Solid State Communications 204 (2015) 19–22

Contents lists available at ScienceDirect

Solid State Communications

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

Enhanced energy-storage properties of $(1-x)[(1-y)(Bi_{0.5}Na_{0.5})TiO_3$–$y(Bi_{0.5}K_{0.5})TiO_3]$–$x(K_{0.5}Na_{0.5})NbO_3$ lead-free ceramics

Jigong Hao, Zhijun Xu*, Ruiqing Chu, Wei Li, Juan Du, Peng Fu

College of Materials Science and Engineering, Liaocheng University, Liaocheng 252059, People's Republic of China

ARTICLE INFO

Article history:
Received 15 October 2014
Received in revised form
1 December 2014
Accepted 3 December 2014
Communicated by T. Kimura
Available online 11 December 2014

Keywords:
A. Ferrelectrics
B. Sintering
D. Energy-storage
D. Temperature stability

ABSTRACT

In this work, we designed a series of compositions within peudocubic region based on ternary $(1-x)[(1-y)(Bi_{0.5}Na_{0.5})TiO_3$–$y(Bi_{0.5}K_{0.5})TiO_3]$–$x(K_{0.5}Na_{0.5})NbO_3$ (BNKT100*y*–*x*KNN) system for energy storage applications. Results showed that the KNN substitution into BNKT100*y* induced a significant disruption of the ferroelectric order, and tended to enhance the energy storage density of the ceramics. With the external electric field, the energy storage density increased drastically, and a maximum value of 1.20 J/cm^3 at 100 kV/cm was achieved in BNKT100*y*–*x*KNN ($y=0$, $x=0.16$) samples. Furthermore, BNKT100*y*–*x*KNN ($y=0$, $x=0.16$) ceramics not only exhibited high energy density but also possessed fatigue-free behavior and temperature-independent characteristic. Temperature-dependent structural analysis suggested that the good energy-storage properties insensitive to temperature can be ascribed to the stable relaxor pseudocubic (antiferroelectric-like) phase over a wide temperature range. These results indicate that BNKT100*y*–*x*KNN system should be a promising lead-free material for energy-storage capacitor application.

1. Introduction

High-energy storage materials are urgently needed in a large variety of applications such as electrical vehicles, mobile electronics and different types of pulsed power technologies [1,2]. Antiferroelectric (AFE) materials undergoing a reversible transition between the antiferroelectric and ferroelectric states under an alternating electric field [3,4] are currently used in energy storage applications [5–9], due to the small remanent polarization and large charge–discharge displacements compared with conventional dielectrics. However, AFE materials that have been extensively studied are mostly lead-based, such as, $Pb(Zr,Ti)O_3$ (PZT), $Pb(Zr,Sn,Ti)O_3$ (PZST) and $(Pb,La)ZrO_3$ (PLZ) [7–9]. With the highlights of the global environmental problems, environment-friendly materials will become the mainstream demand for future development [10,11].

As a lead-free piezoelectric material, $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT) with strong ferroelectric properties draws considerable attention in recent years [12]. BNT has a ferroelectric (FE) rhombohedral structure at room temperature (RT) [13] and shows an AFE-like behavior (the so-called "AFE" phase of BNT does not actually exist because no corresponding crystallographic evidence was found in the *in situ* TEM study [14]; recently, it has been clarified with a "non-polar" phase [15], which is an ergodic relaxor state [15,16]) at its depolarization temperature T_d of ~220 °C, where constricted hysteresis loops appear, while for pure BNT ceramics, the excellent ferroelectric properties with large remanent polarization P_r at RT are not a satisfactory characteristic for its application in energy storage. Therefore, to design BNT-based energy storage materials, it is desirable to shift the T_d down to or below RT and thus obtain the AFE-like phase at RT. Recently, Zhang et al. lowered the transition temperature T_d by introducing $(K_{0.5}Na_{0.5})NbO_3$ (KNN) and $BaTiO_3$ (BT) into BNT system and obtained AFE featured materials at RT with "slanted" *P*–*E* hysteresis loops [17,18]. Our recent studies [19,20] demonstrated that components $(Bi_{0.5}K_{0.5})TiO_3$ (BKT) and KNN intrinsically changed the structural nature of the BNT-based system with the shift of MPB from MPB(I) between FE rhombohedral and FE tetragonal phases to MPB(II) between FE rhombohedral and AFE-like (relaxor pseudocubic) phases as shown in Fig. 1. Near MPB(II), a significant jump of electric-filed-induced strain was achieved due to emergence of AFE-like phase and the shift of T_d down to room temperature.

