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Preparation and characterization of ceramic nanocomposites in the PZT–BT system

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Abstract

Nanocomposites of the $(1-x)$PZT-xBT system were fabricated by the bimodal particle concept. The effect of fabricating conditions on structural characteristics and dielectric properties of the ceramics was investigated using XRD, SEM, and a standard dielectric measurement. The ceramic–solid solutions and -nanocomposites in the PZT–BT system were comparatively explored. It was clearly seen that the microstructures and the dielectric properties of PZT–BT ceramic-nanocomposites are totally different from those of ceramic–solid solutions. The dielectric behavior of ceramic-nanocomposites displayed superimposition of two phase transitions with a lower maximum value of the dielectric constant than that of the solid solutions.

Keywords: B. Nanocomposites; C. Dielectric properties; D. PZT; BT

1. Introduction

Piezoelectric ceramics (e.g. $Pb(Zr_x,Ti_{(1-x)})O_3$, $BaTiO_3$ and its related compounds), which are widely used as transducers, pressure sensors and actuators, suffer from mechanical and electrical deterioration in service because of fatigue damage. When piezoelectric devices are used in severe circumstances, such as high stress or high power applications, problems that are related to reliability (i.e. degradation of electrical properties and fatigue fracture) become more critical and important. Therefore, it is necessary to investigate the electrical behavior of piezoelectric ceramics and to design microstructure that possesses excellent electrical properties. Both $BaTiO_3$ (BT) and $Pb(Zr,Ti)O_3$ (PZT) are among the most common ferroelectric materials and have been studied extensively since the late 1940s [1,2]. These two ceramics have distinct characteristics that make each individual ceramic suitable for different applications. The compound PZT has highly desirable piezoelectric properties which can be applied in transducer applications. Furthermore, it has a high T_C of 390 °C which allows piezoelectric devices to be operated at relatively high temperatures. BT is a normal ferroelectric material which exhibits a high dielectric constant, a lower T_C (~120 °C) and better mechanical properties [1–3]. Thus, mixing PZT with BT is expected to decrease the sintering temperature of BT-based ceramics, allowing a desirable move towards electrodes of lower cost [4]. Moreover, the nano-reinforced structure is believed to improve densification and mechanical properties of the ceramic composite. Therefore, ceramic-nanocomposites of the lead zirconate titanate–barium titanate ($(1-x)$PZT-xBT) system with various compositions, were fabricated using a modified mixed-oxide synthetic route and a bimodal particle concept. The effect of processing parameters on the arrangement of phases, microstructural evolution and electrical properties of the ceramics was carefully investigated using XRD, SEM and dielectric measurements.

2. Experimental procedure

Ceramic-nanocomposites in the system $(1-x)$PZT-xBT ($0.1 \leq x \leq 0.5$; $\Delta x = 0.1$) have been fabricated from PZT powder and BT nanopowder, employing a normal sintering method. Reagent grade PbO, ZrO_2, TiO_2 and $BaCO_3$ powders (Fluka, >99% purity) were used as starting materials. Powder of each end member (PZT and BT) was first formed in order to avoid unwanted pyrochlore phases. For the preparation of BT

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nanopowder, a vibratory laboratory mill (McCrone Micronizing Mill) powered by a 1/30 HP motor was employed for 30 h with zirconia media in ethanol. The well-mixed powder was calcined at 1300 °C for 2 h in an alumina crucible. With a modified mixed-oxide method [5], the PZT powders were prepared using a lead zirconate ($PbZrO_3$) as precursor in order to reduce the occurrence of undesirable phase. Pure $PbZrO_3$ phase was first formed by reacting PbO with ZrO_2 at 800 °C for 2 h. $PbZrO_3$ powder was then mixed with PbO and TiO_2 and milled, dried and calcined at 900 °C for 2 h to form single phase PZT.

The $(1 - x)$PZT–xBT mixed powders were then formulated from the BT and PZT components by employing the similar mixed-oxide procedure. In the mixing process, the calculated relevant proportions of constituents were weighed, suspended in ethanol and intimately mixed in a ball-mill with zirconia media. Drying was carried out for 2 h and the dried powder was then ground into the fine powders. The powders were then isostatically cold-pressed into pellets with a diameter of 15 mm and a thickness of 2 mm at a pressure of 4 MPa and sintered at 1200 °C for 2 h.

