International Journal of Materials and Chemistry 2013, 3(2): 39-43
DOI: 10.5923/j.ijmc.20130302.04

Effect of Zr/Ti Ratio Content on Some Physical Properties of Low Temperature Sintering PZT−PZN−PMnN Ceramics

Le Dai Vuong[*], **Phan Dinh Gio, Truong Van Chuong, Dung Thi Hoai Trang, Duong Viet Hung, Nguyen Trung Duong**

Department of Physics, College of Sciences, Hue University, 77 Nguyen Hue street, Hue city, Vietnam

---

Abstract Low-temperature sintering of $0.8Pb(Zr_xTi_{1-x})]O_3 - 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ + 0.7 % wt Li_2CO_3 (PZT-PZN-PMnN) ceramics was prepared by using Li_2CO_3 as the sintering aid. Their structure and physical properties were investigated according to the Zr/Ti ratio content. From X-ray diffraction patterns showed that samples formed a phase perovskite structure without secondary phases. The electromechanical coupling factor (k_p), the maximum dielectric constant (ε_{max}), the piezoelectric constant (d_{31}) and the mechanical quality factor (Q_m) increased with the increase of Zr/Ti ratio content and reaches to the highest value at the ratio content of Zr/Ti = 48/52. At this ratio content, the ceramic has the optimal electromechanical properties: the ε_{max} = 19500, the k_p = 0.62, the d_{31} = 140 pC/N and the Q_m = 1112.

Keywords Crystal Structure, Dielectrics, Piezoelectrics, Electromechanical Coupling Factor

---

1. Introduction

Last several decades have witnessed extensive study on the relaxor ferroelectrics since their discovery by Smolenskii *et al.*[1], owing to their significant technical importance on the application of electromechanical devices such as multilayer ceramic capacitors, electrostrictive transducers, micro displacement positioners. $Pb(Mn_{1/3}Nb_{2/3})O_3$ (PMnN) and $Pb(Zn_{1/3}Nb_{2/3})O_3$ (PZN) are members of lead-based relaxor ferroelectric family with different cations on the B-site of perovskite lattice. These materials are ferroelectric materials that have characteristics as high dielectric constant, the temperature at the broad phase transition point between the ferroelectric and paraelectric phase (the diffuse phase transition) and the strong frequency dependency of the dielectric properties. Gao Feng *et al.*[2] investigated 0.8PZT – (0.2–x)PZN – xPMnN ceramics with compositions close to the morphotropic phase boundary (MPB). The optimized results of k_p (0.57), ε (842) and Q_m (1020) were obtained at 0.075 mol $Pb(Mn_{1/3}Nb_{2/3})O_3$, which is a new promising material for piezoelectric transformer. The Zr/Ti ratio is known to affect some properties strongly such as the elastic constant, the permittivity, the coupling factor, etc. These properties take extreme values when Zr/Ti ratio corresponds to the composition of the MPB which separates the tetragonal (*T*) and rhombohedral (*R*) phases towards Ti-rich and Zr-rich sides, respectively[3,4]. Rangson Muanghlua *et al.*[5]. studied the effect of Zr/Ti ratio on the structure and ferroelectric properties of $0.07Pb(Mn_{1/3}Nb_{2/3})O_3$-$0.6Pb(Ni_{1/3}Nb_{2/3})O_3$-$0.87Pb(Zr_xTi_{1-x})O_3$ ceramics. From XRD analysis and ferroelectric properties measurements indicated the existence of the MPB composition between x = 0.50. At this composition, the ceramics exhibits the highest ferroelectric properties. Yoo and Lee[6] also reported that the PZT-PNN-PMnN ceramics were strongly influence by the Zr/Ti ratio. They found that the electromechanical coupling factor k_p, the piezoelectric constant d_{33} and the mechanical quality factor Q_m increased with the increase of Zr/Ti ratio and then decreased after the ratio exceeded 50/50. Recently, Fares Kahoul *et al.*[7] studied the structure and electrical properties of $Pb_{0.98}Sm_{0.02}[(Zr_x,Ti_{1-x})_{0.98}(Fe_{1/2}Nb_{1/2})_{0.02}]O_3$ ceramics with the composition near the MPB. They found that the k_p, d_{31} and Q_m of the ceramics are enhanced with the increase of Zr/Ti ratio. At Zr/Ti ratio of 55/45, the ceramics has the optimal electromechanical properties, k_p = 0.631, d_{31} = 120.10^{-12}C/N, Q_m = 462.

