ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 8, February 2014

Study Structure, Microstructure and Temperature Dependence of Some Physical Properties of ZnO Doped PZT–PMSN Ceramics

Nguyen Dinh Tung Luan, Le Dai Vuong
Faculty of Chemical and Environmental Engineering, Hue Industry College, Hue City, Vietnam
Department of Physics, College of Sciences, Hue University, Hue City, Vietnam

Abstract*—The 0.9Pb $(Zr_{0.49}Ti_{0.51})$ O3 – 0.1Pb $[(Mn_{1/3}Nb_{2/3})_{0.7}(Sb_{1/2}Nb_{1/2})_{0.3}]O_3$ + 0.25%wt ZnO (PZT-PMSN + ZnO) ceramics has been prepared by the Columbite and Wolframite method. Experimental results showed that ceramic samples have pure perovskite phase with rhombohedral structure and average grain size of this sample is large. We have used the impedance resonance technique to measure the impedance spectra of ZnO doped PZT-PMSN ceramic specimens over temperatures ranging between 30ºC and 290ºC. The temperature behavior of the main piezoelectric parameters, such as the electromechanical coupling factor k_p, the mechanical quality factor Q_m, the dielectric permittivity ε (real and imaginary part), the loss tangent $\tan\delta$ and the piezoelectric charge constants d_{33} and d_{31} of this piezoelectric material was investigated. The results showed that temperatures under 120°C do not influence these parameters, which indicate that every transducer made from this type of material may be successfully used up to this temperature. Between 120°C and 220°C, the piezoelectric properties undergo more or less important changes, mainly due to the depoling effect and above that, at temperatures over 220°C, they degrade very rapidly, tending to zero.

***Index Terms*—PZT-PSbN-PMnN, temperature behavior, electromechanical coupling factor, mechanical quality factor.**

I. INTRODUCTION

Piezoelectric transducer materials are commonly characterized at room temperature by resonance measurements as outlined in the IEEE Standard on Piezoelectricity Std 176-1987 [1]. A small AC signal is used to excite a strain wave in the material via coupling to the piezoelectric coefficient. At a critical frequency determined by the sample dimensions a resonance occurs. The resonances are determined experimentally by monitoring the electrical impedance or admittance of the sample as a function of the frequency. The measurement is very practical in that the dielectric, and piezoelectric constants can be determined from one measurement [2,3,4,5]. However, in many applications, a transducer may be operated at temperatures above and below room temperature, depending on the application. It is therefore useful to know the temperature dependence of the material properties of the transducer material in order to predict the transducer response as a function of temperature. The best material for high frequency is, of course, the ceramics with constant resonance frequency to withstand thermal shock during soldering process. For the successful application of surface mount devices type high frequency filters, the stability in temperature coefficient of resonant frequency is needed as well because the resonant frequency of the filter can be suddenly changed by the thermal shock [4,5]. This investigates the behavior of the main parameters (k_p, Q_m, ε, d_{ij}) of these materials up to the Curie temperature, where they become paraelectric and, therefore, in active from the piezoelectric point of view.

II. EXPERIMENTALS

A. Specimen preparation

PZT – PMSN + x %wt ZnO ceramics were prepared from reagent grade raw material oxides via the Columbite and Wolframite method in order to suppress the formation of pyrochlore phase [6, 7, 8]. The processing of synthezise was through three steps:

Step 1: Synthezise $MnNb_2O_6$ and $Sb_2Nb_2O_8$

$MnCO_3$ and Nb_2O_5; Sb_2O_3 and Nb_2O_5 were mixed and acetone milled for 20 h in a zirconia ball mill and then calcined at 1200°C for 3 h to form $MnNb_2O_6$ and $Sb_2Nb_2O_8$. The material was acetone-ground for 10 h in the mill and dried again.

Step 2: Synthezise PZT – PMSN calcined powders

Reagent grades PbO, ZrO_2, TiO_2 were mixed with $MnNb_2O_6$ and $Sb_2Nb_2O_8$ powders by ball mill for 20 h in acetone. The mixed powders were dried and calcined at 850°C for 2 h and then the calcined powders were ground by ball mill in acetone for 24 h.

Step 3: Synthezise PZT – PMSN + 0.25 wt% ZnO ceramics

The PZT – PMSN calcined powders were mixed with 0.25 wt% ZnO, and acetone-milled for 8 h in the zirconia ball mill and then dried. The ground materials were pressed into disk 12mm in diameter and 1.5mm in thick under 100MPa. The samples were sintered in air at 950°C for 3 h in an alumina crucible to form PZT – PMSN + 0.25 wt% ZnO ceramics.