Densities of sintered ceramics were measured by Archimedes method and X-ray diffraction (XRD using CuK_α radiation) was employed to identify the phases formed. The grain morphology and size were directly imaged using scanning electron microscopy (SEM). For electrical measurements, silver paste was fired on both sides of the polished samples at 750 °C for 12 min as the electrodes. Dielectric properties of the sintered ceramics were studied as a function of both temperature and frequency. The capacitance was measured with a HP4284A LCR meter in connection with a Delta Design 9023 temperature chamber and a sample holder capable of high temperature measurement. Dielectric constant (ε_r) was calculated using the geometric area and thickness of the discs.

3. Results and discussion

XRD patterns of all sintered ceramic-nanocomposites are shown in Fig. 1. Here the peak positions and intensities of the XRD patterns vary according to the amount and chemical composition of the phases present. It is seen that the diffraction peaks shifted towards a higher angle with increasing x and the XRD peaks of all ceramic-nanocomposites are broader than those of solid-solution case in our earlier work [6]. These can be interpreted in terms of co-existing perovskite phases, i.e. PZT, BT and their reacted intermediate phases. Moreover, with careful observation, it is found that the sintered samples of $0.3 \leq x \leq 0.5$ nanocomposites exhibit the perovskite structure with traces of unwanted phase ($\bigtriangledown$) occurring at $2\theta \sim 28°$. It is believed that this unwanted phase is ZrO_2 matched with JCPDS file no. 37-1484 [7]. Compositional fluctuations due to the evaporation of lead oxide within surface regions are believed to be responsible for the occurrence of free ZrO_2 phase in the sintered $(1 - x)$PZT-xBT ceramics of $0.3 \leq x \leq 0.5$ nanocomposites. Another possibility was put forward by Fushimi and Ikeda [8], who suggested that melting of PT-PZ solid solution can change from congruent to incongruent and induce ZrO_2 to form at ~1340 °C. On the other hand, Brankovic et al. [9] suggested that incomplete reaction of the starting precursors can also result in the persistence of free ZrO_2 phase. Since no trace of ZrO_2 has been observed for sintered samples of $x = 0.1$ and 0.2, it is believed that the segregation of ZrO_2 may be associated with loss of Pb content and also depend on the level of BT content, similar with observations made in other perovskite systems [10,11].

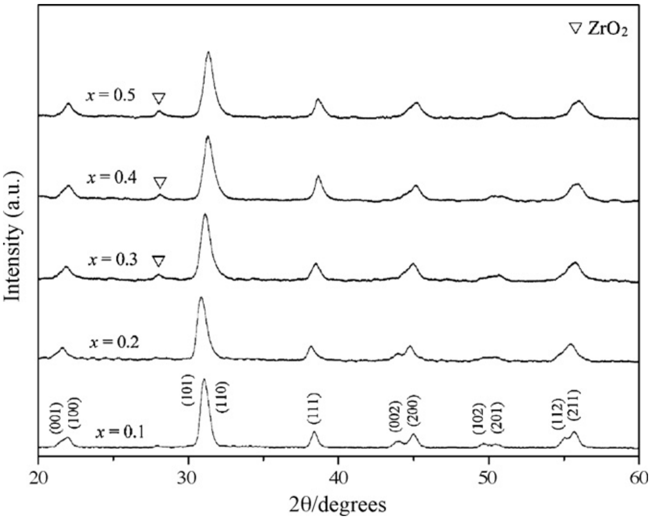

Fig. 1. XRD patterns of the $(1 - x)$PZT-xBT ceramic-nanocomposites sintered at 1200 °C for 2 h.

The microstructural morphology of $(1 - x)$PZT-xBT ceramic-nanocomposites was initially examined by SEM. Micrographs of as-fired surface of all ceramic-nanocomposites are shown in Fig. 2(a–e). In general, high porosity, heterogeneous microstructures consisting mainly of two ranges of particles (in respect of size and shape) were found in all samples. A distribution of very small spherical BT particles (brighter phase with diameter ~200–500 nm) is found over the PZT grains, especially for rich-BT samples. Large pore-sizes of the order of 2 μm were also observed. These poorly sintered samples could be attributed to several factors, including the effect of different particle size fractions between the two end components, ineffective mixing and the use of low density green bodies produced by conventional uniaxial die-pressing.

