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PZT-based materials with bilayered structure: preparation and ferroelectric properties

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Abstract

In the present work, bilayered PZT-based ceramic materials were successfully produced via dry pressing and sintering. The densification, compositional phase, and microstructure of the materials prepared were investigated. Ferroelectric properties of the materials were measured and the relationship between property and layer volume composition was discussed. The present work reported a simply method to fabricate ferroelectric materials incorporating good parameters, such as higher remanent polarization, dielectric constant, and lower dielectric loss, which meet the material demand of both higher performance and longer service time.

Keywords: Bilayered materials; Ferroelectric properties; PZT

1. Introduction

Lead zirconate titanate (PZT) ceramics are widely accepted as useful ferroelectric materials which have a wide range of applications in piezoelectric, pyroelectric and photoelectric devices.[1] PZT ceramics are always doped with additives to improve and optimize their basic properties for special applications. The effect of dopants on properties is a complex matter, but in general, two important types of them, donor dopant and acceptor dopant, can be classified based on the aliovalent substituent in lattices. Donor dopants with higher charge than that of the ions they replace, are compensated by cation vacancies to keep the electric neutrality, whereas acceptor dopants with lower charge than that of the ions they replace, are compensated by oxygen vacancies.[2–11] It is noted that usually higher remanent polarization, dielectric constant, piezoelectric constant, and pyroelectric constant are the features of donor-doped materials, while acceptor-doped materials are of lower dielectric loss and mechanical loss (higher mechanical quality factor).[5]

In practical application of PZT-based components, both high performance and long lifetime of the material are required. However, it is difficult for a monolithic material to attain this requirement due to its physical limitation. For example, high piezoelectric constants are needed for materials to realize best utility and conversion of energies in the application of actuators or transducers. This can be achieved by donor-doping. On the other hand, low dielectric and mechanical losses are also needed to make sure the component works in a long period of time, where material design is emphasized on acceptor-doping for this purpose. If one expect to achieve a component with both high performance and long service time, the process of direct mixture of both donor-doped and acceptor-doped powders is however not feasible because the compensation of the donors and acceptors would occur and hence deteriorate the materials properties. In an attempt to achieve a component combining both better performance and longer service time, layered-structure PZT-based ceramics, therefore, were designed and fabricated in the present work. Another research significance related to layered ferroelectric materials, as reported by Zhu et al.,[12,13] is that there exists interdiffusion between layers. With this phenomenon, the material, to a certain extent, can be considered as a functionally graded material (FGM), in which sharp interface and stress or field concentration can be reduced or released.[14]

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The production of multilayered or functionally graded layered ferroelectric materials had been reported in the literature.[14,15] The methods included tape casting and centrifugal casting. In the present work, a simple method, i.e. dry pressing and sintering, was used. The material prepared included two layers. One layer was designed to expect to possess high remanent polarization, because high remanent polarization is the base for ferroelectric material showing good performance. The other layer was expected to possess low dielectric loss, because low loss is suitable for long lifetime working. The material sintering behavior is studied and the phase and the structure of the bilayered ceramic are analyzed. The ferroelectric properties (remanent polarization, dielectric constant, and dielectric loss) were measured and the relationship between property and layer volume ratio is discussed.

2. Experimental procedure

Two PZT-based ceramic compositions were designed and used. One was expected to have high remanent polarization and dielectric constant, $Pb(Zr_{0.525}Ti_{0.475})O_3 + 0.005Y_2O_3 + 0.005Nb_2O_5$, termed as powder A in the present work. The other was expected to have low dielectric loss, $Pb(Zr_{0.525}Ti_{0.475})O_3 + 0.00375Y_2O_3 + 0.00375Nb_2O_5 + 0.005WO_2 + 0.5$ wt.%MnO_2, termed as powder B. Powders A and B were synthesized from commercially available PbO, ZrO_2, TiO_2, Y_2O_3, Nb_2O_5, WO_2, and MnO_2 powders (Coors Ceramics, USA). The weighted powders for each composition were mixed for 24 h with zirconia balls as the grinding media and ethanol as the solvent in a planetary ball miller (Restch, USA). After milling, the resultant slurry was dried in an oven and then the powders were calcined in a high-temperature furnace (Carbolite, UK) at 850 °C for 2 h. After sieving, the calcined powders A and B were weighed according the ratio of 1:1 (0.25 g each). Powder A was fed first in a 10 mm stainless steel die and subjected to pressure to obtain a flat surface. Then powder B was fed on the flat surface of powder A. The bilayered powder was uniaxially pressed under 120 MPa. Monolithic pellets A and B were also formed from powers A and B using same methods and conditions for the investigation on material sintering behavior and property comparison. The monolithic compacts A and B were sintered at different temperature of 1120, 1130, 1140, and 1150 °C, isothermally held for 2 h in a high-temperature furnace (Carbolite, UK). After the investigation on the sintering behavior of the monolithic ceramics, the bilayered compacts were sintered at 1150 °C for 2 h. During sintering, all the compacts were placed in a covered alumina crucible that contained $PbZrO_3$ disks to produce a PbO-excess atmosphere.