The research results of the above authors clearly showed the significance of Zr/Ti ratio in controlling the electromechanical properties of the PZT-based ceramics. In this paper, we investigated the effect of Zr/Ti ratio content on some physical properties of the low temperature sintering PZT-PZN-PMnN ceramics.

---

[*] Corresponding author:
ledaivuongqb@gmail.com (Le Dai Vuong)

2. Experimental Procedure

The general formula of the material was $0.8Pb(Zr_xTi_{1-x})O_3 - 0.125Pb(Zn_{1/3}Nb_{2/3})O_3 - 0.075Pb(Mn_{1/3}Nb_{2/3})O_3$ + 0.7 wt% Li_2CO_3, where x is 0.46, 0.47, 0.48, 0.49, 0.50 and 0.51. They are denoted by M46, M47, M48, M49, M50 and M51, respectively.

The raw materials including powders (purity of 99%) of ZrO_2, TiO_2, Nb_2O_5, ZnO and MnO_2 for the given composition were weighted by mole ratio and the powders were mixed and milled (the PM 400/2 milling machine) for 8 h using ziconia balls and ethanol as the medium, then were calcined. Thereafter, PbO was added and milled again. Powders were calcined at 850°C for 2 h, then the sintering aid, Li_2CO_3 was added[8] and milled again for 16h. The ground materials were pressed into disk 12mm in diameter and 1.5mm in thickness under 100 MPa. The samples were sintered in a sealed alumina crucible with $PbZrO_3$ coated powder at temperature 950°C for 2h.

The crystalline phase was analyzed using an X-ray diffactometer (XRD, D8 ADVANCE). The microstructure of the samples was examined by using a scanning electron microscope (SEM). The density of samples was measured by Archimedes method. The samples were poled in a silicone oil bath at 120°C by applying 30 $kVcm^{-1}$ for 20 min, then cooled at this electric field. They were aged for 24h prior to testing. The piezoelectric properties were determined by the resonance and antiresonance technique using an impedance analyzer (Agilent 4396B and RLC HIOKI 3532). The calculation equations are as follows:

$k_p = [2.51(f_p - f_s)/f_p]^{1/2}$ and $Q_m = f_p^2[2\pi Z_{\min} C_s f_s (f_p^2 - f_s^2)]^{-1}$,

where f_s and f_p are resonant and antiresonant frequencies (Hz), and Z_{min} and C_s are resonant impedance (ohms) and electrical capacitance (farads). The dielectric properties were measured by RLC HIOKI 3532.

3. Results and Discussion

3.1. Phase Analysis and Microstructure

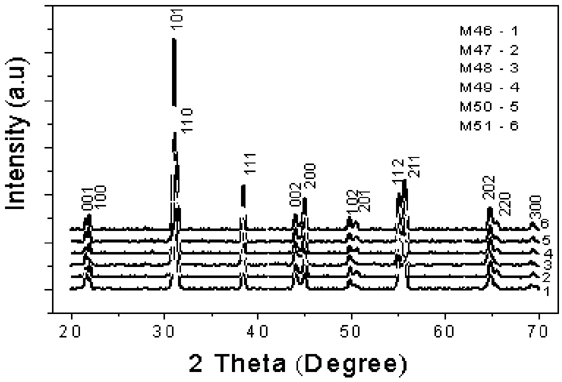

Figure 1. X-ray diffraction patterns of the ceramics with different Zr/Ti ratio contents

Figure. 1 shows X-ray diffraction patterns (XRD) of the PZT–PZN–PMnN ceramics with the variation of Zr/Ti ratio content. All the samples showed a tetragonal perovskite phase without any secondary phase. The lattice parameters for various compositions were calculated using the least square method from the double (002) and (200) peaks of tetragonal structure and results for the tetragonality c/a of perovskite phase are shown in Figure 2. The c/a ratio decreases with increasing Zr/Ti ratio content, indicating that the tetragonality of PZT-PZN-PMnN ceramics decreased when Zr increased.

