Journal of the European Ceramic Society xxx (xxxx) xxx–xxx

Contents lists available at ScienceDirect

Journal of the European Ceramic Society

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

Original Article

Influence of $K_{0.5}Bi_{0.5}TiO_3$ on the structure, dielectric and ferroelectric properties of $(Ba,Ca)(Zr,Ti)O_3$ ceramics

Mohammed N. Al-Aaraji[a,b,*], David A. Hall[a]

[a] School of Materials, University of Manchester, M13 9PL, Manchester, UK
[b] Ceramics and Construction Materials Department, College of Materials Engineering University of Babylon, Al Hillah, Iraq

ARTICLE INFO

Keywords:
Lead-free ceramics
Ferroelectric
Core-shell
Relaxor
Dielectric

ABSTRACT

A new lead-free ferroelectric solid solution between $(Ba,Ca)(Zr,Ti)O_3$ (BCZT) and $K_{0.5}Bi_{0.5}TiO_3$ (KBT) has been systematically investigated in terms of its phase transformations, microstructure, dielectric and ferroelectric properties. The incorporation of KBT into BCZT was found to enhance the sintering behavior, although secondary phases of $K_4Ti_3O_8$ and $BaBi_4Ti_4O_{15}$ were detected at high KBT contents. Chemical heterogeneity was also observed in the form of core-shell grain structures comprising tetragonal ferroelectric BCZT-rich cores with pseudo-cubic relaxor ferroelectric KBT-rich shell regions. Temperature-dependent dielectric property measurements revealed that the BCZT-KBT ceramics exhibited both normal and relaxor ferroelectric behaviour simultaneously, associated directly with the core-shell structure. Ferroelectric hysteresis measurements indicated that the remanent polarisation and coercive field were strongly dependent on KBT content. In common with other lead-free relaxor ferroelectrics, increasing temperature led to the formation of constricted polarisation-electric field hysteresis loops, indicating the occurrence of a reversible electric field-induced nanopolar to long-range ordered ferroelectric state.

1. Introduction

Lead zirconate titanate, abbreviated Pb(Zr, Ti)O_3 or PZT, still represents one of the most important categories of ferroelectrics, despite its long history of use over more than a half century. It is widely used in applications such as electro-mechanical actuators, sensors, ultrasonic transducers and electro-optic devices [1,2]. PZT ceramics possess outstanding ferroelectric, piezoelectric and pyroelectric properties. However, the high content of lead, which is well-known for its toxicity, has created a strong desire in recent years to remove lead oxide as a component of piezoelectric ceramic products [3–6]. Therefore, it is necessary to develop new lead-free piezoelectric ceramics in order to substitute PZT in certain applications [7,8]. The main candidate ceramic materials for this purpose are based on $(K_{0.5}Na_{0.5})NbO_3$ (KNN), $BaTiO_3$ (BT), and $(Bi_{0.5}Na_{0.5})TiO_3$ (BNT). Many investigations have been conducted on the synthesis and properties of these materials as pure compounds, modified by minor dopants, or in the form of solid solutions with other ABO_3 perovskites [4,9].

Barium titanate-based solid solutions modified with calcium and zirconium oxides, abbreviated as BCZT have attracted attention in recent years due to their promising piezoelectric properties. Therefore, they represent one of the most promising candidates for lead-free piezoceramic materials [5,10,11]. It was reported by Srinivas that the BCZT, $(Ba_{0.85}Ca_{0.15})(Zr_{0.1}\ Ti_{0.9})O_3$, ceramic exhibits a piezoelectric charge coefficient, d_{33}, in the region of 600 pC/N at room temperature, albeit with a low Curie temperature of just 85 °C. It was prepared by the conventional solid state reaction method using a sintering temperature of 1500 °C [12]. The high piezoelectric coefficient (d_{33}) of this composition is attributed to the coexistence of rhombohedral and tetragonal phases. It is reported that the high piezoelectric activity in such materials is found in the region of the morphotropic phase boundary (MPB) and is associated with enhanced ferroelectric domain wall mobility [13,14].

