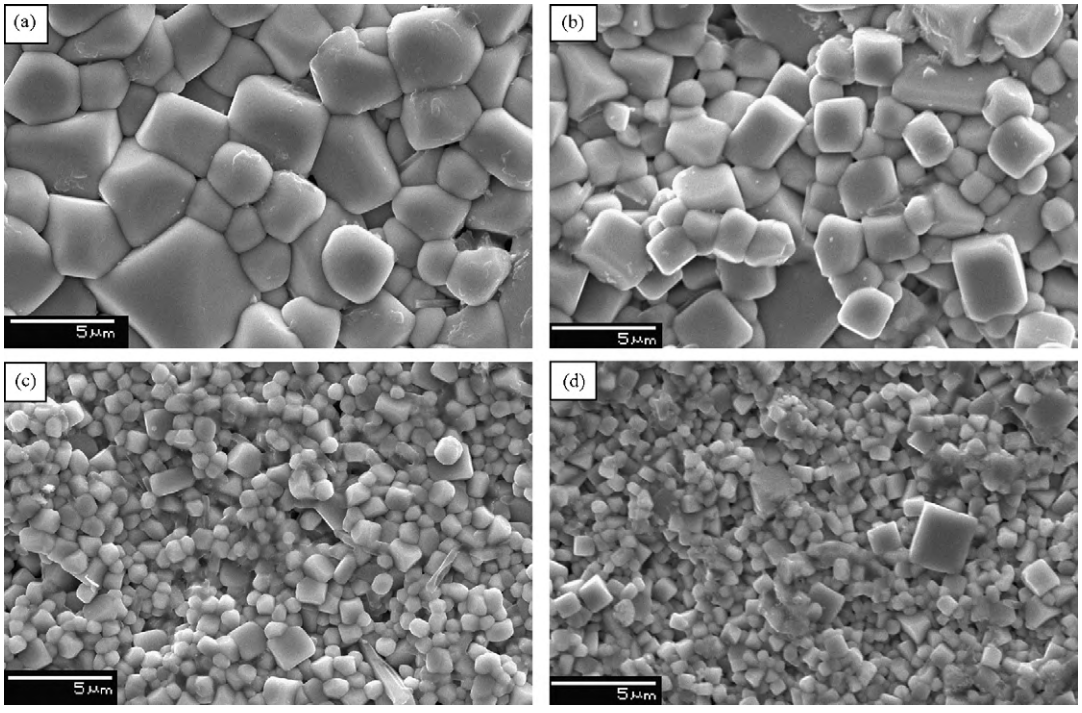

Fig. 3. SEM micrographs of $(NaBi_{(1-x)}K_x)_{0.5}Ti_{(1-x)}Nb_xO_3$ ceramics, (a) $x = 0.02$, (b) $x = 0.04$, (c) $x = 0.06$, (d) $x = 0.08$.