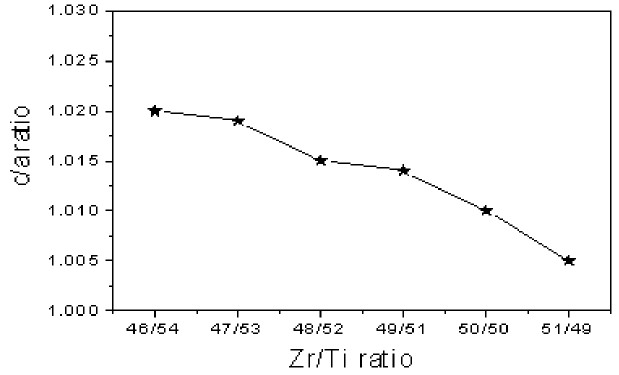

Figure 2. The tetragonality c/a of the ceramics as a function of Zr/Ti ratio

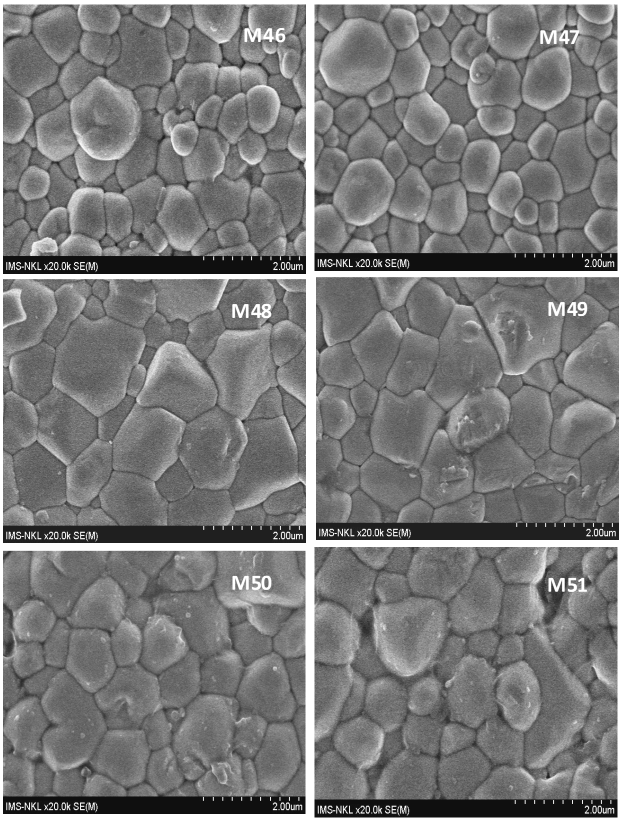

Figure 3. Microstructures of samples with the different Zr/Ti ratio contents

Figure 3 shows the SEM image of the fractured surface of PZT–PZN–PMnN ceramics at different Zr/Ti ratio contents. It is observed from the micrographs that the average grain size of samples are increased with the increasing amount of Zr/Ti ratio (Table 1). It is explained that the initial and intermediate stages of sintering, densification and grain growth occur through liquid-phase diffusion (Li_2CO_3)[8], and then the liquid phase at the intergranular boundaries gradually dissolves into the grains with grain growth[9,10]. However, figure 3 also shows that further increasing the Zr/Ti content to 51/49 gives rise to an abnormal grain boundary, and the average grain size is reduced.

Table 1. The average grain size of ceramic samples

Samples	Average grain size (μm)
M46	0.80
M47	0.90
M48	1.18
M49	1.16
M50	1.02
M51	1.00

3.2. The Ceramic Density

The densities of the samples containing different amounts of Zr/Ti ratio were measured, and the results are shown in Figure 4. As seen, the densities of the ceramics are in the range from 7.80g/cm^3 to 7.86g/cm^3 (94-97 % theoretical density) and dependent on Zr/Ti ratio content. When Zr/Ti ratio content increases, the density of samples increases and achieves the highest value (7.86g/cm^3) at the ratio of Zr/Ti = 48/52, and then decreases. This may be explained from microstructures of ceramic samples. When the amount of Zr/Ti ratio increased, the ceramic samples became more dense, and at Zr/Ti = 48/52, the ceramic sample was almost fully dense (fig. 3). When the further increasing the Zr/Ti ratio content to 49/51 and above, a large number of pores were present, giving rise to an abnormal grain boundary. Hence, the densities of the ceramics are decreased. The variation in density of the ceramic samples is in good accordance with the microstructure.

