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Microstructure, domain morphology and piezoelectric properties of Si-doped $Pb(Mn_{1/3}Sb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ systems

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Abstract

The microstructure, domain morphology, and piezoelectric properties of Si-doped PMS–PZT ceramics were investigated. TEM results revealed that the domain morphology evolved from the normal herringbone to the micron-sized lenticular shape and to the final "wavy" pattern when SiO_2 content varied from 0 to 1 wt.%. Nano-scaled secondary phases consisting of SiO_2 and $PbSiO_3$ were observed on the grain boundary and twinned ZrO_2 was observed around the PMS–PZT perovskite phase. The mechanism for the formation of the twinned ZrO_2 and the dependence of its content on SiO_2 concentration were studied. The deterioration of the piezoelectric properties was also discussed.

Keywords: PZT; Grain boundaries; Piezoelectric; Ceramics

1. Introduction

The $Pb(Zr, Ti)O_3$ (PZT) system has found wide industrial applications. In order to meet the specific requirements for its applications, extensive research on the modifications of its composition and processes for its preparation has been carried out [1–4]. Researches have reported that the pseudo-ternary crystalline solutions of $Pb(Mn_{1/3}Sb_{2/3})O_3$–$PbZrO_3$-$PbTiO_3$ (PMS–PZT) displayed significantly higher electromechanical coupling factors, higher mechanical quality factors, and higher maximum vibration velocities than that of pure PZT [5–7]. These superior properties make the PMS–PZT system an ideal candidate for high power applications such as piezoelectric transformers, ultrasonic motors, and electromechanical transducers.

With the rapid development of the semiconductor industry, extensive research has been devoted to the integration of ferroelectric films with semiconductor techniques. The epitaxial films on silicon surfaces, due to their piezoelectric properties, have found valuable applications as microelectromechanical actuators and transducers [8]. To optimize the ferroelectric properties, it was essential to understand the interaction between ferroelectric materials and SiO_2. Wright and Francis [9] have reported that metastable polymorph of the pyrochlore phase $Pb_2Ti_2O_6$ was stabilized only in the presence of silicon. When the pyrochlore phase converted to the stable perovskite phase of $PbTiO_3$ at a higher temperature, silicon incorporated in the $Pb_2Ti_2O_6$ lattice diffused out of the freshly nucleated perovskite lattice. Palkar et al. [10] have not observed any change in the crystal structure and the ferroelectric properties of $PbTiO_3$ in the presence of silicon. They assumed that silicon diffused out of the perovskite lattice and was likely located on the grain boundary in an unidentified chemical form. The authors, however, did not provide any evidence to prove the segregation of silicon on the grain boundary.

To better understand the ferroelectric properties, it is necessary to investigate the domain morphology and the microstructure of the specimens. Transmission electron microscope (TEM) provides the most direct method to study the domain structure. It offers much better resolution than scanning electron microscopy (SEM) [11,12]. In this work, the effect of Si doping on domain morphology and microstruc-

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ture, especially the secondary phases on the grain boundary, of PMS–PZT ceramics has been studied.

2. Experimental

All specimens were fabricated by conventional ceramic techniques. The compositions of $Pb_{0.98}Sr_{0.02}(Mn_{1/3}Sb_{2/3})_{0.05}Zr_{0.48}Ti_{0.47}O_3 + x$ wt.% of SiO_2, where x varied from 0 to 1.0, were mixed starting from powdered Pb_3O_4, $SrCO_3$, $MnCO_3$, Sb_2O_3, ZrO_2, TiO_2, and SiO_2 (reagent-grade). The mixtures were wet milled for 4 h using distilled water and ZrO_2 balls as a grinding medium. The mixtures were then calcinated at 850 °C for 2 h. The calcinated powders were re-milled for 6 h and 5–10 wt.% of polyvinyl alcohol (PVA) was subsequently added as a binder. The milled powders were pressed into pellets under 200 MPa. The disks were sintered in a sealed alumina crucible at 1200–1300 °C for 1 h under a protective atmosphere to prevent the evaporation of lead. The sintered pellets were machined into 0.5 mm in thickness and coated with silver electrodes on both sides. They were subsequently fired at 740 °C for 20 min. The specimens were finally poled in an electric field with strength up to 3 kV mm^{-1} for 20 min at 130 °C in silicon oil.

