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Enhanced electrical properties of lead-free BNLT–BZT ceramics by thermal treatment technique

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Abstract

Electrical properties of lead-free solid solution ceramics from the $Bi_{0.4871}Na_{0.4871}La_{0.0172}TiO_3$ (BNLT) and $BaZr_{0.05}Ti_{0.95}O_3$ (BZT) system have been improved by a thermal treatment technique. A modified two step mixed-oxide method was employed for the preparation of the $(1-x)$BNLT–xBZT ceramics, where $x=0.06$, 0.09, 0.12 and 0.20. After sintering at 1125 °C for 4 h, the BNLT–BZT ceramics were annealed at 825, 925 and 1025 °C. The annealing treatment caused an increase in dielectric constant of BNLT–BZT ceramics with $x \leq 0.09$ mol% and with x higher than 0.09 mol% the dielectric value dropped considerably. The ferroelectric properties of all annealed ceramic samples tend to decrease with increasing annealing temperature as confirmed by the slimmer *P–E* loops. The piezoelectric coefficient (d_{33}) increased with annealing temperatures and a maximum value of ~170 pC/N was obtained from the ceramic samples annealed at 1025 °C with $x=0.02$.

Keywords: C. Dielectric properties; C. Ferroelectric properties; C. Piezoelectric properties; D. Perovskites

1. Introduction

Bismuth sodium titanate ($Bi_{0.5}Na_{0.5}TiO_3$:BNT)–barium titanate ($BaTiO_3$:BT) and BNT–BZT based ceramics, as lead-free ABO_3 perovskite ceramics, have been of great interest among researchers lately, due to the awareness of lead pollution during processing [1–4]. However, the electrical properties of BNT–BZT ceramics compared to that of typical BNT or BT ceramics particularly piezoelectric properties are not comparable with those found in the Pb-based ceramics. Thus, the development of these BNT–BZT ceramics in terms of improving their electrical properties to replace the toxic Pb-based has been carried out.

In general, the cationic substitutions at A and B sites in ABO_3 perovskite is considered to be one of the best solutions for improving electrical properties of a typical piezoelectric ceramic [5]. We reported that the addition of 1.72%La_2O_3 into the BNT–BZT and BNT–BT ceramics [6–7], enhanced the piezoelectric constant (d_{33}) and dielectric constant (ε_r) of the ceramics. Chen and Hu [8] studied the $(1-x)$BNBT–xBZT ceramics and found that the doping of A-site ion, Bi^{3+} enhanced their piezoelectric properties.

The modification of the processing technique in the cationic substitutions at A and B sites in ABO_3 perovskite is considered as one of the successful methods. For example, our previous work [6] reported that two step mixed-oxide method, where BNLT and BZT powders were calcined separately before the sintering step, has enhanced the electrical properties of the BNLT–BZT ceramics, overcoming the conventional mixed-oxide method.

The thermal annealing method is also of particular interest as it is an effective way to improve the electrical properties of some lead-free ferroelectric materials such as the B_2O_3-doped BZT ceramics and Bi_2GeO_5 glass ceramics [9–10]. The treatment helps to improve the heterogeneity in composition and microstructure of the ceramics after sintering [9–10].

In this work, the annealing treatment at various temperatures was employed to the $(1-x)$BNLT–xBZT ceramics. The range of x values was chosen near the morphotropic phase boundary (MPB) of the BNLT–BZT system ($x=0.06$, 0.09, 0.12 and 0.20). Effects of annealing temperature on physical and electrical properties of the BNLT–BZT ceramics were investigated.