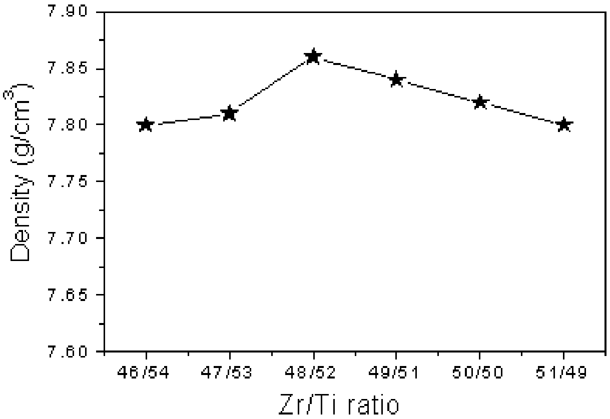

Figure 4. The density of PZT-PZN-PMnN samples as a function of the Zr/Ti content

3.3. Dielectric Properties

The change of Zr/Ti content also significantly affects the piezoelectric and dielectric properties of PZT–PZN–PMnN ceramics.

Figure 5 shows the dependence of dielectric constant ε and dielectric loss tanδ of the ceramic on temperature at 1 kHz. As observed, the dielectric properties exhibited characteristics of a relaxor material in which the phase transition temperature occurs within a broad temperature range. This is one of the characteristics of ferroelectrics with disordered perovskite structure. The maximum dielectric constant ε_{max} increases with increasing Zr/Ti ratio content, and at Zr/Ti = 48/52, the highest dielectric constant ε_{max} of about 19500 and then sharply decreases beyond this point. This can be explained by the increase of grain size effect[10]. The dielectric loss tanδ shows the reversed trend, this appropriate to the characteristics of dielectrics[11].

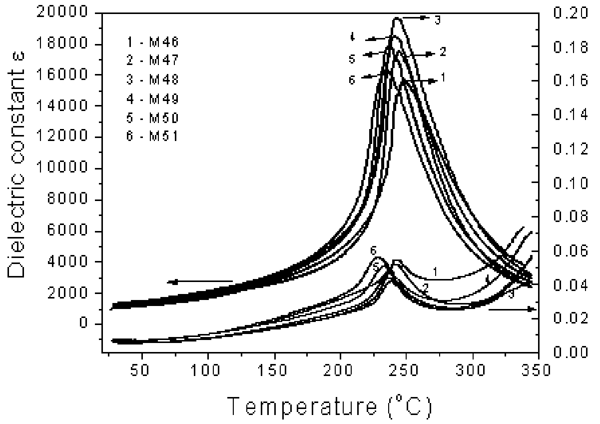

Figure 5. Temperature dependence of the dielectric constant and dielectric loss tanδ at 1 kHz of ceramic

In Figure 6, the change of Curie temperature T_C with the Zr/Ti ratio is shown. With the increase in Zr amount, the Curie temperature decreases because the Curie temperature of $PbZrO_3$ is about 232°C and it is lower than that of $PbTiO_3$, 490°C[11,12].

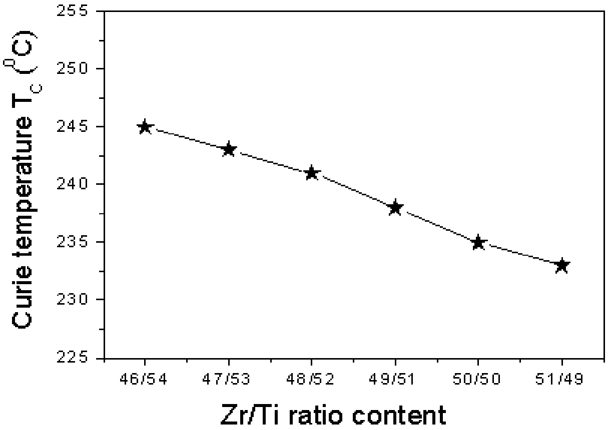

Figure 6. The Curie temperature T_C of PZT-PZN- PMnN ceramics with different amounts of Zr/Ti ratio

Figure 7 shows the temperature dependence of the dielectric constant ε and dielectric loss tanδ of the M48 sample measured at frequency of 1kHz, 10kHz, 100kHz and 1MHz, respectively. It show that the shape of the ε peaks was broad, which is typical of a case diffuse transition with frequency dispersion. When the measured frequency increased, the maximum of ε_{max} was decreased and shifted to higher temperature while dielectric loss increased near the Curie point, which is typical of a relaxor material[13].

