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Ceramics International 39 (2013) S35–S39

CERAMICS INTERNATIONAL

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Influence of Ca substitution on microstructure and electrical properties of $Ba(Zr,Ti)O_3$ ceramics

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Available online 16 October 2012

Abstract

In the present work, lead-free $(Ba_{1-x}Ca_x)(Zr_{0.04}Ti_{0.96})O_3$ ($x=0.00$–0.09) ceramics were fabricated via a solid-state reaction method. The microstructure and electrical properties of the ceramics were investigated. The microstructure of the BCZT ceramics showed a core shell structure at compositions of $x=0.03$ and 0.06. The substitution of small amount of Ba^{2+} by Ca^{2+} resulted in an improvement of the piezoelectric, dielectric and ferroelectric properties of the ceramics. The orthorhombic–tetragonal phase transition was found in the composition of $x \leq 0.03$. Piezoelectric coefficient of $d_{33} \sim 392$ pC/N and lowest $E_c \sim 3.3$ kV/cm with highest $P_r \sim 14.1$ μC/cm^2 were obtained for the composition of $x=0.03$ while its Curie temperature (T_C) was as high as 125 °C. However, the ferroelectric to paraelectric transition temperature had slightly shifted towards room temperature with increasing Ca^{2+} concentration.

Keywords: C. Dielectric properties; C. Diffusion; C. Piezoelectric properties

1. Introduction

For a half century, Pb-based piezoelectric ceramics, such as lead zirconium titanate [$PbTiO_3$–$PbZrO_3$ (PZT)], have dominated the field of piezoelectric ceramics worldwide. However, the volatilization of PbO during processing and the waste products containing Pb cause a series of environmental problems. For this reason, numerous researchers have been developing a number of lead-free piezoelectric ceramics to substitute the Pb-based ceramics.

Ferroelectric, dielectric and piezoelectric properties of barium zirconium titanate, $BaZr_xTi_{1-x}O_3$ (BZT), a classical perovskite-type compound, has been extensively studied fundamentally and as a material for applications in electronic devices.

Recently, many researchers have reported that the substitution of Ca^{2+} to replace Ba^{2+} in $Ba_{1-x}Ca_xTiO_3$ solid solutions can cause a slight change in T_C, but has strongly lowered the orthorhombic to tetragonal T_{O-T} transition temperature, which is of great value in improving the temperature stability of piezoelectric materials for many practical applications [1,2]. Liu et al. [3] reported that a high piezoelectric coefficient (d_{33} about 300–600 pC/N) was achieved in Ca doped BZT ceramics. Unfortunately, their optimal composition with high d_{33} values exhibited a low T_C (93 K), which limited their use in real applications.

In order to obtain excellent piezoelectric properties and a high T_C, we redesigned the $(Ba_{1-x}Ca_x)$ $(Zr_{0.04}Ti_{0.96})O_3$ (BCZT) system. The effect of Ca doping on the structure, microstructure, dielectric, piezoelectric and ferroelectric properties of the BCZT lead-free ceramics were systematically studied.

2. Experimental procedure

The $(Ba_{1-x}Ca_x)(Zr_{0.04}Ti_{0.96})O_3$ (BCZT) ceramics for $x=0.00$, 0.03, 0.06 and 0.09 were prepared via a solid state reaction method. High purity ($>99.0\%$) powders of $BaCO_3$, $CaCO_3$, ZrO_2 and TiO_2 were mixed, dried and calcined at 1200 °C for 4 h. After that, the calcined powders were pressed into pellets of 10 mm diameter and the pellets were sintered between 1300 and 1450 °C for 4 h. The phase identification and density of the BCZT ceramic samples were investigated using X-ray diffraction (XRD)

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http://dx.doi.org/10.1016/j.ceramint.2012.10.031

and Archimedes' method. Scanning electron microscope (SEM) and energy dispersive spectroscopy (EDS) were used to observe the surface microstructures and quantitative element analysis of selected sintered ceramics with maximum density. The linear intercept method was used to estimate the grain size of ceramics. The dielectric constant (ε_r) and dielectric loss (tan δ) of the samples were measured at 1 kHz for various temperatures from room temperature to 250 °C using a LCZ meter. Polarization and strain were measured as a function of electric field by using a Sawyer–Tower circuit. The ceramic samples were polled in a silicone oil bath at 40 °C at 3 kV/cm for 20 min and the piezoelectric properties were measured at room temperature by using a piezoelectric-d_{33}-meter.