AFE materials with "square" shaped hysteresis loops generally possess higher energy density than those with "slanted" ones. However, it is very difficult for AFE materials with "square" hysteresis loops to withstand over several hundred charge–discharge circulations because it is often cracked due to the phase transition during the charge–discharge process. Therefore, more

* Corresponding author. Tel./fax: +86 635 8230923.
E-mail address: zhjxu@lcu.edu.cn (Z. Xu).

http://dx.doi.org/10.1016/j.ssc.2014.12.004
0038-1098/

"slanted" hysteresis loops and smaller area of hysteresis loops will be helpful to the charge–discharge circulations [21]. Based on the above, to develop the BNT-based materials for energy storage application, it is desirable to design kinds of materials with "slanted" hysteresis loops. Motivated by the above consideration, we designed a series of compositions which lie deep in the peudocubic region based on ternary BNT – BKT – KNN system, as indicated in the phase diagram of this system (Fig. 1). The energy-storage properties of lead-free BNT – BKT – KNN ceramics with AFE-like phase were studied to unveil its potential for energy-storage application.

2. Experimental

$(1\text{-}x)[(1\text{-}y)(Bi_{0.5}Na_{0.5})TiO_3\text{–}y(Bi_{0.5}K_{0.5})TiO_3]\text{–}x(K_{0.5}Na_{0.5})NbO_3$ (abbreviated as BNKT100y–xKNN, series 1, $y=0$, $x=0.10$–0.20; series 2, $y=0.20$, $x=0.10$–0.20) was prepared by a conventional ceramic fabrication process [20]. The crystal structures of the sintered ceramics were determined by X-ray powder diffraction analysis (XRD) (D8 Advance, Bruker Inc., Germany). For the temperature-dependent structural analysis, a reflective XRD apparatus (Bruker D8 Advance) equipped with a furnace was used. The surface morphology of the ceramics was studied by a scanning electron microscope (SEM) (JSM-5900, Japan). For the electrical measurements, silver paste was coated on both sides of the sintered samples and fired at 740 °C for 20 min to form electrodes. The electric-field-induced polarization (P–E) measurements were carried out using an aix-ACCTTF2000FE-HV ferroelectric test unit (aix-ACCT Inc., Germany).

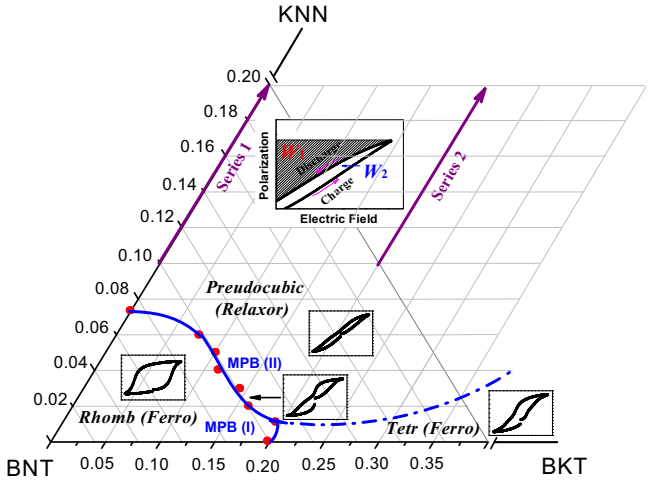

Fig. 1. (Color online) Phase diagram of ternary BNT–BKT–KNN system reported in our recent work [18] and the designed compositions in this study based on the system (inset shows schematic calculation of energy-storage density W_1 and energy loss W_2).