The sintered and annealed samples were ground and cut to 1mm in thick. A silver electrode was fired at 680°C for 10 minutes on the major surfaces of samples. Poling was done in the direction of thickness in a silicon oil bath under 30kV/cm

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 8, February 2014

for 15 minutes at 120°C. The physical and piezoelectric properties of the poled samples were measured after 24 h.

B. Measurements

The Curie temperature of samples were measured between temperature 30°C and 330°C at 1 kHz using LCR meter (RLC HIOKI 3532). The electromechanical coupling factor and mechanical quality factor were produced by measuring resonance and ant resonance frequency with an impedance analyzer (Agilent 4396B). The temperature coefficients of piezoelectric properties were measured in the temperature range from 30 to 290°C and calculated by measuring the resonant frequency of specimen using an impedance analyzer (Agilent 4396B) in thermostatic chamber. Calculated equation [4] is as follows:

$$\frac{\Delta\alpha}{\alpha_{30^0C}} = \frac{\alpha(30^0C)-\alpha(t^0C)}{\alpha(30^0C)}x100\%$$, in which, α is symbol of f_r, Q_m, k_p, d_{ij}.

III. RESULTS AND DISCUSSION

A. Structure and microstructure

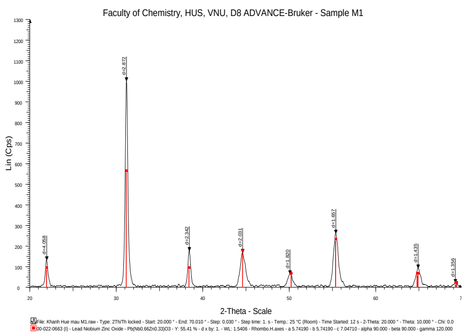


Fig. 1 XRD pattern of PZT-PMSN + 0.25 wt% ceramic

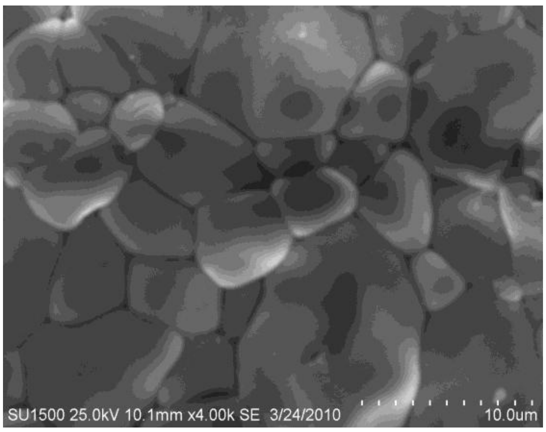


Fig. 2 SEM of PZT-PMSN +0.25 wt% ceramic

Fig.1 shows XRD pattern of the PZT – PMSN + 0.25 %wt ZnO ceramic. As observed, ceramic have pure perovskite phase with rhombohedral structure. Average grain size of this sample is large as given in Fig. 2.

