



Li-modified Ba_{0.99}Ca_{0.01}Zr_{0.02}Ti_{0.98}O₃ lead-free ceramics with highly improved piezoelectricity



Yong Zhang^{a, b}, Hua-Jun Sun^a, Wen Chen^{a, *}

^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, School of Materials Science and Engineering, Wuhan University of Technology, Wuhan, 430070, PR China

^b Department of Materials Science and Engineering, The Pennsylvania State University, University Park, PA, 16802, USA

ARTICLE INFO

Article history:

Received 7 August 2016

Received in revised form

6 October 2016

Accepted 7 October 2016

Available online 8 October 2016

Keywords:

BCZT

Lead-free ceramics

Li⁺ ion doping

Microstructure

Electrical properties

ABSTRACT

In this paper, Ba_{0.99}Ca_{0.01}Zr_{0.02}Ti_{0.98}O₃ lead-free ceramics with highly enhanced piezoelectricity have been obtained at an optimized Li⁺ ion doping content by means of elaborately adjusting the microstructure. The introduction of Li⁺ ions significantly improves the sinterability due to the emergence of oxygen vacancies and the formation of eutectic liquid phase. The sintering temperature is reduced by 100–150 °C compared with other literatures. The highest piezoelectric coefficient d_{33} and planar mode electromechanical coupling factor k_p can be increased up to 340 pC/N and 44%, which are stem from outstanding ferroelectric activity ($P_r = 9.8 \mu\text{C}/\text{cm}^2$, $E_c = 220 \text{ V}/\text{mm}$) and dielectric property ($\epsilon_r = 2250$, $\tan \delta = 1.35\%$). In addition, the Curie temperature T_c is still maintained about 120 °C. A plausible mechanism concerning the defect dipoles, polarization rotation, and ferroelectric phase transition is constructed in this work to well state above mentioned phenomena.

© 2016 Elsevier B.V. All rights reserved.

1. Introduction

According to the difference of crystal structure, piezoelectric ceramics could be divided into four major categories: Perovskite structure, tungsten-bronze structure, bismuth layer structure, and pyrochlore structure ceramics. Among these, perovskite ABO₃ structure ceramics especially attracted people's attention since last several decades. As a distinguished representative, lead-zirconate-titanate (Pb(Zr_{1-x}Ti_x)O₃ or PZT) based system almost dominates the piezoelectric material's various applications, such as pulse power capacitors, sensors, actuators, ultrasonic transducers, energy harvesters, and so on [1–5]. However, as the exponential booming of the use of lead-based electronic components, the pollution derived from toxic elements gradually becomes a thorny issue. Thus, the research on the lead-free ceramics was carried out vigorously based on this background [6].

So far, the widely studied lead-free piezoelectrics can be categorized into three main families: (1) K_{0.5}Na_{0.5}NbO₃ (KNN), (2) Na_{0.5}Bi_{0.5}TiO₃ (NBT), and (3) BaTiO₃ (BT) [3,7–9]. Each system has its unique advantages and features. For the KNN system, it exhibits very high Curie temperature ($T_c = 420 \text{ °C}$), good ferroelectric

properties ($P_r = 33 \mu\text{C}/\text{cm}^2$), and large electromechanical coupling factors [10]. However, the relatively low piezoelectric coefficient, $d_{33} \sim 80 \text{ pC}/\text{N}$, and difficulties in fabrication impede its development as a commercial piezoelectric material [11]. NBT is also considered as a promising lead-free alternative due to its strong ferroelectric properties of a large remnant polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) and high Curie temperature ($T_c = 320 \text{ °C}$). The main drawback lies on that the poling process of this material is not easy to proceed, due to its high conductivity. As the earliest discovered lead-free piezoelectric ceramic system, BT has a relatively high electromechanical coupling factor and highest piezoelectric coefficient ($d_{33} \sim 190 \text{ pC}/\text{N}$). Yet, the low Curie temperature ($T_c = 120 \text{ °C}$) restricts its actual usage temperature range [10].

