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ScienceDirect

Ceramics International 40 (2014) 2731–2735

CERAMICS INTERNATIONAL

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Effect of $SrZrO_3$ on phase structure and electrical properties of $0.974(K_{0.5}Na_{0.5})NbO_3–0.026Bi_{0.5}K_{0.5}TiO_3$ lead-free ceramics

Tao Huang, Dingquan Xiao*, Chao Liu, Fangxu Li, Bo Wu, Jiagang Wu, Jianguo Zhu

Department of Materials Science, Sichuan University, Chengdu 610064, PR China

Received 12 August 2013; received in revised form 11 October 2013; accepted 12 October 2013
Available online 22 October 2013

Abstract

$(0.974-x)(K_{0.5}Na_{0.5})NbO_3–0.026Bi_{0.5}K_{0.5}TiO_3–xSrZrO_3$ lead-free piezoelectric ceramics have been prepared by the conventional solid state sintering method. Systematic investigation on the microstructure, crystalline structures as well as electrical properties of the ceramics was carried out. With the addition of $SrZrO_3$, the rhombohedral–orthorhombic phase transition temperature of the ceramics increases. Both the rhombohedral–orthorhombic and orthorhombic–tetragonal phase transitions of the ceramics were modified to be around room temperature when $x\sim0.05$, and as a result remarkably strong piezoelectricity has been obtained in $0.924(K_{0.5}Na_{0.5})NbO_3–0.026Bi_{0.5}K_{0.5}TiO_3–0.05SrZrO_3$ ternary system, whose piezoelectric parameters were $d_{33}=324$ pC/N and $k_p=41\%$.

Keywords: C. Piezoelectric properties; Lead-free ceramics; Phase boundary; KNN; $SrZrO_3$

1. Introduction

Lead-based piezoelectric ceramics, such as lead zirconate titanate (PZT), have been widely used in various applications such as sensors, actuators and transducers due to their excellent piezoelectric properties [1,2]. It is well known that the dielectric and piezoelectric properties of ceramics usually maximize around the tetragonal–rhombohedral morphotropic phase boundary (MPB)—a phase boundary that a narrow composition region with orthorhombic or monoclinic phase separating rhombohedral and tetragonal phases in solid solutions—for widely used PZT-based ceramics [3]. However, the lead has been restricted from many commercial applications because of its toxicity. Lead-free piezoelectric ceramics are widely investigated for the environmental protection and human health [4], in which the (K, Na)NbO_3 (KNN) based ceramics have received considerable attention because of their excellent piezoelectric properties and high Curie temperature [5–23]. KNN undergoes several phase transitions with increasing temperature: rhombohedral to orthorhombic (R–O) transition at −123 °C, orthorhombic to tetragonal (O–T) transition at 200 °C, and tetragonal to cubic (T–C) transition at 410 °C, respectively [10,24]. Thus, it is expected that KNN based lead-free ceramics with piezoelectric properties comparable with that of lead-based piezoelectric ceramics could be developed via forming similar MPB in this system.

However, most of the researchers focus on modifying the orthorhombic–tetragonal phase transition temperature ($T_{O–T}$) down to around room temperature, and the properties obtained are still inferior compared to lead-based piezoelectric ceramics [6–9,11–18]. In order to get similar MPB in KNN based lead-free ceramics, both the rhombohedral–orthorhombic phase transition temperature ($T_{R–O}$) and the orthorhombic–tetragonal phase transition temperature ($T_{O–T}$) of the ceramics should be modified to be around room temperature. The usual way to decrease $T_{O–T}$ near room temperature has been conducted by forming solid solutions with compounds such as $Bi_{0.5}Na_{0.5}TiO_3$, $Bi_{0.5}K_{0.5}TiO_3$, $LiSbO_3$, $LiTaO_3$, $BaTiO_3$ etc. [8,14–18]. Among them, $Bi_{0.5}K_{0.5}TiO_3$ falls into the tetragonal ferroelectric and seems to broaden the tetragonal phase zone by shifting $T_{O–T}$ downward, where the optimum content of BKT is in the range of 0.02–0.03 [14]. It was reported that $SrZrO_3$ has an ABO_3 perovskite structure and exhibits an orthorhombic structure at room temperature [25], effectively shifting the $T_{R–O}$ of KNN ceramics to be above room temperature [19].

*Corresponding author. Tel.: +86 28 85412415; fax: +86 28 85416050.
E-mail address: nic0402@scu.edu.cn (D. Xiao).

