A QUICK ROUTE FOR THE SYNTHESIS OF PMN-PZT POWDERS

A. Izadpanahi[1] *, S. Baghshahi[2] and A. Shalbaf Zadeh[1]

* *info@izadpanahi.com*

Received: June 2015 Accepted: August 2016

[1] Department of Materials Science and Engineering, Science and Research, Islamic Azad University, Tehran, Iran.
[2] Materials Science and Engineering Department, School of Engineering, Imam Khomeini International University, Qazvin, Iran.

Abstract: *In the following research, Lead magnesium niobate relaxor ferroelectric (PMN-PZT) ceramic powders were synthesized using the combustion method grand urea as the fuel for the first time. The starting materials used were lead nitrate, magnesium acetate, niobium oxide, zirconium nitrate, titanium oxide. The raw materials were first mixed using the general formula of (1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPb($Zr_{0.52}Ti_{0.48}$)O_3, with x= 0.3. The synthesized powders were characterized using XRD, SEM and FTIR spectroscopy techniques. The X-ray diffraction patterns revealed that the structure of the prepared samples were tetragonal at 500,600,700 and 800 °C. However, the monoclinic phase was detected in the samples calcined at 800 °C and the amount of pyrocholore phase also drastically decreased at this temperature. The band gap widths of the samples were measured via UV spectroscopy in the wave number range of 400-4000 cm^{-1}. The results show that by increasing the calcination temperature, the band gap width of the prepared samples decreases. SEM micrographs verify that by rising the calcination temperature, the structure of the prepared samples becomes more homogenous.*

Keywords: *PMN-PZT, Combustion Method, Urea, Electro-Ceramic, Band Gap Width.*

1. INTRODUCTION

Lead magnesium niobate ferroelectric relaxors (PMN) exhibits desirable dielectric properties, low loss, a wide dielectric peak, non-hysteric behavior, and a low sintering temperature [1, 3, 5]. On the other hand, lead zirconate titanate (PZT) has unique dielectric, electerostrictive, and electromechanical characteristics [2, 3, 5, 8]. It also has higher electromechanical coupling compared to PMNs. These types of ceramics are considered to be some of the most important piezoelectric materials, which have been widely used in creating ultrasonic power sources, actuators for small displacement systems, piezoelectric motors, and medical equipment [4, 7].

However, there are some disadvantages to PMN such as low electro-mechanical coupling and a low working temperature. Also there are some undesirable characteristics to PZT as well, including low dielectric properties and a high Curie temperature which results in it being unsuitable for working at low temperatures. Therefore, one can expect the composite of PMN and PZT to have the advantages of both [6]. Modifying PMN compositions by PZT, results in an increase in the piezoelectric coefficient in the range of 600 – 700 pCN^{-1} [7]. Additionally, by increasing electrochemical coupling, the dielectric efficiency improves [9]. It has been reported that a desirable combination of [(1-x)Pb($Mg_{1/3}Nb_{2/3}$)O_3-xPb($Zr_{0.52}Ti_{0.48}$)O_3] leads to the morphotropic phase boundary with $0.27<x<0.34$ [10, 11].

PMN-PZT composites are made by different methods. In the simplest one, used by Yamirian et al [12] and others [6,14], PMN and PZT powders were separately synthesized and then used as starting materials for preparing PMN-PZT. In this method, a certain amount of PMN and PZT were mixed using ball-mill and then sintered. However, the powders prepared by this method are not well homogenized but are agglomerated. Moreover, pyrochlore phases are observed in the structure.

The sol-gel method was also used [13,14], for preparing xPMN – (1 − x) PZT ceramics, where x varied from 0 to 0.3 to avoid the formation of pyrochlore phase during the calcination process, employing the columbite method. P. Moetakef et al [6] synthesized PMN-PZT ceramic using a seeding method,in which PbO, MgO and Nb_2O_5

[DOI: 10.22068/ijmse.13.3.54]

were added to the previously prepared PZT sol, resulting in the formation of a PMN-PZT gel. The gel was then fired to vaporize the organic contents in order to obtain the PMN-PZT powder.