The densities of the sintered components were measured by a MD-200S densimeter (Mirage, Japan). A X-ray diffractometer (Rigaku, Japan) with Cu K_α radiation was used to reveal the phases of the calcined powders and sintered samples A and B. With this equipment, the lattice constants of the achieved components were also determined to calculate material theoretical density. The relative densities of the sintered samples were obtained from the ratio of the measured density to the calculated theoretical density. The microstructure of the sintered bilayered sample was examined by a JSM-5410 SEM (Jeol, Japan). For the measurement of ferroelectric properties, different thickness ratios of A to B (3:1, 1:1, and 1:3) in the bilayered component were obtained by grinding the two surfaces of the samples. The total thickness of the bilayered component was ground to 0.6 mm and silver paste (Agar, UK) was applied on both surfaces. For property comparison, the sintered monolithic components were also ground to a 0.6 mm in thickness and then were applied using silver paste. The P–E hysteresis loop, and the dielectric constant and dielectric loss were measured using a RT 6000HVA Radiant ferro-tester (Radiant, USA) and a HP4194A impedance/gain-phase analyzer (HP, USA), respectively.

3. Results and discussion

3.1. Analysis of calcined powders

In the present work, the PZT-based powders A and B were synthesized by solid-state reaction (850 °C for 2 h). The quality of synthesis has a direct influence on the properties of PZT ceramics. Fig. 1 shows the XRD patterns of the calcined powers A and B. It can be seen that PZT materials with perovskite structure were formed from both powders and no other phase was detected. This indicates that a good synthesis was achieved.

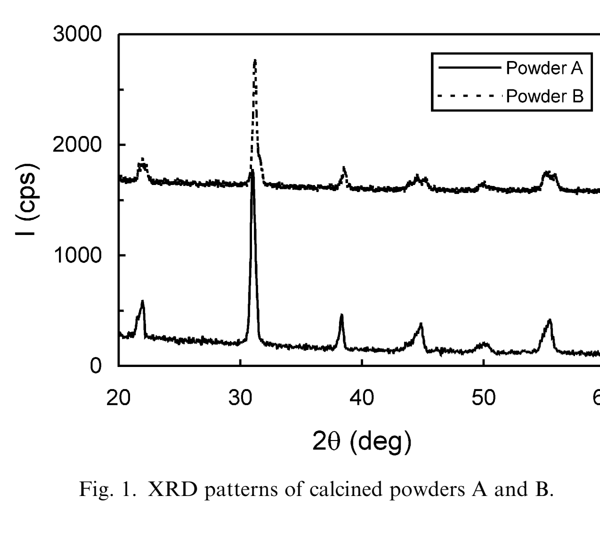

Fig. 1. XRD patterns of calcined powders A and B.

3.2. Analysis of sintered compacts

The theoretical densities of monolithic A, monolithic B, and bilayered materials, labeled as A–B, were calculated as 7.984, 7.988, and 7.986, respectively. The relative density results of the prepared samples are shown in Fig. 2. It is noted that the densities of monolithic samples A and B are close in the investigated sintering temperature range and they both increase with the increase of sintering temperature. Almost same relative densities were obtained for the monolithic ceramics A and B at 1150 °C. As a result, the bilayered materials were also sintered at this temperature, and the relative density is also shown in Fig. 2. The density values indicate nearly consistent densification rates of samples A, B, and A–B during sintering. In the present work, flat and crack-free bilayered materials were achieved, which resulted from the nearly consistent densification behavior of the two layers and therefore no or minimum thermal stress was induced during sintering. Furthermore, all the samples attain over 96% relative density after sintered at 1150 °C, which indicates that high density components were obtained using the present experimental conditions.