B. Piezoelectric properties of PZT -PMSbN + ZnO ceramic at temperature room

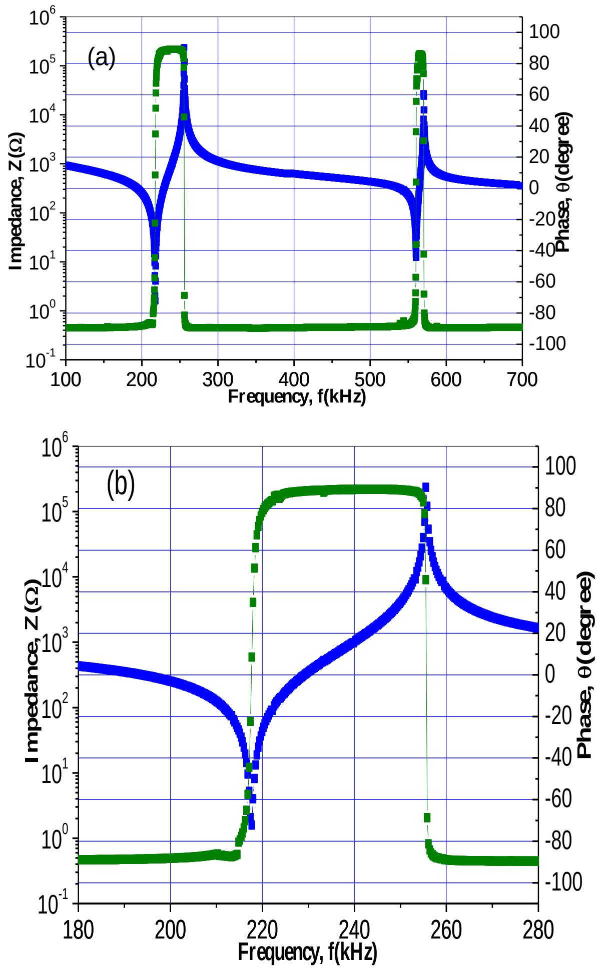


Fig. 3 shows the spectrum of piezoelectric resonance frequency of PZT–PMSN + 0.25 wt% ZnO ceramic at temperature room

From these resonant spectra (Fig. 3), electromechanical coefficients k_p, piezoelectric coefficients d_{31}, d_{33} mechanical quality factor Q_m were determined. It is given in Table 1.

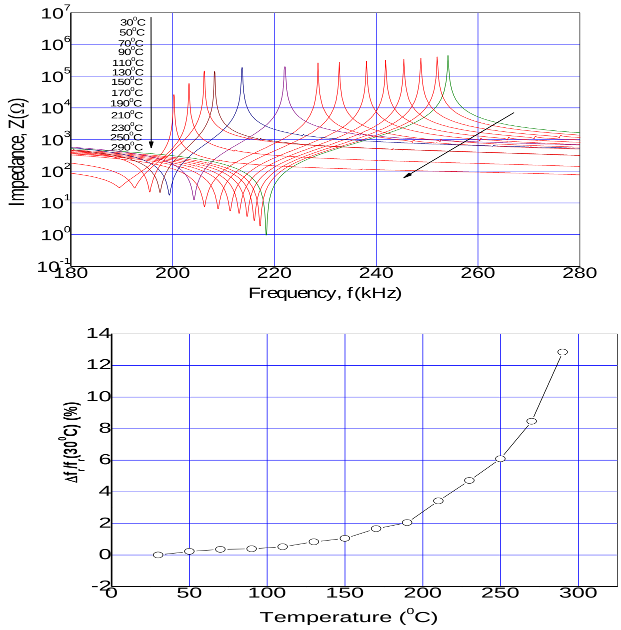
Table 1. Piezoelectric parameters of PZT – PMSN + 0.25% ZnO at room temperature

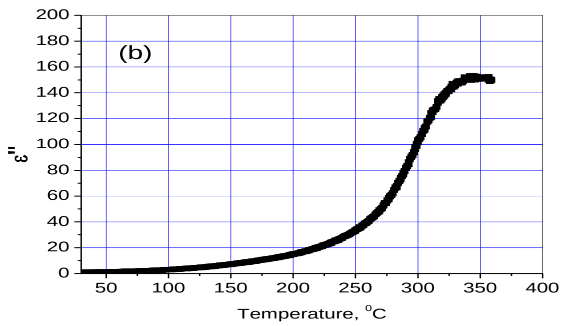
k_p	Q_m	d_{33} (pC/N)	$- d_{31}$ (pC/N)
0.6	2030	217	452

Fig. 4 shows the temperature dependence of the resonant frequency spectrum of PZT -PMSN + 0.25% ZnO ceramics. The resonance peaks move up to lower frequency and the width frequency, Δf = f_a - f_r, rather stability change in the temperature range from 30°C to 120°C. Between 120°C and 220°C, this value slowly decrease and then tending to very small in over 220°C.

C. Temperature denpendence of resonant frequency

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 8, February 2014





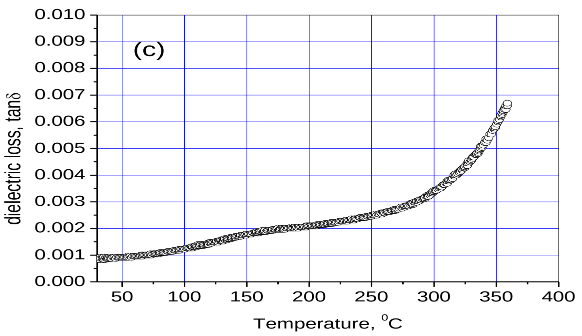


Fig. 4. Temperature dependence of resonant frequency spectrum and $\Delta f_r/f_r(30^oC)$.