In another method, developed by Juhyun Yoo et al [15] and also by Jin –Chen Shaw [16], the raw materials including PbO, MgO, Nb_2O_3, TiO_2 and ZrO_2 were ball milled and then calcined at 850°C. The drawback of this method was the formation of pyrochlore phase to a considerable amount which resulted in a sharp drop in piezoelectric properties. In a method used by Koval et al [17], the raw materials including Nb_2O_3 and MgO were first combined and then calcined to make coloumbate phase ($MgNb_2O_3$) [18]. The formation of coloumbate phase is also possible by the mixing of Nb_2O_3, MgO, TiO_2 and ZrO_2 powders. The important point in this method is the reaction between raw materials in the absence of lead oxide at a temperature of about 1000°C. Next, the resultant coloumbate was ball milled with the other raw materials to form the PMN-PZT composite and calcined at a temperature lower than 850°C.

The co-precipitation method was also used by Byeong Woo Lee [19]. In this method, by preparing a solution of raw materials and controlling the pH, the composition of PMN-PZT was formed at 700 °C. The most important drawbacks of this method are the incompletion of the deposit, the need for exact control of pH, and also the difficulty of making the solution from the raw materials.

In this research we have tried to minimize the pyrochlore phase in the PMN-PZT composites as well as have the structure close to the morphotropic boundary gel combustion by using urea as the fuel.

The prepared samples were characterized using X-Ray Diffraction (XRD), Fourier Transformation Infrared (FTIR) and Scanning Electron Microscope (SEM) techniques.

2. EXPERIMENTAL

The xPMN-(1-x)PZT composition (x=0.3),at near morphotropic boundary, was synthesized using niobium oxide [Nb_2O_5](99.9% *Aldrich*), magnesium acetate [$(CH_3COO)_2Mg.4H_2O$], lead nitrate [$Pb(NO_3)_2$, zirconium nitrate [$ZrO(NO_3)_2$], titanium oxide [TiO_2] and urea [$CO(NH_2)_2$] (all 99.9% Merk) as the fuel. The materials were first mixed with certain portions. Then urea (with a melting point of 135°C) was heated up separately to about 250°C. The mixture of the starting materials was added to the melting batch. As the heating continued, ignition occurred at a temperature of about 400 to 600°C within 55 minutes. At this stage, the organic materials were extracted and dry yellowish-brown foam was obtained. The foam was ball-milled for 3 hours and calcined at 500, 600, 700 and 800 °C for about 90 minutes with a 10°C/min thermal gradient.

The structure of the prepared samples was analyzed by an x-ray diffraction technique with Cu-kα in the range of 4-60 deg. Then the percentages of pyrochlore and perovskite phases were calculated using the following relation (1).

$$\%Pyrochlore = \frac{I_{\text{pyrochlore}}}{I_{\text{pyrochlore}} + I_{\text{perovskite}}} \qquad (1)$$

The samples were also characterized by FTIR spectroscopy in the wave number range of 400–4000 cm^{-1}. Lambert's law was used to calculate the absorption coefficient to draw the $(\alpha hv)^2$ versus photon energy(hc/λ) by which the band gap widths of the prepared samples were determined. The morphology of the samples was investigated using SEM.

3. RESULTS AND DISCUSSION

3. 1. Phase Analysis

The XRD patterns of the synthesized powders are shown in Fig. 1.

In all samples the XRD data verify the presence of pyrochlore phase. As can be seen in Fig. 1, the samples prepared at 800°C have the lowest pyrochlore phase (1.35%). Pyrochlore phase with the formula $Pb_{1.83}Nb_{1.71}Mg_{0.29}O_{6.39}$ has the XRD identification card no. 33-0769. The percentages of pyrochlore and perovskite phases of the samples, at all mentioned calcined temperatures, can be calculated using the relation (1).