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2. Experiment procedure

A modified two step mixed-oxide method was employed to fabricate the lead-free ceramics with compositions of $(1-x)(Bi_{0.4871}Na_{0.4871}La_{0.0172}TiO_3)$–$x(BaZr_{0.05}Ti_{0.95}O_3)$ where $x=0.06$, 0.09, 0.12 and 0.20. High purity (> 99.0%) powders of Bi_2O_3, Na_2CO_3, La_2O_3, TiO_2, ZrO_2 and $BaCO_3$ were used as starting materials. The BNLT and BZT powders were separately calcined at 900 °C and 1250 °C for 2 h, respectively in order to produce highly pure powders of both phases. Both powders were then combined and mixed again corresponding to the above formula by wet ball-milling. After drying, the resulting powders were made into pellets by uniaxially pressed in a stainless steel mould, using the pressure applied at 1 t for 10 s and subsequently sintered at 1125 °C in normal atmospheric pressure for 4 h with constant heating and cooling rate of 5 °C/min. This sintering condition was chosen according to our previous work [6] as the resulting samples showed maximum density with no trace of any second phase and abnormal grain growth. After that, the sintered ceramic samples were thermally annealed at 825, 925 and 1025 °C in an electric furnace with constant heating and cooling rate of 5 °C/min and with a dwell time of 4 h.

The bulk density and phase formation of the annealed BNLT–BZT ceramic samples were measured by Archimedes' method and an XRD technique, respectively. For electrical property characterizations, two circular surfaces of all annealed ceramics were ground to obtain parallel faces and then coated with silver paste as electrodes for electrical contact. The room temperature dielectric constant and dielectric loss of the annealed samples were measured at 1 kHz using an LCZ meter (HP4276A). The ferroelectric hysteresis (*P*–*E*) loops were also measured at room temperature by using a ferroelectric tester with controlled modified Sawyer–Tower circuit. Prior to piezoelectric measurements, the ceramic samples were poled at 50 °C in a silicone oil bath by applying a DC electric field of 4.0 kV/mm for 15 min. The piezoelectric coefficient of the samples was measured using a piezo d_{33}-meter.

3. Results and discussion

The density and porosity of the BNLT–BZT ceramics annealed under various annealing temperatures are shown in Fig. 1. It can be clearly seen that the annealing treatment slightly enhances the bulk density of the annealed samples having BZT content $(x) \leq 0.09$ mol%, while those density of the annealed ceramics of $x > 0.09$ mol% decreases with increasing annealing temperature. The opposite trend is found in the porosity of the annealed samples which is consistent with the bulk density data. The porosity rates (porosity (%)/annealing temperature (°C)) of the annealed samples with $x \leq 0.09$ mol% are negative while those of the samples with $x > 0.09$ are positive. The porosity rate of the higher BZT content ($x > 0.09$) samples was found to be higher than that of the lower BZT content samples. It is interesting that the annealed ceramics with $x=0.09$, which is a composition at MPB, exhibit a nearly constant porosity rate, while after this point the porosity rate is positive.

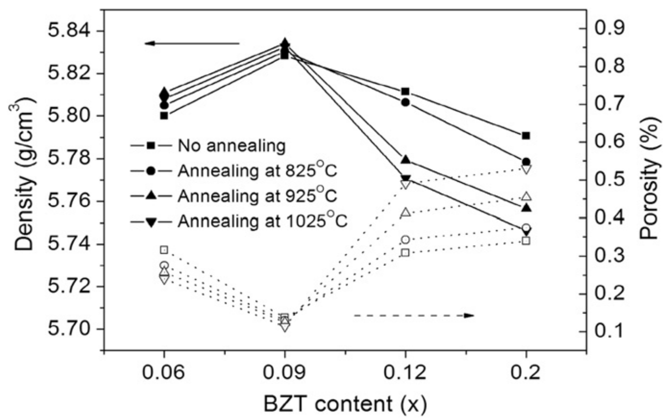

Fig. 1. Density and porosity of the annealed ceramics.