In recent years, BaTiO₃-based lead-free system has aroused wide concern among the people since the report of a surprisingly high piezoelectric coefficient of $d_{33} \sim 620 \text{ pC}/\text{N}$ (the composition is Ba(Ti_{0.8}Zr_{0.2})O₃-(Ba_{0.7}Ca_{0.3})TiO₃) [12]. The excellent piezoelectric property could be attributed to the proximity of morphotropic phase boundary to the tricritical triple point. However, the relatively low Curie temperature ($\sim 93 \text{ °C}$) and high sintering temperature (1450–1500 °C) dramatically restrict its practical applications [13–15]. So, in order to push BaTiO₃-based lead-free system towards better real-life application, three main requirements (gratifying electrical property, a relatively high Curie temperature and

* Corresponding author.

E-mail address: chenw@whut.edu.cn (W. Chen).

lowest possible sintering temperature) should be satisfied. Until now, worldwide researchers have devoted much effort on this issue (seeking for a comparatively better conjunction among these three key requests) and some delightful achievements have been obtained in succession [16–18].

In this paper, we would also like to report our research results on this issue, hoping to accelerate the practical process of BaTiO₃-based lead-free ceramics. Li⁺ ions were intentionally introduced into Ba_{0.99}Ca_{0.01}Zr_{0.02}Ti_{0.98}O₃ to reduce the sintering temperature and facilitate the densification process. Meanwhile, to clarify the origin of Li-doping induced improvement of piezoelectricity and sinterability, the piezoelectric, dielectric, ferroelectric properties, and microstructure evolution were well characterized to illustrate its favorable effects.

2. Experimental details

In this work, the ceramics were fabricated by the traditional solid state technique. All the starting materials (including BaCO₃, CaCO₃, ZrO₂, TiO₂ and LiF) were supplied by Sinopharm Chemical Reagent Co., Ltd and used as received. First, the raw materials were weighted precisely according to the designed composition of Ba_{0.99}Ca_{0.01}Zr_{0.02}Ti_{0.98}O₃ and placed in a polyethylene jar. The planetary ball milling process (deionized water was chosen as the liquid medium) was proceeded for 12 h to thoroughly mix the raw powders. Then, the obtained slurry was dried at 80 °C convection oven for one day to remove the moisture and subsequently calcined at 1100 °C for 4 h. Thereafter, LiF was introduced into the pre-sintered powders and planetary ball milled for another 12 h. The acquired viscous liquid was dried and mixed sufficiently with 5 wt% polyvinyl alcohol (PVA) organic binder solution. Last, the granular powder was compressed into disks (diameter: 10 mm, thickness: 1 mm) and sintered at 1250 °C for 4 h to form ceramics. All the ceramics were shaped into disks with the same thickness (0.3 mm) before electrical characterization. For the measurement of electrical properties, both sides of the ceramics were coated with silver paste.

Various facilities were employed to characterize the phase structure, morphology and electrical properties. Bulk densities of the sintered ceramics were measured by the Archimedes method. XRD patterns (Cu K α radiation, PANalytical X'Pert PRO, Holland) were recorded to examine the crystalline structure. Sample's surface was well polished before phase structure analysis. The Rietveld analysis of the XRD pattern was done by FULLPROF software package (MDI Jade 2010). Field emission scanning electron microscope (FE-SEM, Hitachi S-4800) was used to reveal the microstructure. For better observation effect, a thin layer of gold (~10 nm) was pre-deposited on the surface. Dielectric and ferroelectric properties were recorded by the dielectric/impedance analyzer (Novocontrol, Germany) and a Radiant Precision Workstation with Sawyer Tower Circuit (Radiant Technologies, USA), respectively. The piezoelectric coefficient d_{33} was characterized using a quasi-static piezoelectric coefficient testing meter (ZJ-3A, Institute of Acoustics, Chinese Academy of Sciences, China). The planar mode electromechanical coupling factor k_p was calculated by a resonance-anti-resonance method using an 4294A impedance analyzer. Prior to the measurement of piezoelectric performance, all the ceramics were polarized by a DC voltage source (3.5 kV/mm) for 40 min and then left in ambient environment for one day.