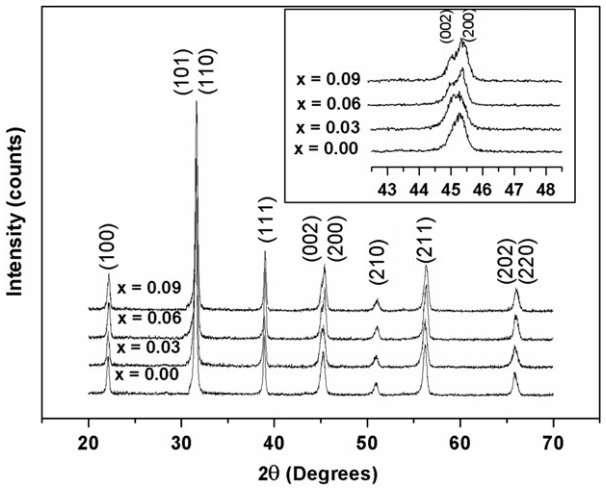

Fig. 1. XRD patterns at 2θ ranging from 20°–70° and inset: a reduced range for 43°–48° of BCZT ceramics.

3. Results and discussion

The XRD patterns for 2θ ranging from 20°–70° and smaller range of 43°–48° for the BCZT ceramics with different compositions are shown in Fig. 1. All of the ceramics show patterns suggesting that Ca and Zr diffuse into the $BaTiO_3$ lattices during sintering to form a solid solution of highly pure perovskite structure. At room temperature, the BCZT ceramic for $x=0.00$ possessed orthorhombic structure seen as a single peak of the (200) between 2θ of 43–48°. It is also noticed that ceramics with $x=0.03$ possess a mixture of orthorhombic and tetragonal structure. When Ca was added ≥ 0.06, BCZT ceramics showed a tetragonal structure, with splitting of (002)/(200) peaks between 2θ of 43°–48°.

The SEM micrographs of the BCZT ceramics are shown in Fig. 2. As can be seen here, samples with a high density and low porosity are obtained from solid state reaction method. However, it was found that the core-shell could be observed at compositions of $x=0.03$ and 0.06. Also, the addition of Ca inhibited grain growth as shown in Fig. 2b and c for the SEM and EDS of the BCZT ceramics with $x=0.03$ and 0.06. The Zr-rich phase with a trace of Ca noticeably occurred at the grain boundary as confirmed by EDS, which led this phase to form the core-shell structure. However, the XRD could not detect the phase of these core shells which may be due to the very small amount of this phase in the ceramic samples.

Fig. 3 shows the temperature dependence of the dielectric constant and dielectric loss for the BCZT ceramics at 1 kHz. The BCZT ceramics for $0.00 \leq x \leq 0.03$ display two obvious polymorphic phase transitions corresponding to the orthorhombic to tetragonal (T_{O-T}) and tetragonal to

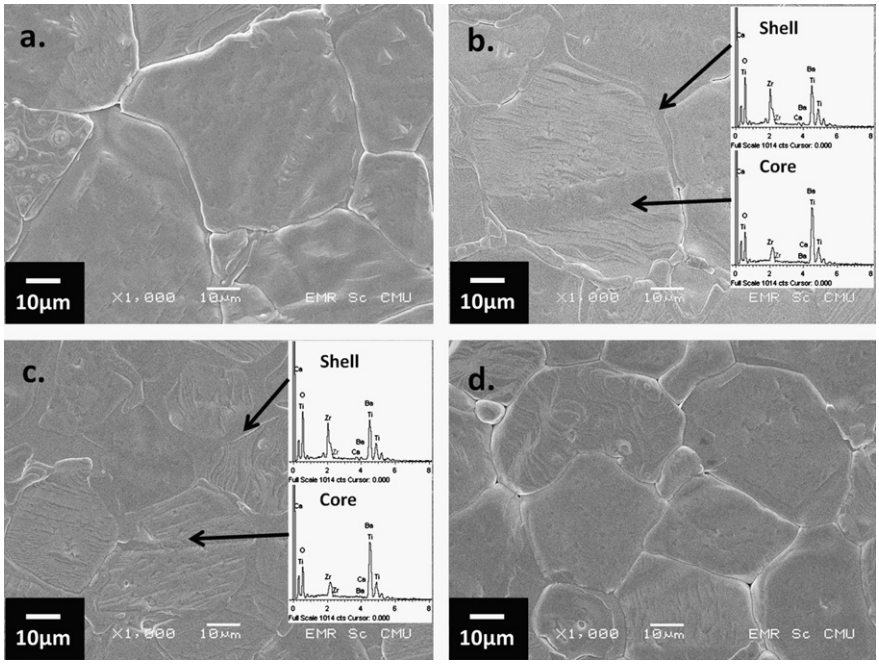

Fig. 2. The SEM and EDS of the BCZT ceramics: (a) $x=0.0$, (b) $x=0.03$, (c) $x=0.06$, and (d) $x=0.09$.