The decreasing trend in the bulk density or positive porosity rate of higher BZT content $(x) > 0.09$ mol% samples may be due to the excess amount of Zr^{4+} ion, which may react with oxygen in the atmosphere during annealing treatment and form a ZrO_2 phase. This in turn leads to a large amount of oxygen vacancies and free volumes left in the bulk ceramic, giving rise to the decrease in density of these ceramics where $x=0.12$ and 0.2 mol%. This hypothesis is confirmed by the SEM micrographs of the 0.12 mol% sample surface annealed at 1025 °C, as seen in the inset of Fig. 2b, showing the white long needle like shape of ZrO_2 crystals. Moreover, the related XRD patterns of this 0.12 mol% sample at various annealing temperatures show the existence of ZrO_2 peaks at $2\theta = 28°$ along with the major peaks of perovskite phase.

To investigate phase formation, the XRD technique was employed to examine ground samples at room temperature. The XRD patterns of the annealed samples with $x \leq 0.09$ mol% exhibit a pure perovskite phase as shown in Fig. 2a while a small amount of a secondary ZrO_2 phase occurs in the annealed samples with $x \geq 0.12$ mol% (Fig. 2b). Moreover, the amount of secondary ZrO_2 phase increases with increasing annealing temperature.

We believe that the high BZT contents $x > 0.09$ mol% of MPB composition lead to the high degree of heterogeneity in the BNLT–BZT composition especially at grain boundaries. Therefore, it is highly possible that these annealed samples may have more defects than those of the lower BZT content samples; therefore, they may decompose easily to form ZrO_2 crystals at grain boundaries as previously discussed. This observed result corresponds to the density data, where the density decreases considerably at higher annealing temperature for the annealed samples with higher x content.

The dielectric properties at room temperature of the annealed BNLT–BZT ceramics with various annealing temperatures are graphically presented in Fig. 3. It can

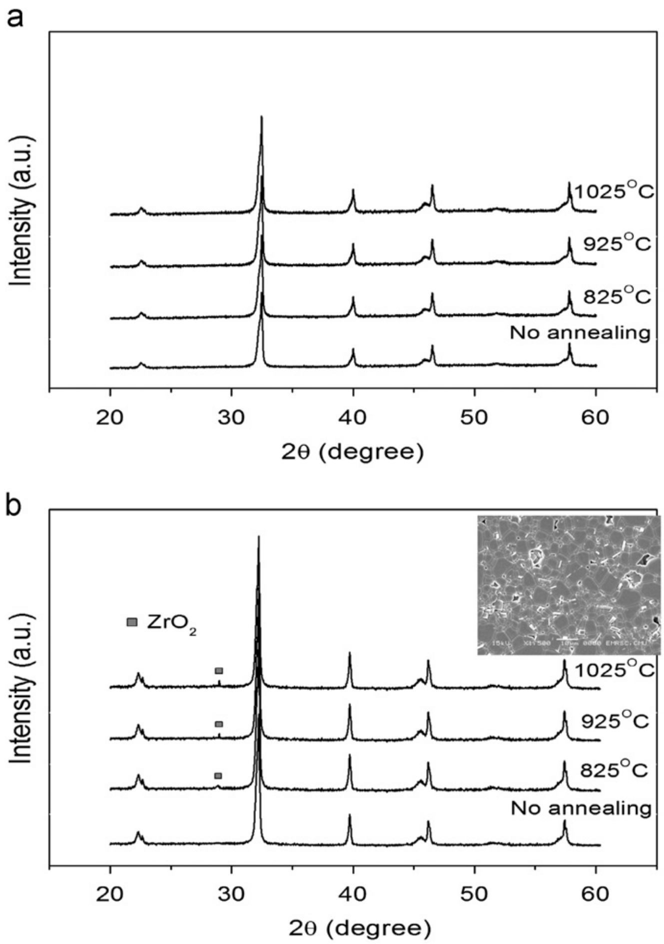

Fig. 2. XRD patterns of ceramics with (a) 0.09 mol% and (b) 0.12 mol% BZT content annealed at different temperatures.