[DOI: 10.22068/ijmse.13.3.54]

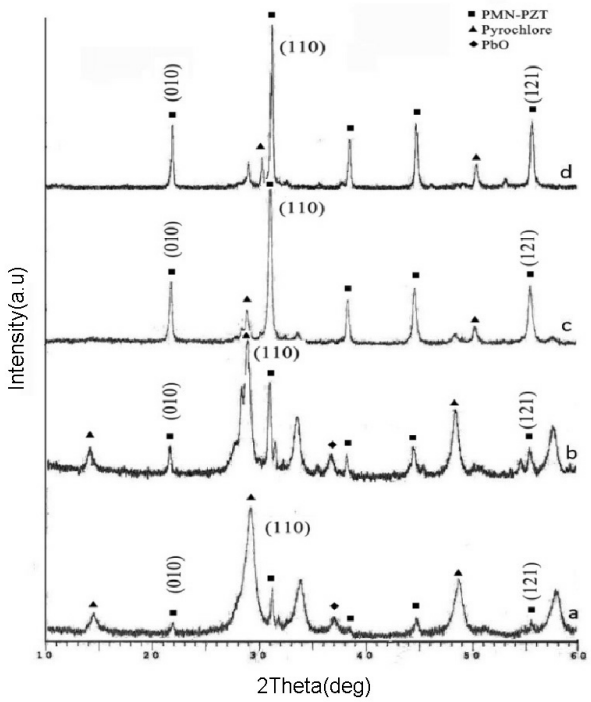

Fig. 1. The X-ray diffraction patterns of the synthesized powders calcined at 500, 600, 700 and 800°C temperatures.

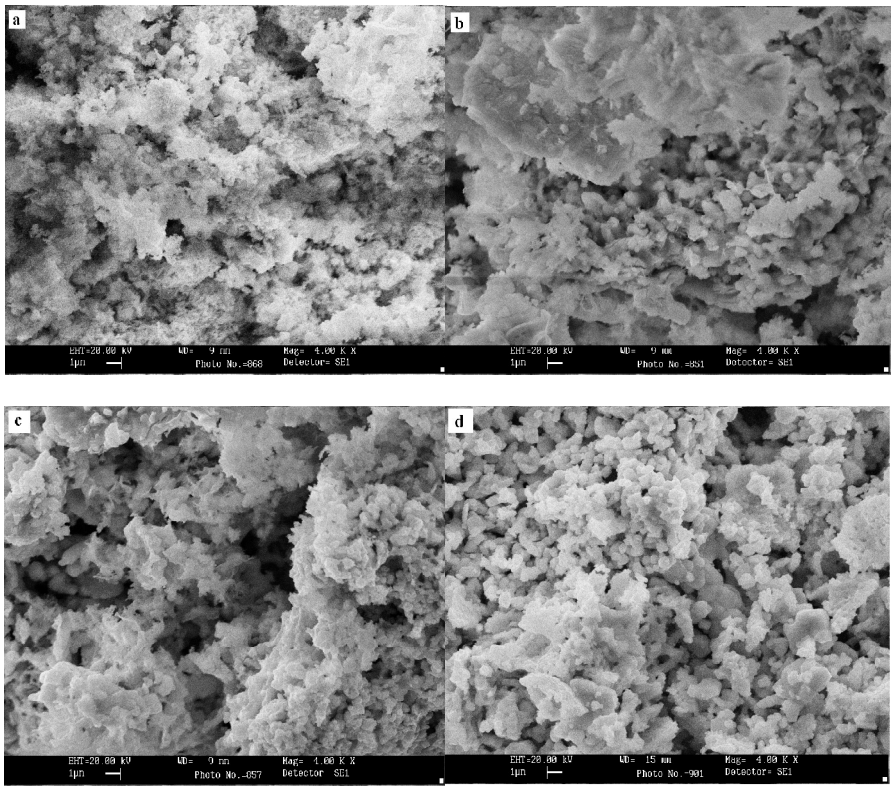

Fig. 2. SEM images of the calcined powders at different temperatures a) 500, b) 600, c) 700 and d) 800°C.

