Perovskite Formation and Dielectric Responses in PZN Modified PMF-PZT Ceramics

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Abstract: PMF-PZN-PZT (0.01Pb(Mo1/3Fe2/3)O3-xPb(Zn1/3Nb2/3)O3-(0.99-x)P(Zr0.53Ti0.47)O3 piezoelectric ceramics), where x = 0.00, 0.01, 0.03, 0.05 and 0.07 were prepared by a conventional mixed-oxide method. The results show that the pure perovskite phase forms in these ceramics. X-ray diffraction analysis indicated that the phase of the material is a MPB (morphotropic phase boundary) structure. The effects of PZN content on the crystal structure and electrical properties were investigated. Optimal dielectric properties were achieved at composition x = 0.07 ceramics by calcination at 800 °C and sintering at 1,180 °C, with a curie temperature of approximately 430 °C. These results clearly show the significance of PZN in controlling the electrical responses of the PMF-PZN-PZT system.

Key words: Perovskit, dielectric properties, MPB, Curie temperature.

1. Introduction

Lead zirconate titanate Pb(Zr,Ti)O3 ceramics are the important piezoelectric materials applied and are widely used in electronic sensors, actuators, resonators and filters [1, 2]. To improve their piezoelectric properties, lead-based complex perovskite structure compounds are dissolved into PZT (Pb(Zr,Ti)O3) ceramics [3, 4]. Compared to the PZT ceramics, multiple compounds have many merits such as low sintering temperature and excellent electrical properties. Moreover, because of the addition of the third and the fourth components, the piezoelectric properties can be adjusted over a wide range.

PZN (Pb(Zn1/3Nb2/3)O3) is typical relaxor ferroelectrics with high dielectric constants and relatively low sintering temperatures [5, 6]. Kaneko investigated Pb(Zn1/3Nb2/3)O3-xPb( Zr0.47Ti0.53)O3 ceramics [7] with compositions close to the MPB (morphotropic phase boundary) and pointed out that these ceramics have large electromechanical coupling factors kp.

However, the small mechanical quality factor Qm constrained their use to high power piezoelectric devices such as multilayer piezoelectric transformers and piezoelectric motors. It is necessary to optimize the piezoelectric properties of PZN-PZT ceramics for high power device applications.

The structure and piezoelectric properties of PMF-PZT (Pb(Mo, Fe)O3) ceramics combined with PZN have not been reported. It is expected that PMF-PZT piezoelectric ceramics with additions of PZN may have excellent piezoelectric properties with higher mechanical quality factors. In this paper, PZN and PMF were added to PZT ceramics to form solid solutions, and the effects of different amounts of PZN on the microstructure and electrical properties of the PMF-PZT ceramics were investigated.

2. Experiments

The ceramics of the 0.01 Pb(Mo1/3Fe2/3)O3-xPb(Zn1/3Nb2/3)O3-(0.99-x)P( Zr0.53Ti0.47)O3. They were
obtained by the conventional mixed oxides method. The oxide powders were mixed by ball milling for 6 h; and then, calcined at 800 °C for 2 h at the following heating and cooling rates: 2 °C/min. and submitted to a new ball-milling step, for 6 h. Then, pressed into pellets with a pressure of 2,500 kg/cm³ in a cylindrical stainless steel mold using a hydraulic press. The size of those pellets was 13 mm in diameter; while the thickness is 1 mm. Pellets were packed into covered alumina crucibles. The inner space of the crucibles was filled up with the powders of PbZrO₃, in order to prevent intensive evaporation of the lead during the sintering. A typical sintering schedule consisted of heating rate of 2 °C/min to 1,100 °C, 1,150 °C and 1,180 °C, for 120 min and natural cooling in the furnace.

The phase structure of the powders and ceramics were analyzed via XRD (X-ray diffraction; Bruker-AXS D8) using CuKα radiation (λ = 1.5406 Å) in a wide range of Bragg angles (20° ≤ 2θ ≤ 60°) at a scanning rate of 2 °/min. Densities of sintered pieces were calculated from the sample dimensions and weights. The microstructures of the sintered samples were examined using SEM (scanning electron microscopy). The dielectric properties of the samples were measured using an automated measurement system. An LCR meter (Good Will Instrument Co., Ltd.). It was used to measure the dielectric properties over a wide temperature range using high temperature measurement cell.