Specimens for TEM were prepared from ceramic bulks by mechanical grinding, dimple grinding, and ion-milling. To minimize ion-induced damages, the ion-milling was carried out using Ar^+ ions of 4 kV and a discharge current of 1 mA. The specimens were finally coated with carbon. Microstructure and domain morphology were analyzed using a JEM-2010 transmission electron microscope (JOEL, Japan) equipped with an energy dispersive spectrometer (Link-ISIS, Oxford) operated at 200 kV. Piezoelectric properties were measured using the resonance–antiresonace method with a precision impedance analyzer (HP 4294A).

3. Results and discussion

Fig. 1 shows the bright field TEM micrographs of PMS–PZT ceramics containing different amount of SiO_2 that are taken at room temperature. With the increase in the amount of SiO_2, significant changes in the domain size and morphology are observed. Pure PMS–PZT (Fig. 1a) shows a distinct herringbone domain structure of several microns in length and less than 100 nm in width, which might be attributed to the coexistence of the ferroelectric tetragonal and rhombohedral phases in the composition near the morphotropic phase boundary (MPB). The herringbone domain pattern contains many parallel stripes where the adjacent ones are twin-related, which form with mutual nearly 90° angles on both sides of the herringbone pattern [11]. With the addition of only 0.4 wt.% SiO_2, the size of the domain (Fig. 1b) remains similar both in length and width relative to the undoped specimens. However, the morphology of the domain dramatically changes to the micron-sized lenticular shape. These normal micron-sized tetragonal 90° ferroelectric domains are typical for the long-range-ordered ferroelectric state. With the further increase of SiO_2 content, the changes in the domain patterns become more pronounced. When the SiO_2 content reaches 1.0 wt.%, dramatic decrease in the domain size (Fig. 1c) is observed. The length of the domains is less than 400 nm and the width is approximately several hundred angstroms. In addition, the domain boundaries become more "wavy" relative to the lower Si-content specimens that have nearly straight boundaries. The "wavy" domains maintain a significant degree of preferred orientation along a particular family of the crystallographically equivalent polar directions. The waviness in the morphology might be due to the continuous bending of the domain orientation between various equivalent directions on a length scale of ca. 0.2 μm [13]. The similar "wavy" domains have also been observed by Tan et al. [14] in potassium-modified PZT ceramics and by He et al. [15] in Cr_2O_3-doped PZTMN samples.

Fig. 2 shows the bright field TEM images/selected-area diffraction (SEAD) patterns and EDS spectra of the grain boundary taken at room temperature. The diffraction rings (Fig. 2a) indicate that the grain boundary in the pure PMS–PZT ceramics contains significant amount of glass phase and the EDS spectrum (Fig. 2c) suggests that the glass phase contains primarily lead. With the doping of SiO_2 into the PMS–PZT ceramics, significant changes occur on the

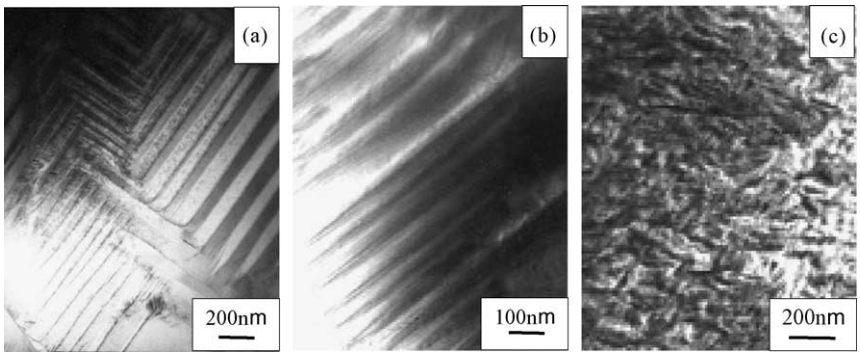

Fig. 1. Bright-field TEM micrographs of PMS–PZT ceramics doped with different amount of SiO_2 taken at room temperature: (a) 0 wt%, (b) 0.4 wt%, (c) 1.0 wt%.