[DOI: 10.22068/ijmse.13.3.54]

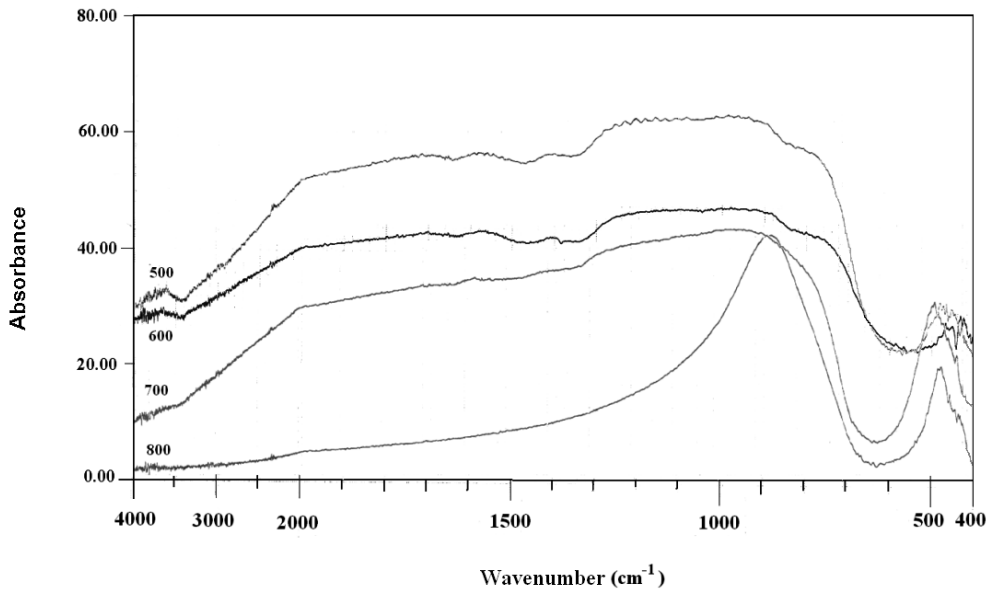

Fig. 3. FTIR spectra of PMN-PZT powders calcined at 500, 600, 700 and 800 °C.

The details of the structural parameters obtained for the samples are given in table 2. The unit cell parameters are in agreement with the results for 0.3PMN-0.7PZT ceramic [10]. The SEM micrographs show that as the calcination temperature increases, the structure becomes more homogenous because of better particle distribution.

3. 2. Optical Properties

In order to obtain the optical energy band gap of the synthesized samples, FTIR diagrams and Lambert's law were used [20, 21, 22]. The Lambert's formula is given as follows:

$$\alpha = -(\frac{1}{t})\ln T \qquad (2)$$

where T is the transmittance coefficient and t is the particle's size. Knowing T and t, the absorption coefficient can be obtained using the Lambert's formula (3) [23, 24]. The value of the band gap can be calculated from extrapolating the linear portion of plotting $(\alpha h\upsilon)^2$ versus (hc/λ).

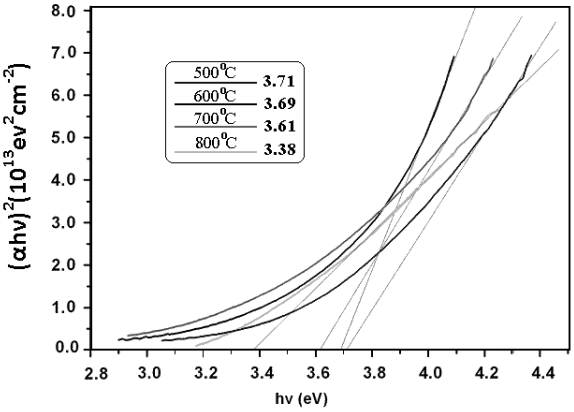

Fig. 4. $(\alpha h\upsilon)^2(10^{13}ev^2cm^{-2})$ graphs based on (hc/λ) for PMN-PZT samples prepared at different calcination temperatures.

$$(\alpha h\upsilon)^2 = C(\frac{hc}{\lambda} - E_g) \qquad (3)$$

The FTIR diagrams of the samples calcined at different temperature are shown in Fig. 3.

