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Investigation of $BiFeO_3$ modified $PbTiO_3$–$Bi(MgZr)O_3$-based complex perovskite ceramics

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ABSTRACT

Bismuth containing crystalline solutions of $(1-x)Bi(MgZr)_{0.5}O_3$–$xPbTiO_3$ (BMZ–PT) and $[(BiFeO_3)_y-(BiMg_{0.5}Zr_{0.5})_{1-y}]_x-[PbTiO_3]_{1-x}$ (BMZ–BF–PT) have been developed using conventional ceramic technology. X-ray diffraction analysis reveals that both the systems possess a perovskite structure, in which tetragonal to rhombohedral phase transformation appears for $x = 0.55$ in BMZ–PT and $y = 0.20$ in BMZ–BF–PT systems. SEM photographs reveal a uniform grain size distribution in the solid solution matrix with the presence of ferroelectric domains in few of the compositions. Ferroelectric hysteresis (polarization–electric field, P–E) loops reveal that increase in $BiFeO_3$ in BMZ–PT systems results in a decrease in residual polarization of the system with change and distortion in the shape of the (P–E) loops.

1. Introduction

Bismuth perovskites have been attracting attention as a family of piezoelectric ceramics in place of the widely used Pb(Zr, Ti)O_3 (PZT) system. The advantages of Bismuth perovskites over PZT are environmentally more friendly materials, a higher mechanical strength and Curie temperature. In this family of materials, bismuth sodium tantanate (BNT) or BNT-based crystalline solutions are considered to be one of the best candidates for lead free or low-lead-content piezoelectric materials due to their strong ferroelectricity [1–4]. However, BNT-based ceramics are difficult to pole due to their large coercive field, and they have a limited range of working temperatures due to a ferroelectric (FE) to antiferroelectric (AFE) transition in the vicinity of $\sim 100 \pm 22$ °C.

Early studies on perovskite-structured $Bi(Me)O_3$–$PbTiO_3$ solid solutions were mostly concerned with compounds containing transition metal Me ions such as Fe^{3+} and Mn^{3+} [1,2]. These materials show high temperature ferroelectric–paraelectric phase transitions but the piezoelectric and dielectric properties were limited or unknown due to their high electrical conductivity, which prevented poling of the ceramics. Recently, Eitel et al. [3,4] investigated more stable valence *B*-site cations in Bi-based perovskites and demonstrated that a material, $BiScO_3$–$PbTiO_3$ (BS–PT), has excellent piezoelectric coefficients ($d33$–500 pC/N) coupled with a high phase transition temperature ($T_c = 450$ °C) at the morphotropic phase boundary (MPB) between the rhombohedral (*R*) and tetragonal (*T*) phases. A recent transmission electron microscopy (TEM) investigation revealed that the FE domain structures and electron diffraction patterns in BS–PT were very similar to those in the $PbZrO_3$–$PbTiO_3$ (PZT) solid solution [5]. The objective of this article is to interpret the structure–property relations in a ferroelectric system $(1-x)Bi(MgZr)_{0.5}O_3$–$xPbTiO_3$ (BMZ–PT). In addition to this, the effect of the addition of $BiFeO_3$ (BF) on microstructural and ferroelectric properties of BMZ–PT binary system has been investigated in this paper.

It must be noted that the introduction of BF to the binary perovskite BMZ–PT creates a ternary system BMZ–BF–PT which is also a perovskite (explained later on by the X-ray diffractograms).

Let us introduce a basic formula for the ternary perovskite according to stoichiometry:

$$[(BiFeO_3)_y-(BiMg_{0.5}Zr_{0.5})_{1-y}]_x-[PbTiO_3]_{1-x}$$

It is here that we must clearly state that by the notation "45–20–55", we mean $x = 0.45$ and $y = 0.20$.

Thus, the concentration of BF is stated as its contribution to BMZ–PT and not to the complete ternary system.

2. Experiment

Polycrystalline samples of BMZ–PT designated as 35–65, 40–60, 45–55, 50–50 and BMZ–BF–PT (BMZ = 45%, BF = 0/05/10/15/20/25/50% and PT = 55%) designated as 45–0–55, 45–05–55, 45–10–

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55, 45–20–55, 45–25–55 and 45–50–55 were prepared by high temperature solid-state reaction technique. PbO, MgO, TiO_2, Bi_2O_3, Fe_2O_3 and ZrO_2 (all Aldrich AR grade) were used as the starting materials. Stoichiometric weights of all starting materials were mixed and ball milled with distilled water for 48 h, using zirconia balls as the grinding media. After drying in vacuum, calcination was carried out at 800 °C for 2 h in air followed by ball milling and drying. A single-phase formation was confirmed by the X-ray diffraction (XRD) technique. The calcined powder was pressed at 100 MPa to form cylindrical pellets using a cold isostatic press (CIP). The pellets were then sintered at 1050 °C for 1.5 h. A PbO-rich atmosphere was maintained by placing $PbZrO_3$ powder in an alumina boat near the test samples in closed crucible configurations in order to minimize the lead loss during sintering. XRD analysis was performed on a PW3710 Philips diffractometer using Cu Kα (λ = 0.15405 nm) radiation in order to examine the phases present in the system. Analysis of the diffraction patterns was conducted using Celref V3 and XFIT software. Sintered pellets were polished to a 1 μm finish and thermally etched for 30 min at a temperature 100 °C below the sintering temperature. Polished surface microstructure was examined by scanning electron microscopy (SEM) (XL30FEG-Philips).