3. Results and discussion

The inset of Fig. 1 shows schematic calculation of energy-storage density W_1 and energy loss W_2. The energy-storage density W_1 is obtained by integrating the area between the polarization axis and the discharge curve of the unipolar P–E hysteresis loops using the equation $W1 = \int EdP$. The energy loss density W_2 caused by the domain reorientation is calculated by integrating the area between the charge and discharge curve of the unipolar P–E hysteresis loops [22]. From the inset of Fig. 1, it is well recognized that the ferroelectrics should be characterized with large saturation polarization P_s, low remanent polarization P_r, and high electric break-down field E_b to achieve a high energy-storage density W_1.

XRD analyses of the sintered and then crushed samples of BNKT100y–xKNN ($y=0$, 0.20; $x=0.10$–0.20) ceramics as presented in Fig. 2(a) show a single perovskite structure without apparent trace of secondary phases. All the peaks could be indexed based on a peudocubic perovskite structure as evident by the undetected splitting of any of the peaks [23], confirming the designed compositions are in the peudocubic region of the ternary BNT – BKT – KNN system. Fig. 2 (b) and (c) provides micrographs of the BNKT100y–xKNN [(b) $y=0$, $x=0.16$; (c) $y=0.20$; $x=0.16$] ceramic representing the typical microstructure observed throughout all the compositions. The microstructure appears homogeneous and almost fully dense without any apparent second phase. By applying the Archimedes method, all samples have a large relative density of $>95\%$.

Fig. 3 shows the P–E hysteresis loops of the BNKT100y–xKNN ceramics with (a) $y=0$, $x=0.10$–0.20 and (b) $y=0.20$; $x=0.10$–0.20. The BNKT100y–xKNN ceramic ($y=0$, 0.20; $x=0.10$) exhibits constricted hysteresis loop, suggesting that the long-range FE order

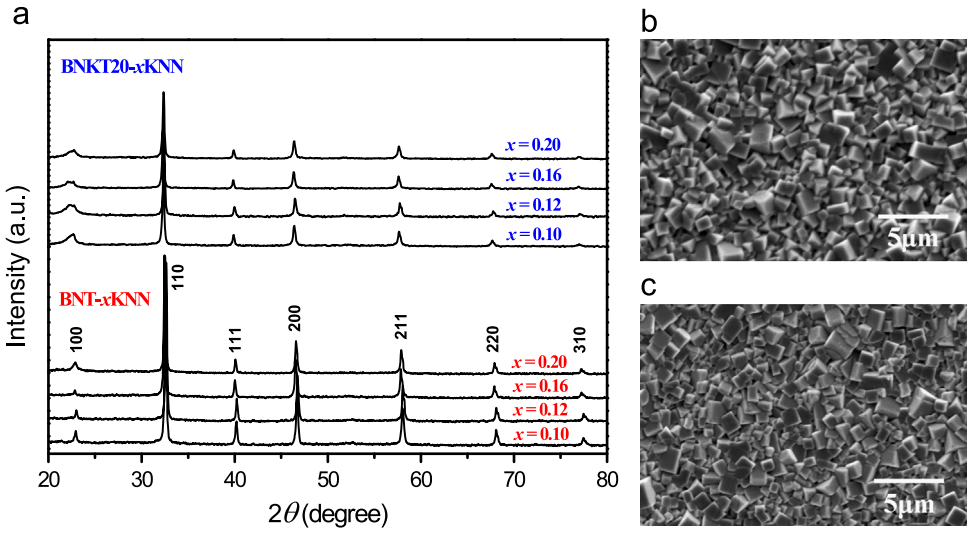

Fig. 2. (Color online) (a) XRD patterns of the BNKT100y–xKNN ($y=0$, 0.20; $x=0.10\sim0.20$) ceramics, (b), (c) micrographs of the BNKT100y–xKNN with $y=0$, $x=0.16$ and $y=0.20$; $x=0.16$.