3. Results and discussion

Fig. 1 depicts the XRD patterns of Ba_{0.99}Ca_{0.01}Zr_{0.02}Ti_{0.98}O_{3-x} mol % Li (BCZT-xLi, $x = 0, 0.4, 0.8, 1.2, 2.0$ and 4.0) ceramics which are all sintered at 1250 °C. It is observed that no obvious secondary impurity phase could be traced within the sensitivity of the

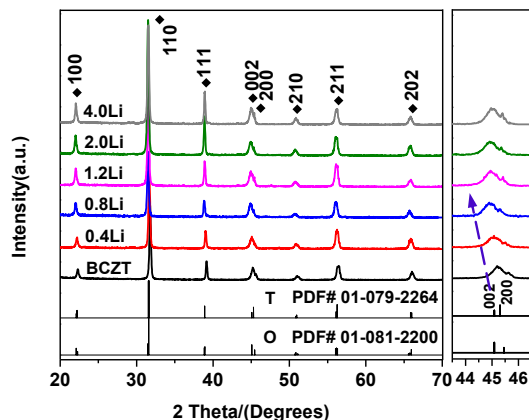


Fig. 1. XRD patterns of BCZT- x mol% Li ($x = 0, 0.4, 0.8, 1.2, 2.0$ and 4.0) ceramics sintered at 1250 °C.

instrument, indicating that Li⁺ ions have diffused into BCZT lattices to form a homogeneous solid solution. A region (ranged from 43.5 to 46.5°) is magnified to illustrate the lattice expansion phenomenon. Two peaks indexed as (002) and (200) locate within this region. The splitting and intensity ratio of these two reflections are considered as the coexistence of tetragonal and orthorhombic phases in different proportions depending on the composition [19]. As can be seen, the right side (200) becomes stronger with the increase of Li⁺ content, confirming a composition-dependent phase evolution from orthorhombic to tetragonal phase [17]. The phase fractions between orthorhombic and tetragonal phase are calculated from the XRD patterns (by Rietveld refinement) and presented in Fig. 2. As can be seen, the proportion of tetragonal phase increases with the increase of x . The coexistence of these two ferroelectric phases has also been reported by other researchers [11,20]. For example, Zhang et al. and Xiao et al. illustrated the phase existence of a tetragonal and an orthorhombic phase for KNN-LS ceramics and BT ceramics, respectively. The Rietveld analysis of the sample ($x = 0.8$) was shown in the inset of Fig. 2. As can be seen, the XRD patterns measured and calculated for the sample fitted well, revealing a good refinement quality.

With increasing Li⁺ content, the reflection peaks shift toward lower angle gradually. To the best of our knowledge, this phenomenon could be elaborated from three different aspects. The first

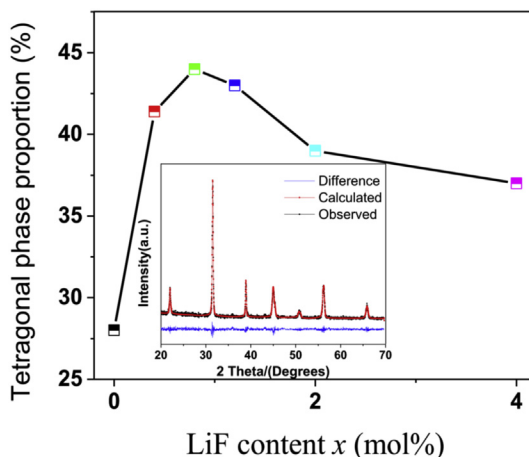


Fig. 2. Tetragonal phase proportion as a function of LiF content (the inset is the Rietveld Refinement of the sample of $x = 0.8$).

Download English Version:

<https://daneshyari.com/en/article/5460968>

Download Persian Version:

<https://daneshyari.com/article/5460968>

[Daneshyari.com](https://daneshyari.com)