Ferroelectric measurements were performed as a function of temperature for all BMZ–BF–PT compositions. High field measurements were conducted at room temperature (22 ± 2 °C) under silicon oil using a computer-controlled function generator (HP 33120A) and a high voltage amplifier (Trek 609D-6). A current amplifier (Stanford Research Systems Model SR570) was used to measure the induced current, which was then integrated numerically to yield the charge Q and then the polarization P. The applied field and induced current waveforms were downloaded to the PC using a Tektronix TDS 420 DSO. Further details of the measure method were given in an earlier publication [6]. The measurements were carried out using a 'burst mode' waveform comprising two complete sinusoidal cycles. This procedure was used in preference to a continuous waveform in order to avoid field-forces deageing effects [7]. The effective high field dielectric coefficients were determined from the measured P–E loops using the method described previously [8].

3. Results and discussions

Fig. 1 shows the room temperature XRD (Cu Kα radiation, λ = 1.5405 Å) patterns of BMZ–PT (35–65, 40–60, 45–55 and 50–50) sintered samples. The peaks in the XRD patterns were found to be sharp with distinct diffraction peaks. The diffraction lines for the system were indexed in different crystal systems and unit cell configurations using a computer programme package POWD-MULT. Standard deviations, $\Sigma\Delta d = d_{obs} - d_{cal}$ where d is the inter-planar spacing, were found to be minimum for tetragonal and rhombohedral structures. All XRDs of BMZ–BF–PT system reveal a pure perovskite structure.

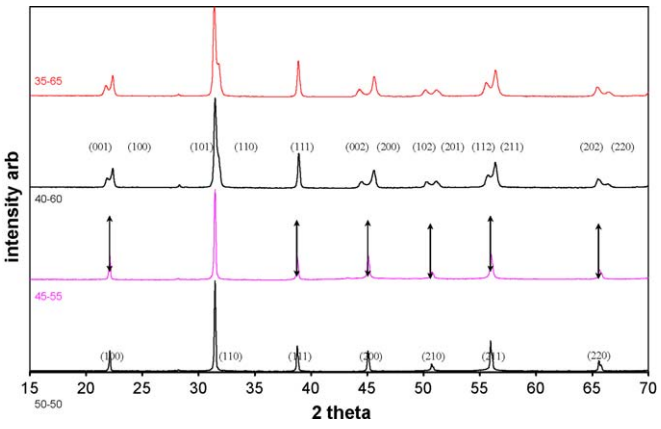

Fig. 1. XRD patterns of BMZ–PT (35–65, 40–60, 45–55 and 50–50) samples sintered at 1050 °C.

A change of structure from rhombohedral to tetragonal between 45–55 and 40–60 compositions is evident from the XRD patterns. Hence, it is inferred from this that morphotropic phase boundary (MPB) lies between these two compositions. The crystal structure as determined from the XRD technique shows that there was a change in structure from rhombohedral to tetragonal structure for $BiFeO_3$ from 15% to 20%. Thus it may be inferred that MPB lies within this region. Tetragonality increases as the $BiFeO_3$ content increases in the respective compositions (as shown in Fig. 2(a) and (b)). Increase in tetragonality with BF content has also been reported earlier [9–11]. The relative density of all the samples were found to be ~95% of the theoretical density.

Fig. 3 shows SEM photographs of BMZ–BF–PT samples. These figures show the uniform grains in the solid solution matrix. Here, black areas are pores and the thin white filaments are a liquid phase of $PbO–Bi_2O_3$ that appeared during sintering situated at the grain boundary region. The liquid phase is in fact an amorphous phase resulting from sintering. The average grain size of all the compositions was found to be in the range of 1.25–1.45 μm. Ferroelectric domains are visible in some of the compositions and they diminish with increase in BF content.

Ferroelectric hysteresis curves for different compositions of BMZ–BF–PT at different temperatures are shown in Fig. 4(a)–(d). P–E loops are more predominant at low temperatures. The remanent polarization Pr (=2.75 cm^{-2} for BF = 0.05, at 50 °C) was found to increase and coercive field was found to decrease with temperature till 100 °C with constriction in the loops. After that at 150 °C the spontaneous and remanent polarization decreases and the loops become more and more conductive as the temperature increases. The decrease in coercive field is due to the defects created near the domain walls. Similar effects were observed by Hagemann [12] and Godefroy et al. [13] for Fe doped $BaTiO_3$. They showed that Fe addition acts as an obstacle to domain wall motion. At 150 °C the loops have a rounded appearance; this is due to the increase in conductivity at higher temperatures. In this case, the ferroelectric behaviour starts to become less clear because the electrical response is dominated by the conduction effects.

Effect of BF on BMZ–PT is to decrease the spontaneous and residual polarization of the system. This is expected as BF is a hardener and hence the loops get constricted. For the compositions with increasing Fe content, we never really approach saturation so that the polarization values generally remain low and the loops that we observe are obtained in the sub-coercive field region. Presence of the hardener impedes the domain wall mobility or domain switching leading to which is evident from the curves for the various compositions. As the BF is introduced in the crystal lattice of BMZ–PT the cut-off low field value increases significantly.

Fig. 5 shows the dielectric-temperature curves of $[(1-x)Bi(MgZr)_{0.5}O_3 - xPbTiO_3$, $x = 0.55–0.80]$, BMZ–PT samples at different frequencies. Samples with compositions nearest to the MPB did not display the largest dielectric constant, but highest dielectric constant was measured in samples with a composition closer to high value of PT. This phenomenon has previously been observed for high Curie temperature BS–PT system, where it was explained in terms of the connectivity between the TiO_6 octahedron and ScO_6 octahedron in the perovskite structure [7]. Fig. 6(a)–(c) corresponds to the typical compositions with BF = 20%, 25% and 50%, respectively for BMZ–BF–PT system. Curie temperature increased with increasing $BiFeO_3$ content in BMZ–BF–PT compositions. Dielectric permittivity decreases with increase in