The significance of the R-T phase transformation in the MPB region was also recognised by Tian, who investigated the effects of Ca content on the phase transition and electrical properties of the system $(Ba_{1-x}Ca_x)(Zr_{0.1}\ Ti_{0.9})\ O_3$ [15]. Keeble identified an intermediate orthorhombic phase for the same composition, which was found to occur over narrow ranges of composition and temperature [16]. The high piezoelectric response of BCZT ceramics was reported by Sutapun, who investigated the phase boundary between rhombohedral and tetragonal phases for the solid solution $0.87BaTiO_3$–$(0.13\text{-}x)BaZrO_3$–$xCaTiO_3$ at x = 0.06 [14].

On the other hand, it should be recognised that the functional

* Corresponding author at: School of Materials, University of Manchester, M13 9PL, Manchester, UK.
E-mail address: mohammed.al-aaraji@manchester.ac.uk (M.N. Al-Aaraji).

https://doi.org/10.1016/j.jeurceramsoc.2017.12.063
Received 14 November 2017; Received in revised form 27 December 2017; Accepted 31 December 2017

properties of BCZT ceramics are affected significantly by temperature-instability, due to the occurrence of the polymorphic phase transformations, and a relatively low Curie temperature. The need for high sintering temperatures for densification of BCZT is also a serious concern, particularly when considering the compatibility with typical electrode and substrate materials used in thick film fabrication.

It has been proposed that the incorporation of bismuth-based perovskite compounds, such as $BiFeO_3$ (BF) and $Bi(Mg_{0.5}Ti_{0.5})O_3$ (BMT) into BCZT could both reduce the temperature-stability of properties and enhance the densification behavior during sintering. Bai observed that incorporation of BMT into BCZT increases the Curie temperature (T_C) to a maximum value of 218 °C for the composition 0.4BCZT-0.6BMT [17]. Similarly, Yi investigated (1-x)BF-(x)BCZT solid solutions and reported that the crystal structure transformed from rhombohedral to pseudo-cubic with increasing x. The morphotropic phase boundary was found to be located in the composition range $0.2 \leq x \leq 0.30$. This composition range was also characterized by relatively large grain sizes and Curie temperatures between 380 and 450 °C [18].

Recently, Cai [19] investigated the influence of the tetragonally-distorted perovskite ferroelectric $(K_{0.5}Bi_{0.5})TiO_3$ (KBT) on the structural and electrical properties of $(Ba_{0.85}Ca_{0.15})(Ti_{0.93}Zr_{0.07})O_3$ (BCZT), for KBT contents up to 8 mol%. The ceramics were prepared by conventional solid state reaction method with a sintering temperature of 1280 °C. It was reported that the composition 0.96BCZT-0.04KBT exhibits promising ferroelectric and piezoelectric properties, but there was no singnificant change in the Curie temperature. Yuan also found that KBT was an effective additive to enhance the sintering behaviour of undoped barium titanate ceramics [20].

There are currently no reports on the properties of BCZT-KBT solid solutions for KBT contents greater than 8 mol%., although it is anticipated that useful functional properties could be obtained by tailoring the ratio of these two ferroelectric perovskites. Intermediate compositions in the BCZT-KBT system could potentially combine the high Curie temperature of KBT (~380 °C) with the high piezoelectric activity of BCZT, whilst avoiding drawbacks such as problems in the processing of KBT ceramics and the low T_C of BCZT.

The aim of this investigation was to develop new lead-free piezoelectric materials with high performance and high Curie temperature from (1-y)$BCZT_x$-(y)KBT solid solutions. Two BCZT compositions were investigated in the ternary system of $0.87BaTiO_3$–(0.13-x)$BaZrO_3$–$xCaTiO_3$ (abbreviated $BCZT_x$) having two different Ca/Zr contents (x = 0.02, 0.06), prepared by solid state reaction and conventional sintering. The first composition ($x = 0.02$, Ca/Zr = 0.18) was located in the orthorhombic region whereas the second one ($x = 0.06$, Ca/Zr = 0.86) was near to the orthorhombic (O)-tetragonal (T) phase boundary. Both of these BCZT ceramics were prepared in the unmodified form and with additions of KBT up to 65 mol%. The evolution from normal ferroelectric to relaxor behaviour with increasing KBT content is discussed in the context of the observed core-shell type microstructures.