[DOI: 10.22068/ijmse.13.3.54]

As seen, a broad band is observed for each spectrum in the range of 600 to 1000 cm^{-1} which indicates that the maximum absorption occurs at about 638 cm^{-1}. The FTIR absorption band in related to the octahedral structure[25, 26] is reported as showing the formation of perovskite phase at all different calcination temperatures [27,28].

Regarding Fig. 4 and table 3, it is clear that the band gap width of PMN-PZT powders decreases by increasing the calcination temperature.

4. CONCLUSION

In this research, ferroelectric PMN-PZT relaxor powders were synthesized by the combustion method that uses urea as the fuel. The XRD patterns show that by increasing the calcination temperature to 800 °C the presence of the pyrochlore phases decreases to 1.35%. Also, in addition to the decrease of the pyrochlore phases, the peak related to monoclinic phase is detected. It was also seen that by increasing the calcination temperature, the band gap width decreases from 3.71eV at 500 °C to 3.83eV at 800 °C. The SEM micrographs show that the structures of prepared powders are more homogenous for the powders at higher temperatures.

The use of the combustion method via urea, results in more homogeneity of the oxides mixture, and a decrease in the synthesis time to 55 minutes minimizing the amount of pyrochlore phase present in the samples structures. Also, the low calcination temperature needed in this method causes the loss of lead oxide to be minimal. It must be noted that the starting materials for this method are costly. However, this method is less expensive than the whole sol-gel or gel combustion method.

REFERENCE

1. Cross, L. E., "Relaxor Ferroelectrics: an Overview". Ferroelectrics. 1994, 151, 305-320.
2. Moulson, A. J. and Herbert, J. M., "Electroceramics in Materials, Properties, Applications", 2nd ed., Wiely, England, 2003.
3. Yimnirun, R., Ananta S., Tipakontitikul R., "Perovskite phase transformation in $0.65Pb(Mg_{1/3}Nb_{2/3})O_3$-$0.35PbTiO_3$ nanoparticles derived by sol-gel". J. Appl. Phys., 2006, 6, 307–311.
4. Ouchi, H., Nagase K. and Hayakawa S., "Piezoelectric Properties of $Pb(Mg_{1/3}Nb_{2/3})O_3$—$PbTiO_3$—$PbZrO_3$ Solid Solution Ceramics". J. Am. Ceram. Soc., 1965, 48, 630-635.
5. Buchanan, R. C., "Ceramic Materials for Electronics", 3rd ed, Marcel Dekker Inc. New York 2004.
6. Moetakef, P. and Nemati, Z., Ali, "Synthesis of pyrochlore free PMN–PZT ceramics via a seeding method". Sensors and Actuators, A., 2008, 141, 463-470.
7. Miclea, C. and Tanasoiu, C., "Effect of lead content on the structure and piezoelectric properties of hard type lead titanate–zirconate ceramics". J. Eur. Ceram. Soc., 2007, 27, 4055–4059.
8. Khaleghian, M., Kalantar, M. and Ghasemi, S. S., "Comparison of Mechanical and Electrical Properties of Piezoelectric Composites PZT/ZnO and PZT/Al Fabricated by Powder Metallurgy". IJMSE, 2015, 12, 71-82.
9. Koduria, R. and Lopez, M., "Ferroelectric and piezoelectric properties of Ag modified PMN-PZT solid solutions". Eur. Phys. J. App. Phys., 2007, 37, 93–99.
10. Takahashi, S., Sasaki, Y. Hirose, S. and Uchino, K., "Stability of $PbZrO_3$-$PbTiO_3$-$Pb(Mn_{1/3}Sb_{2/3})O_3$ Piezoelectric Ceramics under Vibration-Level Change. Japan J. Appl. Phys., 1995, 34, 5328–5331.
11. Belsick, J. R., Halliyal, A. and Kumar, U., "Phase relations and dielectric properties of ceramics in the system PZN-ST-PT". Ceram. Soci. Bull., 1987, 66, 664-667.
12. Yimnirun, R., Anata, S. and Laoratankul, P., "Effects of $Pb(Mg_{1/3}Nb_{2/3})O_3$ mixed-oxide modification on dielectric properties of $Pb(Zr_{0.52}Ti_{0.48})O_3$ ceramics". Mat. Sci. & Eng. B., 2004, 112, 79-86.
13. Paik, D., Komarneni, S. and Abothu, I. R., "Composites of $0.3Pb(Mg_{1/3}Nb_{2/3})O_3$–$0.7Pb(Zr_{0.52}Ti_{0.48})O_3$ prepared by a sol–gel method". J.Mat. Chem., 1997, 7, 1831–1835.
14. Koo Kang, J., Sung Park, Ch. and Wung Lee, J., "Electrical properties of highly oriented