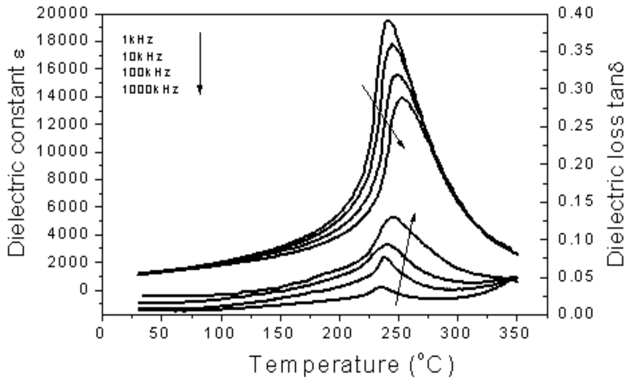

Figure 7. Temperature dependence of relative dielectric constant ε and dielectric loss tan*δ* of M48 sample at different frequencies

3.4. Piezoelectric Properties

To determine piezoelectric property of ceramics, resonant vibration spectrum of samples were measured at room temperature in Figure 8.

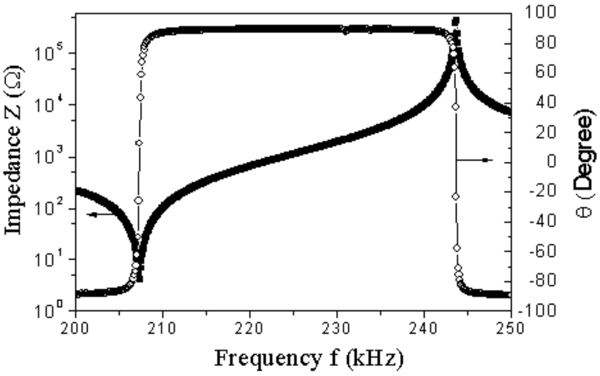

Figure 8. Spectrum of radial resonance of M48 sample

From these resonant spectra, electromechanical coefficients k_p, piezoelectric coefficients d_{31}, mechanical quality factor Q_m and dielectric loss tanδ were determined. Figure 9 shows the changing in the electromechanical coupling factor (k_p), the piezoelectric constant (d_{31}), mechanical quality factor Q_m and dielectric loss tanδ as a function of the amount of Zr/Ti ratio. As can be seen, both k_p and d_{31} show a similar variation with increasing Zr/Ti ratio content. When the amount of Zr/Ti ratio is lower than 48/52, the k_p and the d_{31} are rapidly increased with increasing Zr/Ti ratio content, while the mechanical quality factor Q_m and the dielectric loss tanδ are desreased. The optimized values for k_p of 0.62, d_{31} of 140.10^{-12}C/N, Q_m of 1112 and tan*δ* of 0.005 were obtained at Zr/Ti = 48/52. This is probably related to characteristics of the increasing grain size. As well known, the increased grain size makes domain reorientation easier and severely promotes domain wall motion, which could increase the piezoelectric properties[13]. However, the further increasing of Zr/Ti ratio content gives rise to an abnormal grain boundary and the average grain size is also reduced as shown in Fig. 3. Therefore, electrical properties of PZT-PZN-PMnN ceramics are reduced.

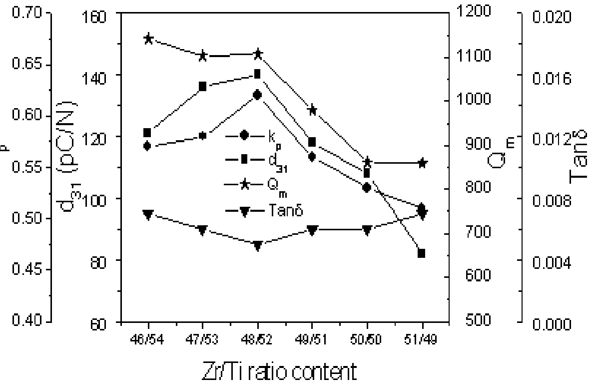

Figure 9. The values of k_p, d_{31}, Q_m, and tanδ of the PZT-PZN-PMnN ceramic samples

4. Conclusions

We have investigated some physical properties of the low temperature sintering $0.8Pb(Zr_xTi_{1-x})O_3–0.125Pb(Zn_{1/3}Nb_{2/3})O_3 – 0.075(Mn_{1/3}Nb_{2/3})O_3$ + 0.7 wt% Li_2CO_3 ceramics. Results of this study are summarized as follows:

- All the specimens displayed a tetragonal perovskite structure without secondary phase. With increasing the Zr/Ti ratio content, the tetragonality c/a was decreased.

- At the Zr/Ti ratio content of 48/52 and sintering temperature (T_s) of 950°C, the density, the electromechanical coupling factor k_p, the dielectric constant ε_{max}, the piezoelectric constant d_{31}, the dielectric loss tanδ and the mechanical quality factor Q_m showed the optimum values of 7.86g/cm^3, 0.62, 19500, 140 pC/N, 0.005 and 1112, respectively. Therefore, they are a promising candidate material used in high power piezoelectric devices.