2. Experimental procedures

Two BCZT solid solutions, corresponding to the formula $0.87BaTiO_3$–(0.13-x)$BaZrO_3$–$xCaTiO_3$ (abbreviated $BCZT_x$) with $x = 0.02$ and 0.06, were prepared in the form of polycrystalline ceramics using the solid state reaction method. Barium carbonate ($BaCO_3$), calcium carbonate ($CaCO_3$), titanium dioxide (TiO_2), and zirconium oxide (ZrO_2) having > 99% purity were used as raw materials. Starting powders were weighed according to the chemical formula of the selected compositions. They were vibro-ball milled with propan-2-o1 for 24 h using zirconia balls as milling media. After drying, the mixed powders were calcined at 1300 °C for 4 h in a covered alumina crucible.

In parallel, a pure $K_{0.5}Bi_{0.5}TiO_3$ powder was prepared using potassium carbonate (K_2CO_3), bismuth oxide (Bi_2O_3) and titanium dioxide (TiO_2) having > 99% purity as raw materials. After weighing, ball-milling and drying of powders, the mixture was calcined at 950 °C for 4 h.

Thereafter, the calcined powders of BCZT in both compositions were mixed separately with different contents of KBT according to the formula (1-y)BCZTx-(y)KBT, with $y = 0$, 0.1, 0.35, 0.50, 0.65 and 1.00. Then, the mixed powders were ball-milled for 4 h. The powder mixtures were dried and mixed with 2 wt% polyethylene glycol (PEG) as a lubricant and binder. Afterwards, the mixed calcined powders including binder were uniaxially pressed in a cylindrical steel die into pellets, 10 mm diameter with around 1.5 mm thickness, under a pressure of 35 MPa for 40 s. The pellets were embedded in calcined powders from the same compositions and heat treated at different temperatures in the range between 1125 °C and 1500 °C for 3–4 h, depending on KBT content, to produce the sintered ceramics. This experimental route follows procedures similar to those employed by Yuan [20].

The bulk density of the sintered samples was measured by the Archimedes method using water as the immersion medium. Phase analysis of sintered pellets was achieved by x-ray diffraction (XRD) using a Philips PANalytical X'Pert-Pro with CuKα radiation having a wavelength of 1.54060 Å. The detection range was 10–80 °2θ with a step size of 0.0167° at room temperature. The surfaces of sintered samples were ground using 1200-grade SiC papers. Then, the samples were annealed at 500 °C for 30 min to eliminate any residual stress that could be induced during preparation. Microstructures of polished and carbon-coated surfaces of sintered samples were characterised by scanning electron microscopy (Philips XL30 FEG-SEM). For electrical measurements, the surfaces of the sintered samples were ground using a similar method to that employed for the XRD samples, to obtain parallel and smooth faces. Then, they were coated with silver paste (C2000107P3, Gwent Electronic Materials) as electrodes. Afterwards, the painted samples were dried in an oven at around 85 °C for 20 min for each face and then heat treated at 550 °C for 30 min to densify the electrodes and ensure good contact with the ceramic surfaces.

The *low-field* dielectric properties of the sintered samples were studied as functions of both temperature and frequency using an automated dielectric measurement system. The computer-controlled dielectric measurement system consists of an LCR-meter (Hewlett-Packard Precision LCR Meter, HP 4284A) connected to the electroded sample by pure silver probes. Samples were heated in a furnace with a heating rate of 2 °C min^{-1}. The parallel capacitance (C_p) and the dielectric loss tangent (tan δ) were determined over the temperature range from 25 to 350 °C, using measurement frequencies from 100 Hz to 100 kHz. *High-field* polarization-electric field (P-E) ferroelectric hysteresis measurements were made using a system based on a HP33120A function generator (Hewlett-Packard, Palo Alto, CA) in conjunction with an HVA1B high voltage amplifier (Chevin Research, Otley, UK) [21]. A burst-mode waveform comprising 4 sinusoidal cycles was employed, with a maximum electric field level up to 6 MV m^{-1}. The samples were immersed in silicone oil during these measurements to avoid electrical arcing.

3. Results and discussion

3.1. Density

The temperatures employed for sintering each composition were determined empirically based on the results of bulk density measurements, as shown in Table 1. The theoretical densities were calculated on the basis of the nominal chemical compositions and the lattice parameters determined from full pattern refinement of the XRD patterns using *Topas* software version 5.0 [22]. Thereafter, the relative densities were calculated, yielding values greater than 92%. It is evident that the required sintering temperatures decreased with increasing KBT content and were greatly reduced (by almost 400 °C), in comparison with pure BCZT ceramics, for the composition with 65% KBT. It has been reported by many researchers that the sinterability of BT-based ceramics at low temperatures can be effectively improved by using single component