Densities in the range 4.80–6.21 g/cm^3 were obtained, which are considerably lower than the values obtained for sintered PZT–BT solid solution ceramics in our earlier work [6]. In order to preserve the ceramics with a nanostructural arrangement, it is possible that the sintering temperature employed in this work is not enough for driving the densification mechanism to achieve dense PZT/BT ceramic-nanocomposites. However, so far, there are no reports on the production of highly dense PZT/BT ceramic-nanocomposites by a pressureless sintering method. Moreover, the scope for improving pressureless sintering by raising the temperature is limited by the melting point of PZT (~1400 °C) whilst the hot-pressing technique can cause severe PbO-volatilization problems [12].

The temperature dependence of the dielectric constant (ε_r) measured at 1 MHz for $(1 - x)$PZT–xBT nanocomposites with

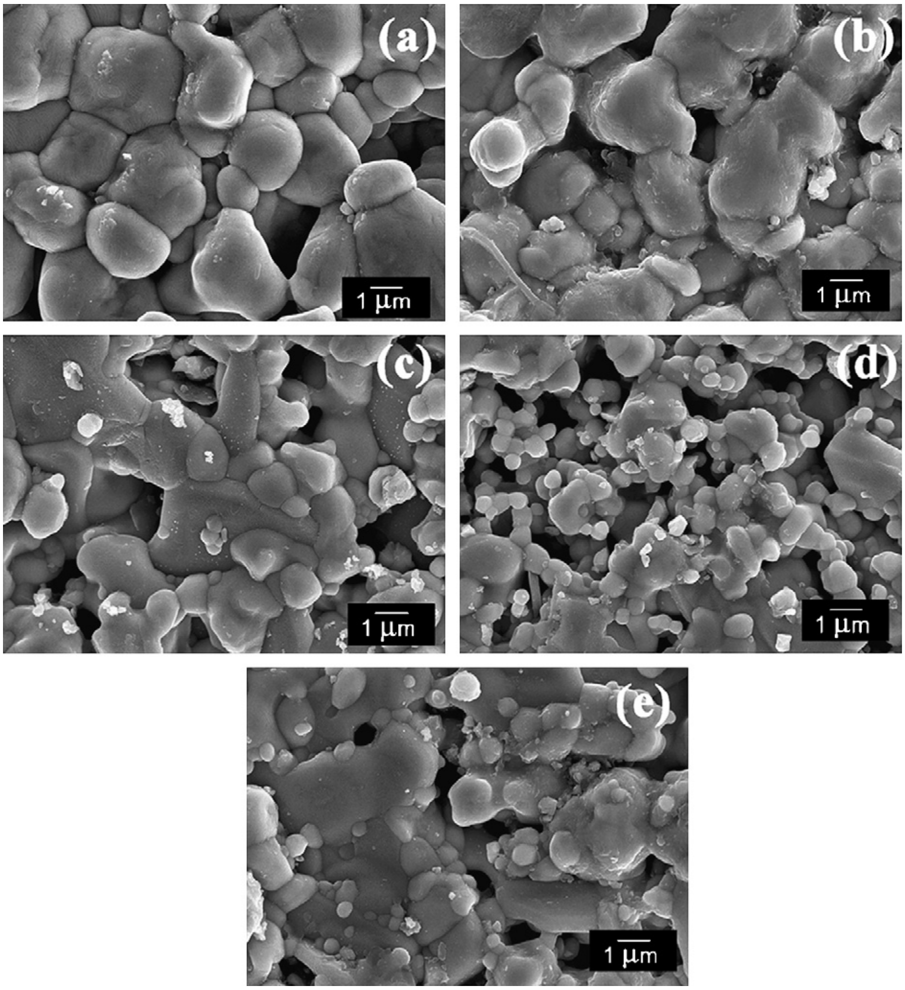

Fig. 2. SEM micrographs of as-fired surfaces of the sintered $(1-x)$PZT-xBT ceramic-nanocomposites with x = (a) 0.1, (b) 0.2, (c) 0.3, (d) 0.4 and (e) 0.5.