3. Results and Discussion

3.1 XRD Analysis

Perovskite phase formation and crystal structure were determined by XRD at room temperature. 0.01Pb(Mo₁/₃Fe₂/₃)O₃-xPb(Zr₁/₃Nb₂/₃)O₃-(0.99-x)Pb(Zr₀.₅₃Ti₀.₄₇)O₃ where x = 0.00, 0.01, 0.03, 0.05 and 0.07 shown in Fig. 1 showing a perovskite structure for all compositions. The pyrochlore phase is not observed in this system. It can be suggested that the MPB where rhombohedral and tetragonal phases coexist.

![Fig. 1 XRD patterns of PMF-PZN-PZT sintered at 1,100 °C, 1,150 °C and 1,180 °C.](image)

It was observed for all the studied compositions, in 2θ range of 38°-50° [8].
3.2 Study of Morphology

Fig. 2 shows the SEM micrographs of PMF-PZN-PZT ceramics. The microstructure of ceramics becomes denser with the increase of PZN content. For the PMF-PZN-PZT ceramics with \( x = 0.0, 0.01 \) and \( 0.03 \), it can be seen from Figs. 2a, 2b and 2d that the ceramics present homogeneous and small grains with a diameter of about (1-2 \( \mu \)m) for the ceramic with \( x = 0.05 \) and 0.07. There are obviously large grains with a diameter of about (5-7 \( \mu \)m). However, the grain sizes increase sharply for the ceramics with \( x = 0.00, 0.01, 0.03, 0.05 \) and 0.07 as seen in Fig. 2. Moreover, the microstructure becomes more uniform with fewer pores. It indicates that PZN can help the grain growth of PMF-PZN-PZT ceramics and the PZN is effective in improving the densification of the ceramics. Generally, the uniform and dense microstructure is helpful for improving the electric properties.

3.3 Sintered Density

The relative density of ceramics sintered in between 1,100 °C and 1,180 °C plotted as a function of PZN concentration is shown in Fig. 3. It can be seen that an increase in the sintering temperature generally increased the density. It seemed therefore that PZN could be used as a sintering aid whose effects on sintering behavior were clearly observed particularly at lower sintering temperatures [9].

3.4 Dielectric Properties

Fig. 4 show the temperature variation of dielectric constant (\( \varepsilon \)) of PMF-PZN-PZT measured at 1 kHz and sintered at 1,180 °C, after incorporation of 0.01 atomic% PZN.

The Curie temperature increases with increase in PZN concentration [10] and takes a maximum of 430 °C. Also, the permittivity increases gradually with the increase in the composition of PZN and takes a
Fig. 3 Variation of density of PMF-PZN-PZT with sintered temperature.

Fig. 4 Variation of dielectric constant with temperature at 1 kHz for all samples sintered at 1,180 °C.

maximum of 36,912.63 for the sample with \( x = 0.07 \), included in the MPB (morphotropic phase boundary). This maximum of dielectric activity can be explained by the presence of several directions of spontaneous polarization relating to the existence of the two structures rhombohedral and tetragonal.

4. Conclusions

In this study, ceramics within the 0.01Pb(Mo\(^{1/3}\)Fe\(^{2/3}\))O\(_3\)-\(x\)Pb(Zn\(^{1/3}\)Nb\(^{2/3}\))O\(_3\)-(0.99-\(x\))Pb(Zr\(^{0.53}\)Ti\(^{0.47}\))O\(_3\) solid solution system (where \( x = 0.00, 0.01, 0.03, 0.05 \) and 0.07) were successfully prepared using a solid-state mixedoxide technique. The results of X-ray diffraction reveal that all the ceramics possess as bi-phase perovskite structure with MPB symmetry. The SEM micrograph showed that the average grain size significantly increases with increasing PZN content. At 1 kHz, a maximum dielectric constant was observed at composition of \( x = 0.07 \), while the transition temperature strongly increased with increasing PZN content.

References


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