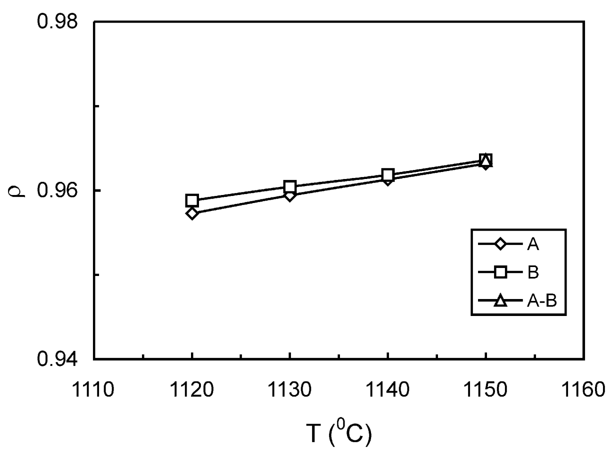

Fig. 2. Variations of relative density with sintering temperature of monolithic samples A and B and bilayered sample A–B.

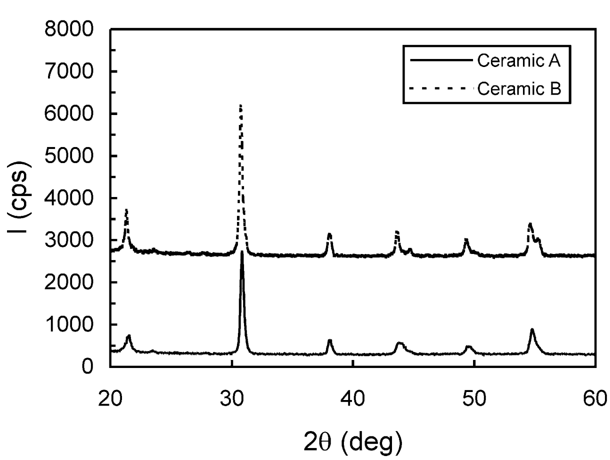

Fig. 3. XRD patterns of sintered samples A and B.

Fig. 3 shows the XRD patterns of the monolithic samples A and B sintered at 1150 °C. It is noted that the peaks occurred in samples A and B are perovskite phases. No other structure can be detected. Therefore, good ferroelectric PZT-based ceramics were achieved in the present work.

Fig. 4 shows the SEM image of the sintered bilayered PZT-based material. It can be seen that a good integration of the material was achieved. The two layers have a smooth transition and no discrete interface can be found. In Fig. 4, material B that shows larger grain size is on the top and material A that shows smaller grain size is at the bottom. Between them, there exist an interdiffusional region where the particles diffuse each other. It can be seen that particles A and B takes on a regular gradient distribution near the diffusional region along the thickness direction. This phenomenon was also reported and explained by Zhu et al.[12,16] in their FGM experiment. It is also noted from Fig. 4 that little porosity can be seen and a high density component was achieved, which is consistent with the obtained density result. Based on the analyses of phase, microstructure,