$0.1 \leq x \leq 0.5$ is shown in Fig. 3. All ceramic-nanocomposites display dielectric peak superimposition of the two phase transitions (T_1 and T_2) with no frequency dependence. The shape of dielectric peak for each composition seems to be the two peaks merged into a mound. The height of the mound was lower than those of solid solutions [6]. The phase transition temperatures, T_1 and T_2, and dielectric data are illustrated in Fig. 3 and list in Table 1. As is well known, the dielectric constant of pure PZT and pure BT showed anomalies at 390 and 130 °C, respectively. Therefore, ceramic-nanocomposites between PZT and BT are expected to show a transition temperature between 390 and 130 °C. An attempt was made to characterize the dielectric temperature of PZT–BT as a function of x. However, difficulties were encountered in indexing the measured dielectric peak broadening obtained. As seen in Fig. 3, with increasing of x, T_1 and T_2 decrease moving toward

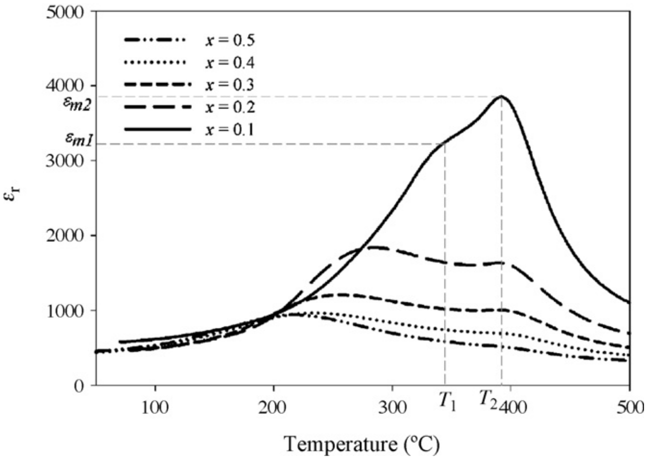

Fig. 3. Comparison of dielectric constant (ε_r) at 1 MHz for $(1-x)$PZT-xBT ceramic-nanocomposites.

Table 1
Dielectric properties of ceramic-nanocomposites in the $(1-x)$PZT–xBT system

Compositions (x)	T_1 (°C)	ε_{m1}	T_2 (°C)	ε_{m2}
0.1	340	3200	392	3800
0.2	285	1800	390	1600
0.3	257	1200	388	1000
0.4	234	960	385	700
0.5	216	940	380	530

ε_{m1} and ε_{m2} are the maximum dielectric constant at T_1 and T_2, respectively (see also Fig. 3).

the Curie temperature of BT. T_1 refers to transition temperature of BT and T_2 refers to transition temperature of PZT. There are various proposals for explaining the dielectric response of composite materials. Ausloos [13] studied effective dielectric constant theories of composite solids. Their work reported that the broad spectrum of dielectric constant is the results of clustering effects, the shape of particle (or cluster) effect and particle heterogeneity effect. In this work, it is possible that the incorporation of BT nanoparticles into a PZT matrix may hinder domain wall motion sufficiently to reduce the dielectric constant [14]. Moreover, the presence of unwanted ZrO_2 phase (confirmed by XRD) and high porosity (confirmed by SEM) are other reasons for the low dielectric constants in ceramic-nanocomposites with composition of $x > 0.2$. However, by neglect accounting for the porosity, the maximum dielectric constant (ε_{max}) of all ceramic-nanocomposites was back-calculated to 100% density for a better comparison with the solid solutions. Although the dielectric values of ceramic-nanocomposites are still lower than those of the solid solutions, the broadening is greater which infers the operating temperature with the moderate dielectric constant (~1000–4000) of these ceramics is much wider in range, suitable for certain electronic devices.

4. Conclusions

Ceramics-nanocomposites in the system $(1 - x)$PZT-xBT were successfully processes by employing the bimodal particle concept. All PZT–BT compositions in this study were of the perovskite structure with tetragonal symmetry. The dielectric properties of all the ceramic-nanocomposites are strongly influenced by the presence of secondary phases and densification mechanism. The dielectric peak shows superimposition of the two phase transitions with no frequency dependence and the dielectric value is lower than that of solid solutions for all compositions, explained by theory of the dielectric response for composite materials. With increasing of x, the phase transition temperatures of all ceramics decrease moving toward to Curie temperature of BT.

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