D. *Temperature dependence of the dielectric properties*

For preventing the transition the ferroelectric phase to occur in operating temperature range of piezoelectric device, the high Curie temperature of 250°C or more is also needed for piezoelectric materials [3,5]. Fig. 5 presents the temperature dependence of real (ε') and imaginary (ε'') parts of dielectric constant and loss tangent (tanδ) of PZT-PMSN + 0.25% ZnO ceramics at 1 kHz. It can be seen that the Curie temperature of 270°C is obtained. It can be noted that the Curie temperature is enough to contribute to the general stability of material characteristics during operation.

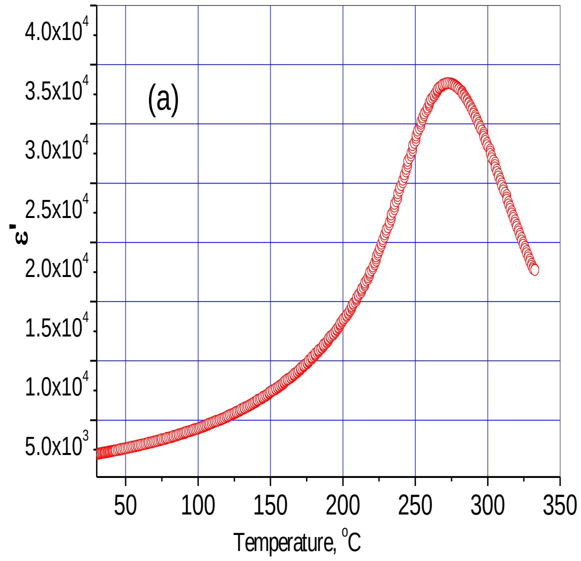


Fig. 5. The temperature dependence of the real (ε') and imaginary (ε'') parts of dielectric constant and loss tangent (tanδ) of PZT-PMSN + 0.25% ZnO ceramics at 1 kHz.

E. Temperature dependence of the piezoelectric properties

Fig. 6 shows the variation of the electromechanical coupling factor k_p with temperature, from room temperature up to the Curie point, situated around 290°C. One observes that up to 120°C, k_p remains constant after which it decreases relatively slowly up to about between 220°C, with a decreasing rate of about 0.4%/°C and above 220°C, the decreasing is rather sudden. At 290°C, the coupling coefficient has a value of just 0.2. This behavior may be understood in terms of the mobility phenomena of ferroelectric domains walls. Until 120°C, the walls are moving insignificantly and so the sample remains practically in the same poling condition as at room temperature. Between 120°C and 220°C, the depoling process takes place rather slowly. Over 220°C, the depoling takes place more rapidly, and the piezoelectric properties decrease in the same manner, tending to zero. What it is most remarkable is the fact that the material doesn't change its coupling factor up to rather high temperatures (for example at 120°C), which makes possible that transducers made with this material to be used, with great efficiency, even at high temperatures.

The piezoelectric constants determined in this experiment are the following: the electromechanical coupling factor (k_p); the mechanical quality factor (Q_m), the charge constants (d_{33} and d_{31}) [8, 9, 10,11]. Fig. 7 illustrates the behavior of mechanical quality factor Q_m with temperature. One can also observe that between the room temperature and 220°C it decrease slowly and steadily after which it remains nearly constant up to about 220°C and then suddenly falls of due the quick depoling of the sample.

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 8, February 2014

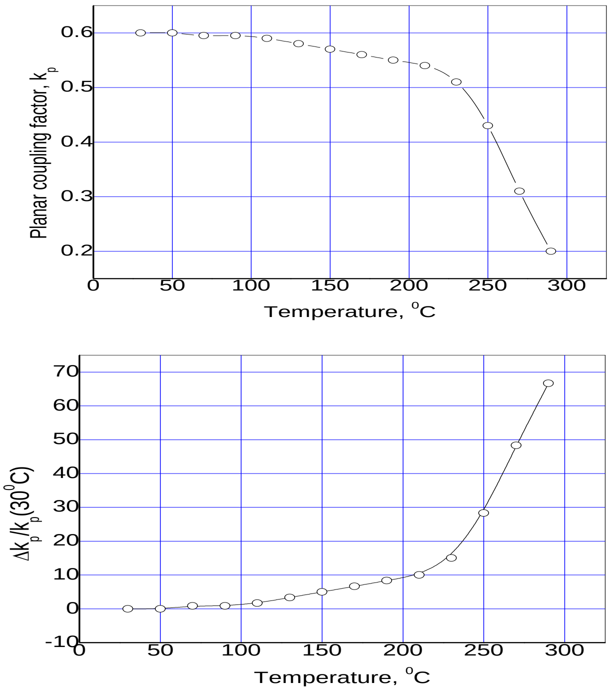


Fig. 6. The temperature dependence of the electromechanical planar coupling factor k_p between room temperature and the Curie point.