REFERENCES

[1] Smolenskii. G. A., V. A. Isupov and A. I. Agranovskaya New ferroelectrics of complex composition of the type $A_2^{2+}(B_I^{3+},B_{II}^{5+})O_6$. I. *Sov. Phys.Solid State*, 1, 1959 150-151.

[2] F. Gao., L. Cheng, Hong R., J. Liu, C. Wang and C. Tian, Crystal structure and piezoelectric properties of $xPb(Mn_{1/3}Nb_{2/3})O_3–(0.2 − x)Pb(Zn_{1/3}Nb_{2/3})O_3–0.8Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramic, Ceramics International 35, 2009, 1719–1723.

[3] H. Kang S., C. W. Ahn, H. J. Lee & I. W. Kim, E. C. Park & J. S. Lee, Dielectric and pyroelectric properties of Li_2CO_3 doped $0.2Pb(Mg_{1/3}Nb_{2/3})O_3 – 0.5Pb(Zr_{0.48}Ti_{0.52})O_3 –0.3Pb(Fe_{1/3}Nb_{2/3})O_3$ ceramics, J Electroceram 21, 2008, 855–858.

[4] Yuhuan Xu, *Ferroelctric Materials and Their Applications* (North-Holland, Amsterdam- London- Newyork-Tokyo), 1991.

[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 55-57, 2008, 125-128.

[6] J. Yoo and S. Lee, Piezoelectric and Dielectric Properties of Low Temperature Sintered $Pb(Mn_{1/3}Nb_{2/3})_{0.02}$ $(Ni_{1/3}Nb_{2/3})_{0.12}$ $(Zr_xTi_{1-x})_{0.86}O_3$ System Ceramics Transactions on electrical and electronic materials 10, 2009, 121-125.

[7] K. Fares, H. Louanes, A. Nora and B. Ahmed, Synthesis and Piezoelectric Properties of $Pb_{0.98}Sm_{0.02}[(Zr_x,Ti_{1-x})_{0.98}$ $(Fe_{1/2}Nb_{1/2})_{0.02}]O_3$ ceramics, Materials Sciences and Applications 3, 2012, 50-58.

[8] Hou Y. D., Chang L. M., Zhu M. K., Song X. M. and Yan H. 2007 Effect of Li_2CO_3 addition on the dielectric and piezoelectric responses in the low-temperature sintered 0.5PZN–0.5PZT systems *Journal of applied physics* 102, 084507.

[9] X. Chao, Z. Yang, C. Kang, Y. Chang, Effects of $BiFeO_3$ addition on electrical properties and temperature stability of low temperature sintered PZT–PFW–PMN ceramics, Sensors and Actuators A 141, 2008, 482–488.

[10] Lee J. S., Choi M. S., Nguyen V. H. Kim Y. S, Kim I. W., Park E. C., Jeong S. J., Song J. S., Effects of high energy ball-milling on the sintering behavior and piezoelectric properties of PZT-based ceramics, Ceramics International 33, 2007, 1283–1286.

[11] Phan Dinh Gio, Vo Duy Dan, Some dielectric, ferroelectric, piezoelectric properties of $0.35Pb(Zn_{1/3}Nb_{2/3})O_3$-$0.65Pb(Zr_x Ti_{1-x})]O_3$ ceramics, Journal of Alloys and Compounds, vol. 449, 1-2, 24-27.

[12] J. Yoo, Y. Lee, K. Yoon, S. Hwang, S. Suh, J. Kim and C. Yoo, Microstructural, Electrical Properties and Temperature Stability of Resonant Frequency in $Pb(Ni_{1/2}W_{1/2})O_3$–$Pb(Mn_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ Ceramics for High-Power Piezoelectric Transformer, Jpn. J. Appl. Phys 40, 2001, 3256–3259.

[13] C.H. Wang, S.J. Chang, P.C. Chang, Effect of sintering conditions on characteristics of $PbTiO_3$–$PbZrO_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zn_{1/3}Nb_{2/3})O_3$, Materials Science and Engineering B 111, 2004, 124–130

[14] Y. D. Hou, M. K. Zhua, C. S. Tian, H. Yan, Structure and electrical properties of PMZN–PZT quaternary ceramics for piezoelectric transformers, *Sensors and Actuators* A 116, 2004, 455–460.