Research Article

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

Nguyen Dinh Tung Luan,¹ Le Dai Vuong,^{1,2} Truong Van Chuong,² and Nguyen Truong Tho²

¹ The Fundamental Science Department, Hue Industry College, Hue City, Vietnam

² Department of Physics, College of Sciences, Hue University, Hue City, Vietnam

Correspondence should be addressed to Nguyen Dinh Tung Luan; ntungluan@yahoo.com

Received 1 August 2013; Accepted 11 December 2013; Published 20 January 2014

Academic Editor: Mohammad Mahroof-Tahir

Copyright © 2014 Nguyen Dinh Tung Luan et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

The $0.9\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3-0.07\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.03\text{Pb}(\text{Sb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (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 $\epsilon_{\max} = 29520$, the $d_{31} = -236 \text{ pC/N}$, the $Q_m = 2400$, high remanent polarization ($P_r = 49.2 \mu\text{C}\cdot\text{cm}^{-2}$), and low coercive field $E_c = 10.28 \text{ kV}\cdot\text{cm}^{-1}$.

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 $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -PZT, $\text{Pb}(\text{Y}_{2/3}\text{W}_{1/3})\text{O}_3$ -PZT, $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ -PZT, $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $\text{Pb}(\text{Ni}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -PZT, $\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3$ - $\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3$ -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, $0.9\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3-0.07\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3-0.03\text{Pb}(\text{Sb}_{1/2}\text{Nb}_{1/2})\text{O}_3$ (PZT-PMnN-PSN) ceramics in the vicinity of MPB were investigated according to the Zr/Ti ratio content. The purpose of this work is to study structure and ferroelectric and piezoelectric properties in the vicinity of the MPB in detail. Furthermore, the width of coexistence of

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.

FIGURE 2: Variations of relative content of the tetragonal and rhombohedra phases with Zr/Ti ratio.

tetragonal and rhombohedra phases and the exact composition of the MPB in chemically homogeneous PZT-PMnN-PSN ceramics were determined.

2. Experimentals

The polycrystalline samples of PZT-PMnN-PSN were synthesized by columbite precursor method. The raw materials including powders (high purity) of PbO (99%), ZrO₂ (99.9%), TiO₂ (99%), MnCO₃ (99%), Sb₂O₃ (99%), and Nb₂O₅ (99.9%) for the given composition were weighted by mole ratio. First, the finely mixed powder of MnCO₃ and Nb₂O₅; Sb₂O₃ and Nb₂O₅ 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, ZrO₂ and TiO₂ 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 PbZrO₃ 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 K α 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_{31}) 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, rhombohedra, and T-R phases were identified by an analysis of the peaks (002 (tetragonal), 200 (tetragonal), and 200 (rhombohedral)) in the 2θ 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 rhombohedra 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 rhombohedra phases.

A transition from tetragonal phase to rhombohedra 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]:

$$M_R = \frac{I_{R(200)}}{I_{R(200)} + I_{T(002)} + I_{T(200)}}, \quad (1)$$

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

With increasing Zr/Ti ratio, tetragonal relative fraction decreases and rhombohedra relative fraction increases. The analysis of the relative phase fraction in the PZT-PMnN-PSN system indicates that tetragonal and rhombohedra 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 ceramics at different Zr/Ti ratios. It is observed from the micrographs that the average grain size of samples are 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 reported 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 $\tan \delta$ 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 $49.2 \mu\text{C}/\text{cm}^2$ and The coercive field (E_c) reaches the minimum value of $10.28 \text{ kV}\cdot\text{cm}^{-1}$ 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 .

FIGURE 6: P - E hysteresis loops of PZT-PMnN-PSN samples.

TABLE 1: Dielectric properties and fitting parameters of PZT-PMnN-PSN ceramics.

Sample	ϵ	$\tan \delta$	$\epsilon'_{\max}$	T_m ($^{\circ}\text{C}$)	T_B ($^{\circ}\text{C}$)	T_C ($^{\circ}\text{C}$)
M046	674	0.023	21343	343	390.3	347.4
M047	699	0.035	21447	337	380.2	342.3
M048	735	0.041	23050	325	375.8	330.8
M049	899	0.044	29520	312	370.4	315.5
M050	887	0.046	29018	298	366.9	304.6
M051	756	0.022	27609	289	348.3	300.1
M052	739	0.023	22348	280	342.5	292.4
M053	692	0.014	21349	271	332.7	281.9
M054	554	0.013	19875	266	325.3	274.4

TABLE 2: Calculated P_r and E_c values of samples.

Sample	E_c (kV/cm)	P_r ($\mu\text{C}/\text{cm}^2$)
M046	11.32	23.0
M047	11.07	27.0
M048	10.37	32.0
M049	10.28	49.2
M050	10.88	46.0
M051	11.85	28.0
M052	12.40	25.0
M053	12.66	19.7
M054	13.45	17.3

piezoelectric coefficient and electromechanical coupling factor around the MPB. From the trend of the variation of piezoelectricity, it reaches the maximum values of $d_{31} = -236 \text{ pC/N}$, $k_p = 0.61$ at $\text{Zr/Ti} = 49/51$.

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.

FIGURE 7: The P_r and the E_c as a function of Zr/Ti ratios.

FIGURE 8: Piezoelectric properties of PZT-PMnN-PSN at various Zr/Ti ratios.

FIGURE 9: Simple diagram phase of PZT-PMnN-PSN system near MPB.

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 rhombohedra, 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 $\epsilon_{\max} = 29520$, the $d_{31} = -236$ pC/N, the $Q_m = 2400$, high remanent polarization ($P_r = 49.2 \mu\text{C}\cdot\text{cm}^{-2}$), and low coercive field $E_c = 10.28 \text{ kV}\cdot\text{cm}^{-1}$.
- (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.