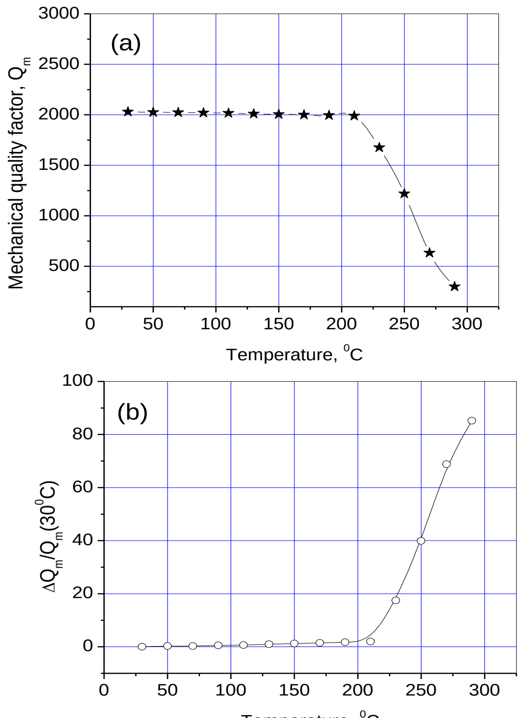


Fig. 7. The temperature behavior of the mechanical quality factor Q_m between room temperature and the Curie point

Table 2. Piezoelectric parameters of PZT–PMSN + 0.25% ZnO between room temperature and the Curie point.

$t(^0C)$	k_p	$\Delta k_p/k_p$ (30^0C)	Q_m	$\Delta Q_m/Q_m$ (30^0C)	d_{33} (pC/N)	$-d_{31}$ (pC/N)	d_h
30	0.600	0.00	2030	0.00	217	452	18
50	0.600	0.00	2025	0.00	217	453	19
70	0.595	0.83	2024	0.83	225	474	20
90	0.595	0.83	2020	0.83	237	505	21
110	0.590	1.67	2017	1.67	243	524	22
130	0.580	3.33	2010	3.33	257	555	23
150	0.570	5.00	2005	5.00	268	594	24
170	0.560	6.67	2000	6.67	295	655	25
190	0.550	8.33	1995	8.33	301	681	29
210	0.540	10.00	1990	10.00	312	705	31
230	0.510	15.00	1676	15.00	326	750	48
250	0.430	28.33	1220	28.33	333	780	54
270	0.310	48.33	633	48.33	341	799	67
290	0.200	66.67	300	66.67	267	630	16

The behavior of the charge constants d_{33} and d_{31} are presented in Fig. 8a while the hydrostatic piezoelectric constant d_h is shown in Fig. 8b. The relation between these three constants is given by the relation: $d_h = d_{33} + 2(-d_{31})$. The coefficient d_h is very important when construction of sonars is involved. The quality of these sonars is given by the great value of dh and by its constant dependence in relation with temperature. In Fig. 8b it is observed that on the entire temperature interval from room up to near the Curie point T_C, it increases steadily with a rate of only 0.05pC/N which could be considered as practically constant. This makes that the discussed material to be very promising for the realization of this type of devices.