0272-8842/$ - see front matter
http://dx.doi.org/10.1016/j.ceramint.2013.10.048

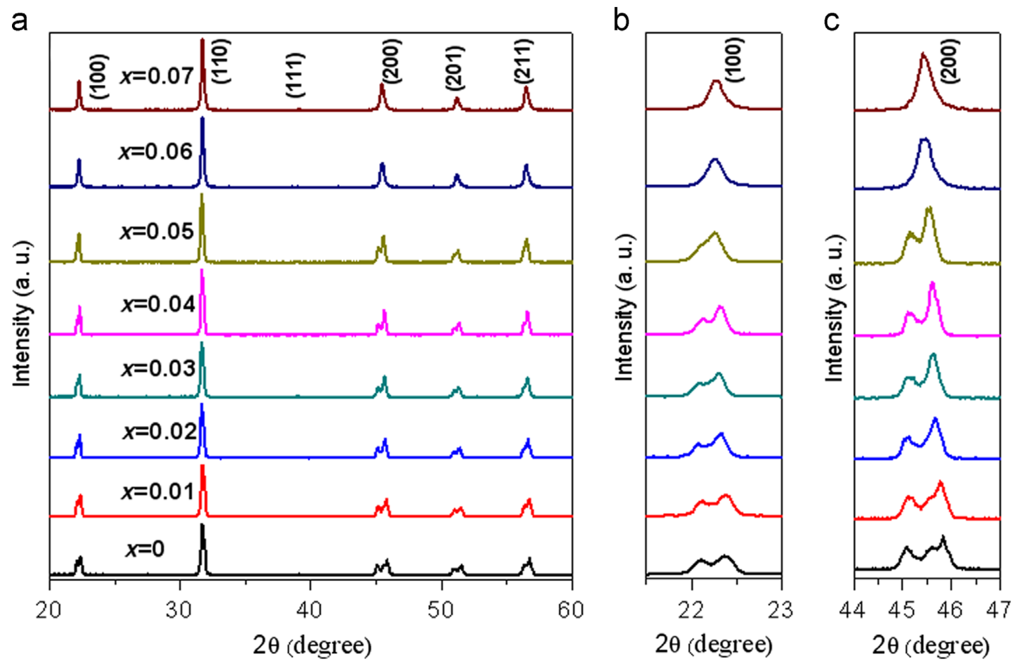

Fig. 1. The XRD patterns of the KNN–BKT–xSZ ceramics in the 2θ range of (a) 20–60°, (b) 21–23°, and (c) 44–47°, respectively.

The purpose of this study is to construct the new phase boundary in $(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ lead-free piezoelectric ceramics and investigate the effect of the phase boundary on their electrical properties. $Bi_{0.5}K_{0.5}TiO_3$ is selected to decrease the T_{O-T} down to be near room temperature, and the $SrZrO_3$ is selected to increase the T_{R-O} to be around room temperature.

2. Experimental procedure

$(0.974-x)(K_{0.5}Na_{0.5})NbO_3$–$0.026Bi_{0.5}K_{0.5}TiO_3$–$xSrZrO_3$ (abbreviated as KNN–BKT–xSZ, $x=0$, 0.01, 0.02, 0.03, 0.04, 0.05, 0.06, and 0.07 respectively) ceramics were prepared by the conventional sintering technique. Na_2CO_3 (99.8%), K_2CO_3 (99%), Nb_2O_5 (99.5%), Bi_2O_3 (99%), TiO_2 (98%), $SrCO_3$ (99%), and ZrO_2 (99%) were used as raw powders weighed according to the stoichiometric ratio of the ceramics. The powders were mixed and milled in ethanol for 24 h with zirconia balls, then dried and calcined at 850 °C for 6 h. The calcined powders were milled again for 24 h. Then, the dried mixtures were added with polyvinyl alcohol as a binder for granulation and pressed into disks with the diameter of 10 mm and the thickness of 1 mm under 10 MPa. After removal of the binder, the disk samples were sintered at 1100–1140 °C for 3 h in air. Silver paste electrodes were coated on both sides of these sintered samples and fired at 700 °C for 10 min. These ceramics were poled at room temperature under a DC electric field of 3–4 kV/mm for 20 min in silicon oil, and the electrical properties of the samples were measured after the poling for 24 h.

The crystalline structure of the ceramics was determined by X-ray diffraction (XRD) using Cu K_α radiation in the θ–2θ scan mode (DX 2700, Dandong, China).The grain morphology of the sintered samples was examined by scanning electron microscopy (SEM, S4800, Hitachi Ltd., Japan). The temperature dependence of the dielectric constant of the ceramics was measured using a LCR meter (Agilent 4980A, USA.). The polarization versus electric field (P–E) hysteresis loops of the ceramics were measured using a Radiant Precision Workstation (USA). An impedance analyzer (Solartron Gain Phase Analyzer) was employed to characterize the dielectric properties, and the piezoelectric coefficient (d_{33}) was measured using a piezo-d_{33} meter (ZJ-3A, China).

3. Results and discussion

Fig. 1(a) shows the XRD patterns of KNN–BKT–xSZ ceramics with different SZ content measured at room temperature. All the ceramics measured exhibit a typical perovskite structure, and no secondary phases were detected. Fig. 1(b) and (c) shows the corresponding XRD patterns of KNN–BKT–xSZ ceramics in the range of 2θ equal to 21–23° and 44–47°, respectively. As shown in Fig. 1(b) and (c), the samples with $x=0$ exhibit the orthorhombic and tetragonal phase coexistence at room temperature [14], which also confirmed the results in Fig. 2(b). The dominant tetragonal phase is obtained for the samples with $x=0.01$–0.05. Only one single peak is observed for the samples with $x=0.06$–0.07. The single peak is a character for either rhombohedral or cubic phase [20], thus the temperature-dependent dielectric and ferroelectric behavior is needed to determine the symmetry of the ceramics with $x=0.06$–0.07 beside the XRD patterns.

The temperature dependence of the dielectric constant (ε_r) at 10 kHz for the ceramics is shown in Fig. 2(a). The T_C almost linearly decreases with x as seen from Fig. 2(a), but it is still