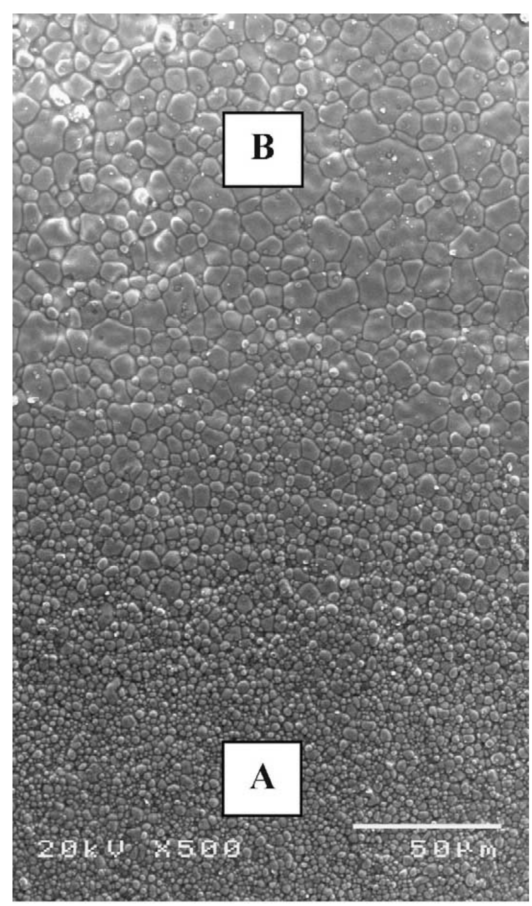

Fig. 4. SEM image of the cross section of sintered bilayered sample A–B.

and density, it can be said that good bilayered materials were prepared by the designed dry pressing and sintering process.

3.3. Ferroelectric properties

As mentioned in Section 2, different thickness ratios of A to B of the bilayered components were achieved by grinding the two surfaces. It is noted that the thickness ratio is equal to the volume ratio of the two layers due to their same diameters in the sintered component. The P–E hysteresis loops, the dielectric constant-frequency, and the dielectric loss-frequency relationships of the bilayered samples with different volume fractions of the two layers and the monolithic samples are shown in Figs. 5–7, respectively. In Fig. 5, the remanent polarization can be read at zero electric field. The values of the remanent polarization, from monolithic sample A, through different ratio of bilayer component, to monolithic B, are listed in Table 1. In Figs. 6 and 7, the dielectric constant and dielectric loss decrease with increasing frequency for all the samples, which are in consistent with the trends reported by Kar et al.[3] and Chen et al.[17] when they sintered PLZT and PZT ceramics respectively.

From Table 1 and Figs. 6 and 7, it is noted that monolithic ceramic A is of high remanent polarization and dielectric constant but high dielectric loss, which is the feature of donor doping. Monolithic ceramic B

Table 1
Remanent polarizations of sintered monolithic and bilayered samples

Composition	Remanent polarization (μC/cm²)
Monolithic A	45.52
0.75A–0.25B	37.50
0.50A–0.50B	29.92
0.25A–0.75B	22.02
Monolithic B	11.40

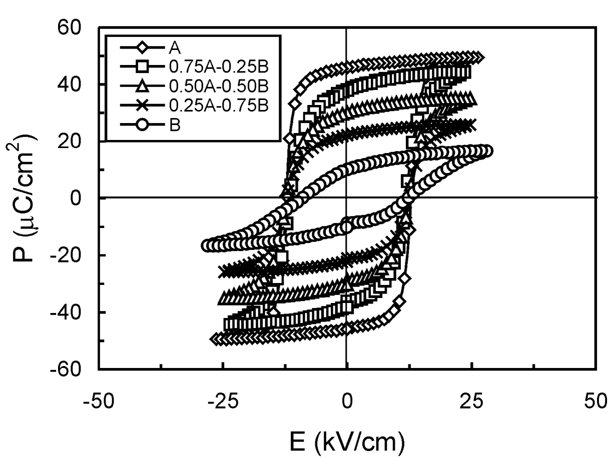

Fig. 5. P–E hysteresis loops of sintered monolithic and bilayered samples.

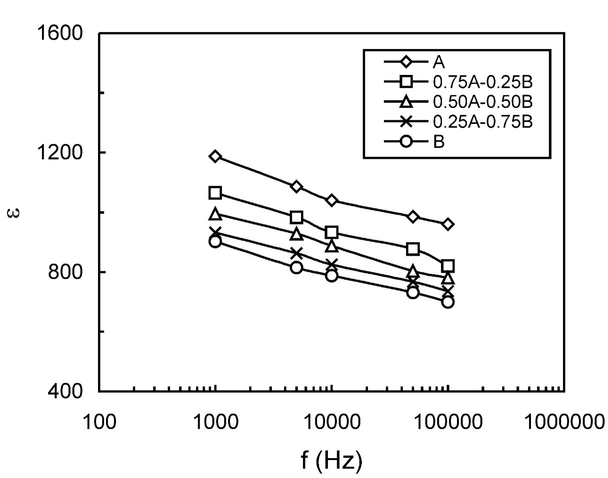

Fig. 6. Dielectric constant–frequency relationships of sintered monolithic and bilayered samples.