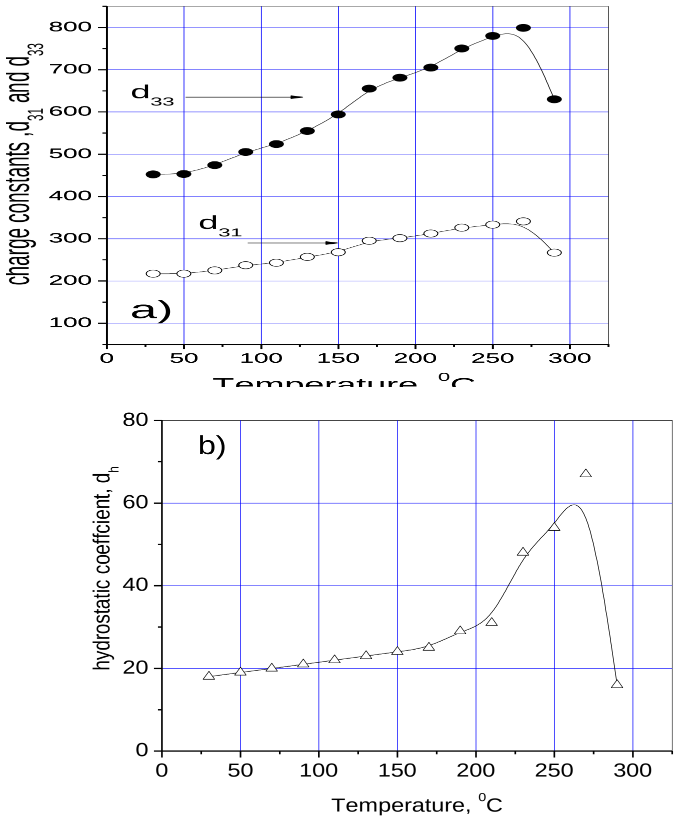


Fig. 8. The temperature dependence of the charge constants d_{33} and d_{31}, and the hydrostatic coefficient d_h between room temperature and the Curie point

ISSN: 2277-3754
ISO 9001:2008 Certified
International Journal of Engineering and Innovative Technology (IJEIT)
Volume 3, Issue 8, February 2014

IV. CONCLUSION

The variation of the main piezoelectric parameters of the PZT - PMSN + 0.25wt% ZnO material was studied as a function of temperature on a large temperature interval, from room temperature up to the Curie point. From this study it was concluded that all these parameters do not present significant variations up to the temperature of 120^{o}C which makes that the transducers made with this material to be perform ant up to this relatively high temperatures. Between 120^{o}C and 220^{o}C, their performances decrease slightly but not so as to be essentially affected. Over 220^{o}C, the transducers cannot be used since the piezoelectric parameters drastically and irreversibly decrease.

REFERENCES

[1] IEEE Standard on Piezoelectricity, IEEE Standard 176–1978, Institute of Electrical and Electronic Engineers, New York.

[2] Jaffe B, Roth R S and Marzullo S 1994 Piezoelectric properties of lead zirconate lead titanate solid solution ceramic J. Appl. Phys. **25** 809 - 810.

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

[4] R. A. Wolf and S. Trolier McKinstrya, Temperature dependence of the piezoelectric response in lead zirconate titanate films, Journal of applied physics, Vol **95** (31) 2004, pp 1397-1406.

[5] YWLi , X L Zhou and FXLi, Temperature dependent mechanical depolarization of ferroelectric ceramics, J. Phys. D: Appl. Phys. 43 (2010) 175501 (8pp).

[6] Nguyen Dinh Tung Luan, Le Dai Vuong, Bui Cong Chanh, "Microstructure, Ferroelectric and Piezoelectric Properties of PZT-PMnSbN Ceramics," International Journal of Materials and Chemistry, Vol. **3,** pp. 51-58, 2013.

[7] Cheng-Che Tsai, Sheng-Yuan Chu, Cheng-Shong Hong, Shih-Fang Chen, Effects of ZnO on the dielectric, conductive and piezoelectric properties of low-temperature-sintered PMnN-PZT based hard piezoelectric ceramics, Journal of the European Ceramic Society **31** (2011) 2013–2022.

[8] Nguyen Dinh Tung Luan, Le Dai Vuong, Truong Van Chuong, and Nguyen Truong Tho, Structure and Physical Properties of PZT–PMnN–PSN Ceramics Near The morphological Phase Boundary, Advances in Materials Science and Engineering, Volume 2014, Article ID 821404, 8 pages.

[9] Le Dai Vuong, Phan Dinh Gio, Truong Van Chuong, Dung Thi Hoai Trang, Duong Viet Hung, Nguyen Trung 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 2013, 3(2): 39-43.

[10] Zupei Yang, Hui Li, Ximei Zong, Yunfei Chang, "Structure and electrical properties of PZT–PMS–PZN piezoelectric ceramics," Journal of the European Ceramic Society, Vol. 26, pp. 3197–3202, 2006.

[11] Le Dai Vuong, Phan Dinh Gio, Nguyen Truong Tho, and Truong Van Chuong. Relaxor Ferroelectric Properties of PZT-PZN-PMnN Ceramics. Indian Journal of Engineering & Materials Sciences, Vol 20, December 2013, pp. 555-560.