Research Article

Structure and Physical Properties of PZT-PMnN-PSN Ceramics Near the Morphological Phase Boundary

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1. Introduction

Lead zirconate titanate (PZT) is one of the most commonly used ferroelectric ceramic materials. The material has been studied intensively since discovery of the miscibility of lead titanate and lead zirconate in the 1950s [1–5]. Due to their excellent dielectric, pyroelectric, piezoelectric, and electrooptic properties, they have a variety of applications in high energy capacitors, nonvolatile memories (FRAM), ultrasonic sensors, infrared detectors, electrooptic devices, and step-down multilayer piezoelectric transformers for AC-DC converter applications [5, 6]. Until now, many ternary and quaternary systems, such as Pb(Ni1/3Nb2/3)O3−PZT, Pb(Y2/3W1/3)O3−PZT, Pb(Mn1/3Nb2/3)O3−PZT, Pb(Mg1/3Nb2/3)O3−PZT, Pb(Ni1/3Nb2/3)O3−PZT, Pb(Ni1/3)O3−PZT, and PZT-PMnSbN, [4, 5, 7–11] have been synthesized by modifications or substitutions to satisfy the requirements of practical applications of piezoelectric transformer.

In ceramics manufacturing technology, piezoelectric PZT system ceramics compositions are mostly near the tetragonal-rhombohedral (T-R) morphotropic phase boundary (MPB). The electromechanical response of these ceramics is known to be most pronounced at the MPB. So, there have been many investigations on the coexistence of two phases near MPB in PZT system [3]. The reports suggested the existence of a range of compositions where both tetragonal and rhombohedral phases are thermodynamically stable [7, 12].

In this study, 0.9Pb(Zr,Ti1−x)O3−0.07Pb(Mn1/3Nb2/3)O3−0.03Pb(Sb1/2Nb1/2)O3 (PZT-PMnN-PSN) ceramics were prepared by columbite method. The phase structure of the ceramic samples was analyzed. Results show that the pure perovskite phase is in all ceramics specimens. The effect of the Zr/Ti ratio on the region of morphotropic phase boundary for PZT-PMnN-PSN ceramics was studied. Experimental results show that the phase structure of ceramics changes from tetragonal to rhombohedral with the increase of the content of Zr/Ti ratio in the system. The composition of PZT-PMnN-PSN ceramics near the morphotropic phase boundary obtained is the ratio of Zr/Ti: 49/51. At this ratio, the ceramic has the optimal electromechanical properties: the $k_p = 0.61$, the $\varepsilon_{\text{max}} = 29520$, the $d_{31} = -236 \text{ pC/N}$, the $Q_m = 2400$, high remanent polarization ($P_r = 49.2 \mu \text{C/cm}^2$), and low coercive field $E_c = 10.28 \text{ kV/cm}$. 

Figure 1: XRD patterns for compositions at (a) 54/46; (b) 53/47; (c) 52/48; (d) 51/49; (e) 50/50; (f) 49/51; (g) 48/52; (h) 47/53; (i) 46/54.
tetragonal and rhombohedral phases and the exact composition of the MPB in chemically homogeneous PZT-PMnN-PSN ceramics were determined.

2. Experimental

The polycrystalline samples of PZT-PMnN-PSN were synthesized by columbite precursor method. The raw materials including powders (high purity) of PbO (99%), ZrO$_2$ (99.9%), TiO$_2$ (99%), MnCO$_3$ (99%), Sb$_2$O$_3$ (99%), and Nb$_2$O$_5$ (99.9%) for the given composition were weighted by mole ratio. First, the finely mixed powder of MnCO$_3$ and Nb$_2$O$_5$; Sb$_2$O$_3$ and Nb$_2$O$_5$ are mixed in a Teflon-mortar for about 10 h in an acetone medium and then calcined at 1200°C in an alumina crucible for 3 h. The calcined powder was then grinded and mixed by mortar again with PbO, ZrO$_2$ and TiO$_2$ for 30 h. The finely mixed powder was calcined at 850°C for 2 h.

The ground materials were pressed into disk 12 mm in diameter and 1.5 mm in thickness under 100 MPa. The samples were sintered in a sealed alumina crucible with PbZrO$_3$ coated powder at temperature 1150°C for 2 h. Scanning electron micrograph of the sample was taken at room temperature. The sintered pellet was polished and silver electroded and connected to an LCR meter (Hioki, Japan) for dielectric measurement. The frequency dependence of dielectric constant and loss tangent were obtained using the LCR meter in the frequency range from 0.1 kHz to 500 kHz. The polarization-electric field ($P$-$E$) hysteresis loops were measured by a Sawyer-Tower circuit at 50 Hz.

As-sintered samples were ground and polished to remove the surface layer for X-ray diffraction (XRD, D/Max-RB, Rigaku, Japan). Cu Kα radiation with a step of 0.01 s was used. The microstructure of the samples was examined by using a scanning electron microscope (SEM). The electromechanical coupling factor ($k_p$), mechanical quality factor ($Q_m$), and piezoelectric coefficient ($d_{33}$) were calculated by using the resonance-antiresonance method. The dielectric constant was calculated from the capacitance and the dimension of the samples.