[DOI: 10.22068/ijmse.13.3.54]

$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ thin films fabricated by the sol-gel method. J. Mat. Res., 2006, 21, 1532-1536.

15. Yoo, J., Lee, Ch., Jeong, Y. and Lee, W. J., "Electrical properties of highly oriented $Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Zr,Ti)O_3$ thin films fabricated by the sol-gel method". Mat. Chem. & Phys., 2005, 90, 386-390.
16. Chen Shaw, J., Liu, K. Sh. and Lin, I. N., "Dielectric behavior at morphotropic phase boundary for PMN-PZT ceramics. Scripta Metallurgica et Mateialia", 1993, 29, 981-986.
17. Koval, V., Alemany, C., Briancin, J. and Brunckova, H., "Effect of PMN modification on structure and electrical response of xPMN–(1x)PZT ceramic systems". J.Euro. Ceram. Soci.,2003, 23, 1157-1166.
18. Su Ha, M., Jong Jeong, S. and Hyuk Koh, J., "Piezoelectric response of compressive loaded multilayer ceramic actuator"., Mat. Chem. & Phys., 2006, 98, 9–13.
19. Lee, B. W., "Synthesis and characterization of compositionally modified PZT by wet chemical preparation from aqueous solution". J. Euro. Ceram. Soc., 2004, 24, 925–929.
20. Ghasemifard, M., Khorrami, Gh., Khorsand, A. and Hossini, S. M., "Microstructural and optical characterization of PZT nanopowder prepared at low temperature". Phys. E., 2009, 41, 1701-1706
21. Swanepoel, R., "Determination of the thickness and optical constants of amorphous silicon". J. Phys. E., 1983, 16, 1214-1222.
22. Prathap, P., Subbaiah, Y. P. and Devika, M., "Optical properties of In_2O_3 films prepared by spray pyrolysis". Chem. & Phys., 2006, 100, 375–379.
23. Bube, R. H., "Electronic Properties of Crystalline Solids", Academic, New York, 1974.
24. Chan, K. Y., Tsang W. S., Mak C. L. and Wong K. H., "Optical studies of $0.65PbMg_{1/3}Nb_{2/3}O_3$–$_{0.35}PbTiO_3$ thin films". J. Euro.Ceram. Soc., 2005, 25, 2313–2317.
25. Thomas, R., Mochizuki, Sh. and Toshiyuki, M., "Perovskite crystallization of sol-gel processed $(Pb,La_{0.06},Gd_{0.02})(Zr_{0.65},Ti_{0.35})O_3$ thin films: Dielectric, ferroelectric and optical properties". J. Mat. Res., 2002, 17,2652.
26. Nimmo, W., Ali, N. J., Brydson, R. M. and Calvert C. C., "Formation of lead zirconate titanate powders by spray pyrolysis", J.Am. Ceram. Soci., 2003, 86, 1474-1480.
27. Leite, E. R., Sousa, C. M. G., Longo, E. and Varela J. A., "Influence of polymerization on the synthesis of $SrTiO_3$: Part I. Characteristics of the polymeric precursors and their thermal decomposition". Ceram. Int., 1995, 21, 143-152.
28. Sakar-Deliormanl, A., Elik, E. and Polat, M., "Solubility and aging of lead magnesium niobate in water". Ceram. Int., 2009, 35, 503–508.

[DOI: 10.22068/ijmse.13.3.54]