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Study on $Pb(Mg_{1/3}Ta_{2/3})O_3$–$Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr_xTi_{1-x})O_3$ high power piezoelectric ceramics near the morphotropic phase boundary

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ABSTRACT

$Pb(Mg_{1/3}Ta_{2/3})O_3$–$Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr_xTi_{1-x})O_3$ quaternary piezoelectric ceramics with different compositions near the morphotropic phase boundary were synthesized using a conventional solid state reaction method. The phases, microstructures, ferroelectric, piezoelectric and dielectric properties of the system were investigated. A transition from rhombohedral to tetragonal phase was observed as the Zr/Ti ratio decreased. The *P*–*E* loops presented pinched shapes at low electric fields and the distortions disappeared at high electric fields. The dielectric study revealed a diffuse phase transition behavior in the ceramics. The optimal dielectric and piezoelectric properties $\varepsilon_r = 817$, $d_{33} = 285$ pC/N, $k_p = 0.55$, $T_C = 302\,^\circ$C, $\tan\delta = 0.4\%$ and $Q_m = 1600$ of the ceramics were obtained at the composition of Zr/Ti = 50/50. Vibration velocity at $\Delta T = 20\,^\circ$C was found as high as 0.74 m/s for this composition, which was almost 2.5 times as that of the commercial hard PZT ceramics.

1. Introduction

Ultrasonic motors, used as compact servomotors for precision positioning, have many advantages over the conventional electromagnetic motors, and are currently widely used in aeronautics, astronautics, and medical applications [1]. Piezoelectric materials used in ultrasonic motors are electrically driven to high mechanical vibration near the resonance frequencies, leading to a temperature rising and deterioration of piezoelectric properties with the increase of their vibration velocities. Therefore, piezoelectric materials are necessary to have high mechanical quality factor (Q_m) [2–4]. Moreover, high piezoelectric coefficient (d_{33}) and electromechanical coupling factor (k_p) are also required for high torque output and efficiency. For piezoelectric properties enhancement, $Pb(Zr,Ti)O_3$ (PZT) based ternary or quaternary systems, such as PZN–PZT [5], PMN–PZT [6], PMN–PZN–PZT [7], PMN–PFW–PZT [8], have been intensively investigated. It is reported that in these systems, ceramics with compositions near the morphotropic phase boundary (MPB) always possess optimum properties. For example, perovskite-structured $Pb(Mg_{1/3}Ta_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (PMgT–PZT) ceramics with compositions near MPB show a dielectric constant (ε_r) and a piezoelectric coefficient of the order of 4000 and 580 pC/N respectively. However, the Q_m of this system is only 70 [9]. On the other hand, the ternary system $Pb(Mn_{1/2}Sb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ (PMS–PZT) presents excellent hard properties, Q_m value of 1755 has been reported in this system under proper sintering conditions [10].

In our previous work, we introduced $Pb(Mg_{1/3}Ta_{2/3})O_3$ into PMS–PZT to form a quaternary system and good properties were obtained [11]. But the piezoelectric properties near the MPB of this system are still not clear. It is well known that the MPB of PZT lies in the region of Zr/Ti ratio around 53/47, but in some ternary or quaternary systems, doping ions will lead to slight shift of the MPB [12]. Therefore, in this study, the effects of Zr/Ti ratio on the structure and electrical properties of the system $Pb(Mg_{1/3}Ta_{2/3})O_3$–$Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr_xTi_{1-x})O_3$ (PMgT–PMS–PZT) was investigated in order to obtain the MPB composition of this system.

In high power devices, such as ultrasonic motors, the used piezoelectric materials usually endure high vibration velocity and large deformation. Thus, measurements under low vibration level may not appropriate to evaluate the performance in high-vibration conditions. Therefore, many investigations have been focused on the high-power properties of the piezoelectric ceramics [13,14]. In our study, the high-power properties of the ceramics near the MPB were also evaluated.