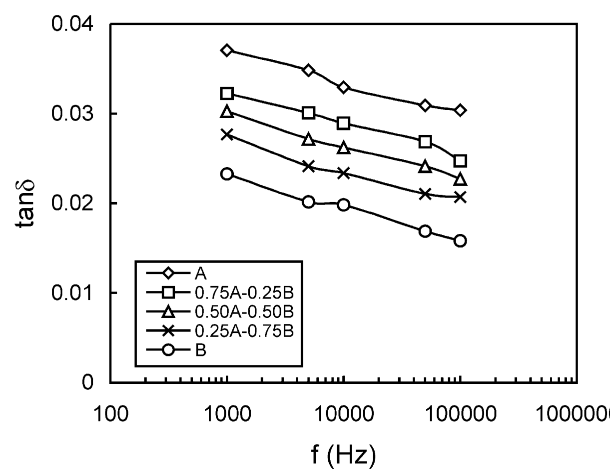

Fig. 7. Dielectric loss–frequency relationships of sintered monolithic and bilayered samples.

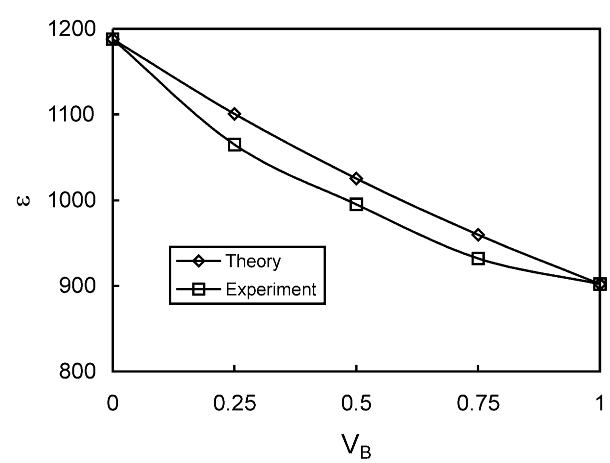

Fig. 8. Variations of dielectric constant with volume fraction of layer B, obtained from experimental measurement and theoretical calculation.

possesses low dielectric loss but low remanent polarization and dielectric constant, which is the characteristics of acceptor doping. The acceptor is MnO_2 in the present work, because Mn^{4+} can occupy B-sites and reduce to Mn^{2+} during sintering, which leads to the creation of oxygen vacancies to keep the electric neutrality.[8] Based on the properties of ceramics A and B, it can be seen that a monolithic material is very difficult to achieve both high ferroelectric parameters and low loss. The bilayered materials, produced in the present work, combine both the merits of monolithic ceramics A and B. Therefore, in the application of ferroelectric component, different volume fraction of the two layers can be selected based on the practical demand, in order to show higher performance and longer operation time.

As the volume fraction of one layer increases, the corresponding characteristic parameter will protrude for the sintered bilayered compacts. However, it should be noted that the property shown in the bilayered materials produced in the present work is not a result of a simple mixing rule of the two monolithic materials. In Fig. 8, as an illustration, the variation of dielectric constant (measured at 1 kHz) with different volume fraction of layer B (V_B) is plotted, and the values calculated from Eq. (1), the ideal capacitance series, are also shown for comparison. It can be seen that the values of the bilayered samples obtained experimentally are lower than the calculated ones. This difference is attributed to the microstructure of the bilayer. As shown in Fig. 4, there exists the transition region between the two layers, which makes the material properties more complicated. The detailed discussion of the interdiffusion effect on material properties is beyond the present work.

$$\varepsilon^{-1} = (1 - V_B)\varepsilon_A^{-1} + V_B\varepsilon_B^{-1} \quad (1)$$

4. Conclusions

In the present work, bilayered PZT-based materials were successfully fabricated by a simple drying pressing and sintering process. The material achieved possesses higher remanent polarization and dielectric constant and lower dielectric loss. The present work provides a simple and feasible method to incorporate both better performance and longer service span in one component, whereas the monolithic material is hard to realize.

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