Acknowledgment

This work is supported by the National Foundation for Science and Technology Development (NAFOSTED), no. 103.02.06.09.

References

- [1] F. Gao, L. Cheng, R. Hong, J. Liu, C. Wang, and C. Tian, "Crystal structure and piezoelectric properties of $x\text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - (0.2-x)\text{Pb}(\text{Zn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - 0.8\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ ceramics," *Ceramics International*, vol. 35, no. 5, pp. 1719–1723, 2009.
- [2] Z. Necira, A. Boutarfaia, M. Abba, H. Menasra, and N. Abdesslem, "Effects of thermal conditions in the phase formation of undoped and doped $\text{Pb}(\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3$ solid solutions," *Materials Sciences and Applications*, vol. 4, no. 5, pp. 319–323, 2013.
- [3] Y. Xu, *Ferroelectric Materials and Their Applications*, North-Holland, London, UK, 1991.
- [4] J. Yoo, Y. Lee, K. Yoon et al., "Microstructural, electrical properties and temperature stability of resonant frequency in $\text{Pb}(\text{Ni}_{1/2}\text{W}_{1/2})\text{O}_3 - \text{Pb}(\text{Mn}_{1/3}\text{Nb}_{2/3})\text{O}_3 - \text{Pb}(\text{Zr,Ti})\text{O}_3$ ceramics for high-power piezoelectric transformer," *Japanese Journal of Applied Physics A*, vol. 40, no. 5, pp. 3256–3259, 2001.
- [5] R. Muanghlua, S. Niemchareon, W. C. Vittayakorn, and N. Vittayakorn, "Effects of Zr/Ti ratio on the structure and ferroelectric properties in PZT-PZN-PMN ceramics near the morphotropic phase boundary," *Advanced Materials Research*, vol. 55–57, pp. 125–128, 2008.
- [6] F. Kahoul, L. Hamzioui, N. Abdesslem, and A. Boutarfaia, "Synthesis and piezoelectric properties of $\text{Pb}_{0.98}\text{Sm}_{0.02}$

- $[(\text{Zr}_y, \text{Ti}_{1-y})_{0.98}(\text{Fe}^{3+}, \text{Nb}^{5+})_{0.02}]\text{O}_3$ ceramics,” *Materials Sciences and Applications*, vol. 3, pp. 50–58, 2012.
- [7] N. D. T. Luan, L. D. Vuong, and B. C. Chanh, “Microstructure, ferroelectric and piezoelectric properties of PZT–PMnSbN ceramics,” *International Journal of Materials and Chemistry*, vol. 3, pp. 51–58, 2013.
- [8] M. Kobune, Y. Tomoyoshi, A. Mineshige, and S. Fujii, “Effects of MnO_2 addition on piezoelectric and ferroelectric properties of $\text{PbNi}_{1/3}\text{Nb}_{2/3}\text{O}_3$ – PbTiO_3 – PbZrO_3 ceramics,” *Journal of the Ceramic Society of Japan*, vol. 108, no. 7, pp. 633–637, 2000.
- [9] S. J. Yoon, A. Joshi, and K. Uchino, “Effect of additives on the electromechanical properties of $\text{Pb}(\text{Zr,Ti})\text{O}_3$ – $\text{Pb}(\text{Y}_{2/3}\text{W}_{1/3})\text{O}_3$ ceramics,” *Journal of the American Ceramic Society*, vol. 80, no. 4, pp. 1035–1039, 1997.
- [10] Y. K. Gao, Y. H. Chen, J. H. Ryu, K. J. Uchino, and D. Viehland, “Eu and Yb substituent effects on the properties of $\text{Pb}(\text{ZrM}_{0.52}\text{Ti}_{0.48})\text{O}_3$ – $\text{Pb}(\text{Mn}_{1/3}\text{Sb}_{2/3})\text{O}_3$ ceramics: development of a new high-power piezoelectric with enhanced vibrational velocity,” *Japanese Journal of Applied Physics*, vol. 40, no. 2, pp. 687–693, 2001.
- [11] Z. L. Gui, L. T. Li, H. Q. Lin, and X. W. Zhang, “Low temperature sintering of lead magnesium nickel niobate zirconate titanate (PMN–PNN–PZT) piezoelectric ceramic, with high performances,” *Ferroelectrics*, vol. 101, no. 1, pp. 93–99, 1990.
- [12] Z. Yang, H. Li, X. Zong, and Y. Chang, “Structure and electrical properties of PZT–PMS–PZN piezoelectric ceramics,” *Journal of the European Ceramic Society*, vol. 26, no. 15, pp. 3197–3202, 2006.
- [13] H. Fan and H. Kim, “Perovskite stabilization and electromechanical properties of polycrystalline lead zinc niobate-lead zirconate titanate,” *Journal of Applied Physics*, vol. 91, no. 1, pp. 317–322, 2002.
- [14] A. Quintana-Nedelcos, A. Fundora, H. Amorín, and J. M. Siqueiros, “Effects of Mg addition on phase transition and dielectric properties of $\text{Ba}(\text{Zr}_{0.05}\text{Ti}_{0.95})\text{O}_3$ system,” *The Open Condensed Matter Physics Journal*, vol. 2, pp. 1–8, 2009.
- [15] L. D. Vuong, P. D. Gio, T. Van Chuong, D. T. H. Trang, D. V. Hung, and N. T. Duong, “Effect of Zr/Ti ratio content on some physical properties of the low temperature sintering PZT–PZN–PMnN ceramics,” *International Journal of Materials and Chemistry*, vol. 3, no. 2, pp. 39–43, 2013.