2. Experimental procedures

Ceramics of $0.05Pb(Mg_{1/3}Ta_{2/3})O_3$–$0.05Pb(Mn_{1/3}Sb_{2/3})O_3$–$0.9Pb(Zr_xTi_{1-x})O_3$, where $x = 0.56$, 0.54, 0.52, 0.50, 0.48, and 0.46, were synthesized by a conventional solid-state reaction method. Pb_3O_4 (99.5%), MgO (4N), Ta_2O_5 (4N), MnO_2 (99.95%), Sb_2O_3 (99.5%), ZrO_2 (4N) and TiO_2 (99%) were weighed stoichiometrically, with 0.5 wt% excess Pb_3O_4 to compensate the lead loss during sintering. The starting

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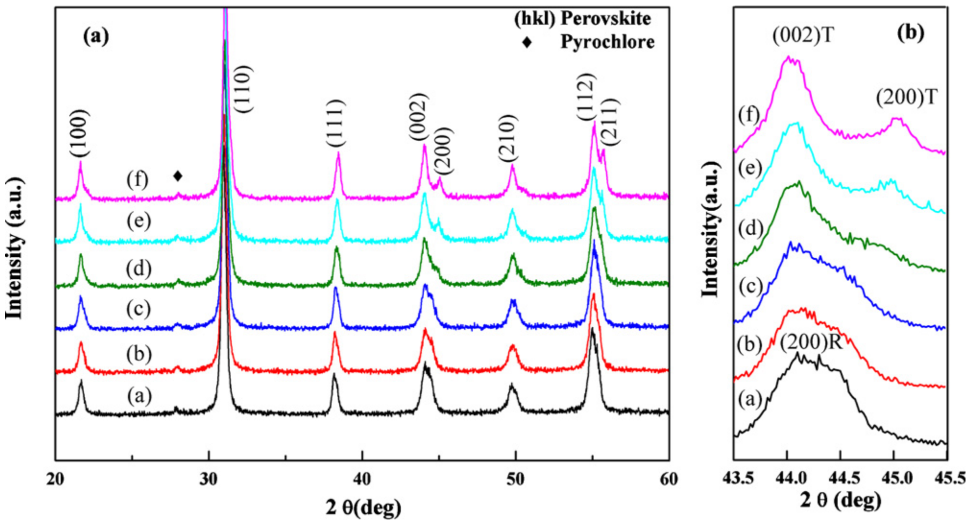

Fig. 1. XRD patterns of 0.05PMgT–0.05PMS–0.9PZT ceramics with different Zr/Ti ratios: (a) Zr/Ti = 56/44; (b) Zr/Ti = 54/46; (c) Zr/Ti = 52/48; (d) Zr/Ti = 50/50; (e) Zr/Ti = 48/52; (f) Zr/Ti = 46/54.

powders were wet-milled for 16 h in ethanol and then the mixtures were dried and calcined at 850 °C for 2 h. The calcined powders were pulverized again for 20 h. With the addition of polyvinyl alcohol (PVA, 5 wt%) as a binder, the ground powders were pressed into pellet samples under uniaxial pressure of 250 MPa. Sintering was carried out at 1240 °C for 2 h in sealed alumina crucibles with the samples covered by their original powders to minimize lead loss. Next, the sintered pellets were cut into 0.8 mm in thickness and printed with silver electrodes on both sides. Electroded samples were subsequently fired at 550 °C for 20 min and poled in silicon oil under a 4 kV/mm electric field for 30 min at 120 °C. The electrical properties of the samples were measured 24 h after poling.

The bulk densities of the sintered samples were measured by the Archimedes method, and all the densities are verified higher than 7.7 g/cm^3. The crystal structures of the sintered samples were analyzed by using an X-ray diffractometer (Bruker D8 Advanced, Cu Kα radiation, λ = 0.15418 nm). For the microstructure observation, the samples were thermally etched at 1150 °C for 15 min and examined by scanning electrical microscopy (SEM, Quanta 200, FEI Company). Piezoelectric measurements were made using a quasi-static piezo-d_{33} meter (ZJ-3A, Institute of Acoustics Academic Sinica). The dielectric constant and loss (tan δ) were measured in the temperature range from room temperature to 600 °C and the frequency range from 1 kHz to 1 MHz by utilizing an impedance analyzer (Agilent 4294A) with a laboratory heating device. Planar coupling coefficient and mechanical quality factor were determined by the resonance and anti-resonance frequencies. Ferroelectric hysteresis loops were obtained at room temperature using a ferro-analyzer (TF2000, aixACCT GmbH). The vibration velocity υ was measured using a Doppler Laser Vibrometer (Polytec PSV-300F, Germany), during which the temperature rise was determined by a infrared radiation thermometer (Victor 303, China).