3. Results and Discussion

3.1. Structure and Microstructure. It is reported that tetragonal, rhombohedral, and T-R phases were identified by an analysis of the peaks (002) (tetragonal), 200 (tetragonal), and 200 (rhombohedral) in the $2\theta$ range 43°–47°. The splitting of (002) and (200) peaks indicates that they are the ferroelectric tetragonal phase (FT), while the single (200) peak shows the ferroelectric rhombohedral phase (FR) [1, 6, 13]. Figure 1 shows the XRD patterns of PZT-PMnN-PSN with Zr/Ti ratio at 54/46 up to 46/54. Triplet peaks indicate that the samples consist of a mixture of tetragonal and rhombohedral phases. A transition from tetragonal phase to rhombohedral phase is observed as Zr/Ti ratio increases. The multiple peak separation method was used to estimate the relative fraction of coexisting phases. The relative phase fraction was then calculated by the following equations [14]:

$$M_R = \frac{I_{R(200)}}{I_{R(200)} + I_{T(002)} + I_{T(200)}},$$

$$M_T = \frac{I_{T(002)} + I_{T(200)}}{I_{R(200)} + I_{T(002)} + I_{T(200)}}.$$  

With increasing Zr/Ti ratio, tetragonal relative fraction decreases and rhombohedral relative fraction increases. The analysis of the relative phase fraction in the PZT-PMnN-PSN system indicates that tetragonal and rhombohedral phases coexist in the composition range for 0.48 $\leq x \leq$ 0.52 as shown in Figure 2.

Figure 3 shows the SEM image of the fractured surface of PZT-PMnN-PSN ceramic at different Zr/Ti ratios. It is observed from the micrographs that the average grain size of samples is increased with the increasing amount of Zr/Ti ratio. However, when further increasing the Zr/Ti ratio to 51/49, the average grain size is reduced. These results are in good agreement with the reports in the literature [15].

3.2. Dielectric and Ferroelectric Properties

3.2.1. The Influence of Zr/Ti Ratio on the Dielectric Properties. Figure 4 shows the temperature dependence of dielectric permittivity and dielectric loss tanδ of PZT-PMnN-PSN system (1 kHz) with Zr/Ti ratios 46/54 up to 54/46, respectively. As shown in Figure 4, all the samples in morphotropic phase boundary region (Zr/Ti = 48/52–52/48) exhibit typical relaxor ferroelectric behavior around. The dielectric responses are characterized by diffuse dielectric peaks and a slight shift of permittivity of maximum toward higher temperature with increasing frequencies.

By comparing the curves in Figure 1, we see that the broadness of dielectric response increases with an increase in Zr/Ti ratio and the largest is at Zr/Ti = 49/51. The temperature of dielectric permittivity maximum also increases with increase of Zr/Ti ratio. All samples have a temperature called
Figure 3: Surface morphologies observed by SEM of PZT-PMnN-PSN ceramics at various ratios of Zr/Ti.

Burn temperature at which dielectric response starts complying Curie-Weiss law and the system starts the transition into paraelectric phase.

Figure 5 shows Curie-Weiss dependence of the permittivity of the samples at temperatures start to $T_B$. The fitting parameters [14] are given in Table 1.

From Table 1, we can see that all the temperature values extend to decrease with the increase of Zr/Ti ratio.

3.2.2. The Influence of Zr/Ti Ratio on the Ferroelectric Properties. Figure 6 shows P-E hysteresis loops of all samples. The well-saturated hysteresis loops were observed, and the values of remanent polarization ($P_r$) and coercive field ($E_c$) were presented in Table 2.

It's demonstrated that the hysteresis loops of all samples are of typical forms characterizing ferroelectric materials. The remanent polarization ($P_r$) reaches the maximum value of 49.2 $\mu$C/cm$^2$ and the coercive field ($E_c$) reaches the minimum value of 10.28 kV·cm$^{-1}$ at Zr/Ti = 49/51 (Figure 7).

4. Piezoelectric Properties

Figure 8 shows the piezoelectric and dielectric properties as a function of Zr/Ti ratio. PZT-PMnN-PSN exhibits high
Figure 4: (a) Dielectric constant and (b) loss tangent of PZT-PMnN-PSN at various Zr/Ti ratios.

Figure 5: Curie-Weiss dependence of the permittivity of the samples at temperatures start to $T_B$. 
piezoelectric coefficient and electromechanical coupling factor around the MPB. From the trend of the variation of piezoelectricity, it reaches the maximum values of $d_{31} = -236$ pC/N, $k_p = 0.61$ at Zr/Ti = 49/51.

Simple diagram phase of PZT-PMnN-PSN ceramics near MPB, which is attractive system displaying excellent piezoelectric and dielectric properties, good electrostrictive effects, and relaxation of ferroelectric phase transition is shown in Figure 9.
5. Conclusion

The results obtained from the experiment are as follows.

(1) PZT-PMnN-PSN ceramics with 7% wt excess PbO were prepared by columbite method.

(2) The structure of ceramics sintered at 1150°C shows the pure perovskite structure in all ceramics specimens; the structure of PZT-PMnN-PSN ceramics was transformed from tetragonal to rhombohedral, with Zr/Ti ratio increased in system.

(3) The composition of PZT-PMnN-PSN ceramics near the morphotropic phase boundary obtained is the ratio of Zr/Ti = 49/51. At this ratio, the ceramic has the optimal electromechanical properties: the $k_p = 0.61$, the $\varepsilon_{\text{max}} = 29520$, the $d_{31} = -236$ pC/N, the $Q_m = 2400$, high remanent polarization ($P_r = 49.2 \mu C/cm^2$), and low coercive field $E_c = 10.28 kV/cm$.

(4) The piezoelectric ceramic with Zr/Ti ratio of 49/51 may be suitable for piezoelectric transformer applications and other high power devices.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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