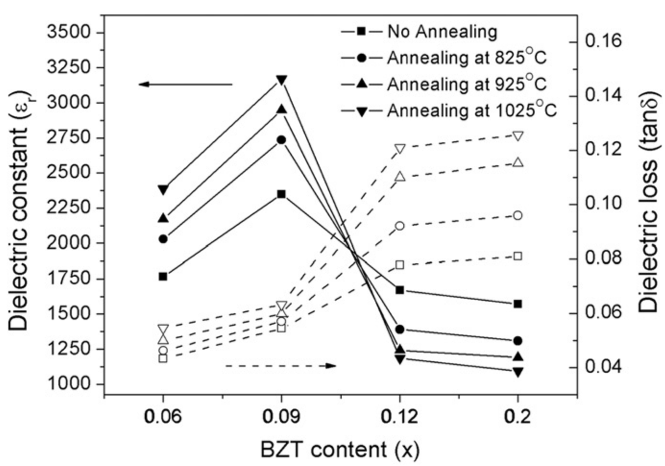

Fig. 3. Dielectric constant and loss at room temperature of the annealed BNLT–BZT ceramics.

be clearly seen that the annealing treatment enhances the dielectric constant (ε_r) for only the ceramic samples with BZT content ≤ 0.09 mol%. For the higher BZT content samples (≥ 0.12 mol%), higher the annealing temperature, the lower is the dielectric constant obtained. This finding is consistent with the density result, thus it can be assumed that the change in ε_r of the annealed samples is related to their densities.

However, the dielectric loss ($\tan\delta$) of all annealed samples increases with increasing annealing temperature. The increasing loss rate in samples with high BZT content ($\geq$ 0.12 mol%) is found to be higher than those of the lower content. This may be a result of the increasing amount of secondary phase ZrO_2 in the high BZT content ceramics with increasing annealing temperature. We suspect that in these high impurity samples, the occurrence of oxygen vacancies and pores may generate more mobile ions, which in turns gives rise to the high dielectric loss.

The plots of the polarization versus electric field (*P–E*) loops at room temperature of the un-annealed and annealed BNLT–BZT ceramics are shown in Fig. 4. In general, the BNLT-based ceramics have a strong ferroelectric property with large remnant polarization (P_r) at room temperature [7]. Therefore, it should be noticed that the *P–E* loops of un-annealed ceramic samples with $x \leq 0.09$ mol% were not fully saturated due to the limitation of our measurement system while those of un-annealed ceramics with $x > 0.09$ mol% were saturated under an applied electric field of 15 kV/cm.

For the annealed BNLT–BZT ceramics, the *P–E* loops change to the slimmer loops with increasing annealing temperature. We suspect that during annealing, the homogeneity of these compositions was enhanced at the atomic scale, giving rise to alteration of the domain switching in these ceramics. However, their *P–E* loop area decreased with increasing annealing temperature which may be due to the formation of ZrO_2 and oxygen vacancies, occurring in the higher annealing temperature samples as confirmed by the XRD result.

The piezoelectric coefficients (d_{33}) of all annealed ceramics are graphically plotted in Fig. 5. The d_{33} values of the un-annealed ceramics where $x = 0.06$, 0.09, 0.12 and 0.20 are 97, 126, 117 and 138 pC/N respectively, which are consistent with the values reported in the previous work [6]. We would like to point out that a significant improvement in the piezoelectric coefficient was achieved by thermal annealing treatment, as the d_{33} values increase significantly with increasing annealing temperature. It is known that easier reorientation of ferroelectric domains during the poling process results in a lower coercive field (E_c) [11]. Therefore, the increase in d_{33} value in this work may be due to the lower E_c which enables the ease in poling the BNLT–BZT ceramics.