3. Results and discussion

3.1. Crystal structure and microstructure

Fig. 1(a) shows the XRD patterns of the PMgT–PMS–PZT ceramics. All the samples present a perovskite structure with minor pyrochlore phase. Meanwhile, the broadening and splitting of the (2 0 0) peak can be seen from fine scans of 2θ between 43° and 46° with the decrease of Zr/Ti ratio (Fig. 1(b)). When the Zr/Ti ratio is greater than 50/50, only one single (2 0 0)R peak is observed. At the Zr/Ti ratio of 48/52, the single peak splits into double peaks of (0 0 2)T and (2 0 0)T, indicating a transition from rhombohedral to tetragonal phase induced by the variation of Zr/Ti ratio. The MPB of this system is around Zr/Ti ratio of 48/52. In PZT based binary ceramics, MPB lies in the region of Zr/Ti ratio around 53/47. When doping ions such as Ta^{5+} (0.64 Å), Mg^{2+} (0.72 Å), Mn^{2+} (0.67 Å) and Sb^{5+} (0.6 Å) dissolve into the crystal lattice, they usually substitute B sites of the perovskite structure and lead to a change in lattice constants and shift the MPB. This phenomenon was also observed in other PZT-based systems [12].

The variation of lattice constants with decrease of the Zr/Ti ratio is shown in Fig. 2. The *a*-axis and the *c*-axis are equal to each other and show little change when the Zr/Ti ratio is greater than 50/50. The lattice is indexed as a rhombohedral structure. As the Zr/Ti ratio decreases, the *c*-axis ascends while the *a*-axis descends consistently, which indicates that the tetragonality of the structure is enhanced.

Fig. 3 presents the SEM micrographs of PMgT–PMS–PZT ceramics with different Zr/Ti ratios. All of them show a dense microstructure with few pores. The observation agrees well with the high density measured by the Archimedes method. A few small diamond-shaped grains with dimensions of about 0.5–1 μm along with the relatively large grains of 1–3 μm dimensions can be observed. The grain size does not vary noticeably with different Zr/Ti ratios. The compositions of these grains were examined by X-ray energy dispersive spectroscopy (EDS). It is found that the contents of Sb and Ta elements in the small grains are much higher than that of the large grains. It is probably because the diffusion of these two elements with high atom weight is hard during the sintering process. Therefore a few small grains with rich contents of these two elements are formed in some regions.

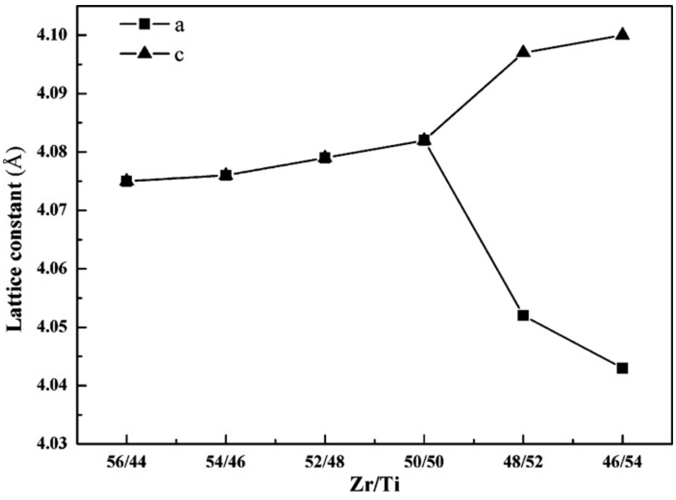

Fig. 2. Lattice constants of PMgT–PMS–PZT ceramics with different Zr/Ti ratios.