4. Conclusions

The effect of thermal annealing temperature on the electrical properties of BNLT–BZT ceramics, which have been fabricated by a modified two step mixed-oxide method, was investigated. Based on our experimental results, it can be clearly seen that the annealing temperature has significant effects on the density and phase formation of ceramics, leading to alteration in their

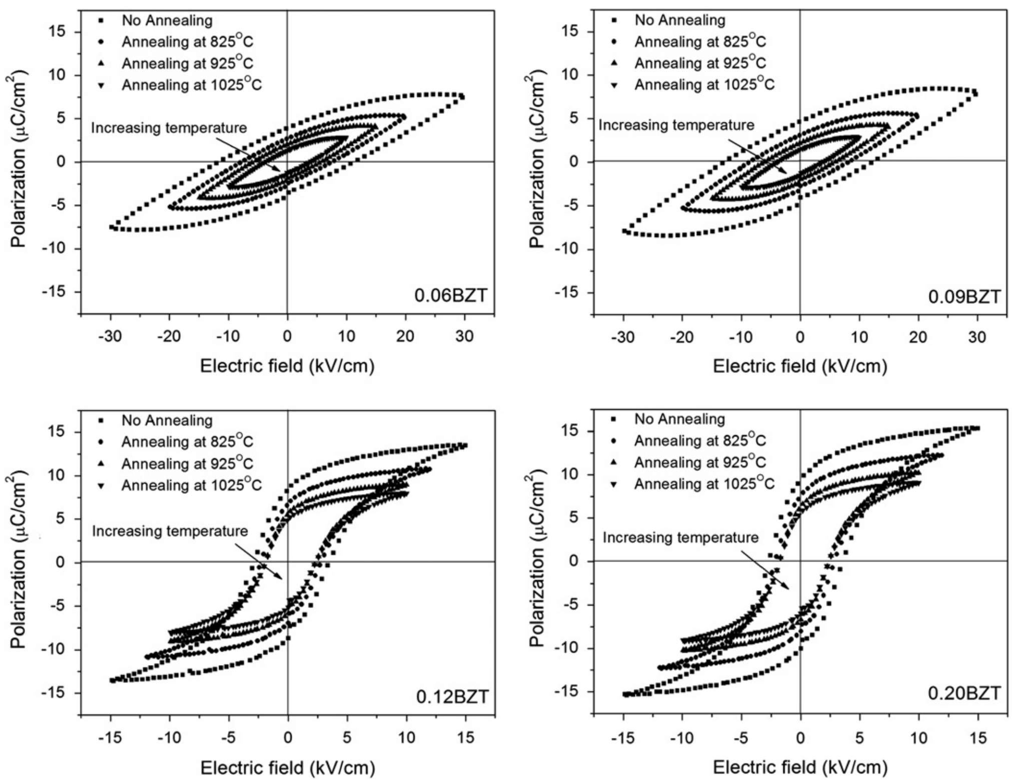

Fig. 4. Polarization versus electric field of the annealed BNLT–BZT ceramics.

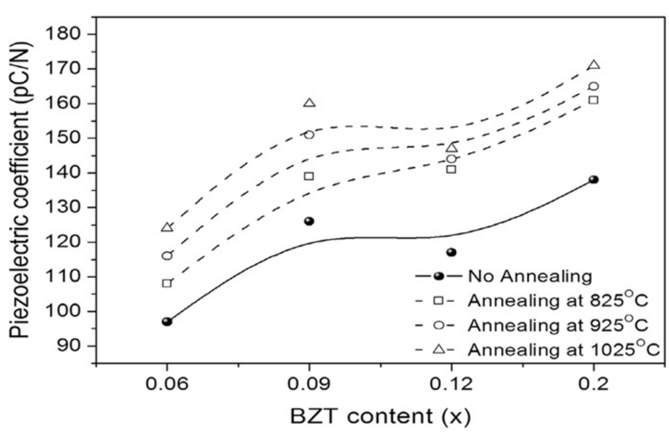

Fig. 5. The d_{33} of the annealed BNLT–BZT ceramics.

electrical properties. The dielectric properties noticeably increase with increasing annealing temperature for the samples with $x \leq 0.09$ mol% while the dielectric values decrease for samples with x higher than 0.09 mol%. The ferroelectric properties of all annealed ceramics decreased with increasing annealing temperature. The piezoelectric coefficient (d_{33}) of all annealed ceramic samples was improved by the thermal annealing method.

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