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Preparation and characterization of nano – porous PMN-PT ceramic

Firas Fouad Abdullah[a]

[a]*Al-Muthanna University / College of Engineering / Department of Civil Engineering / Iraq*
**Corresponding author E-mail: firas77fuad@gmail.com*

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Abstract

The inter-granular-Nano porous 0.65PMN-0.35PT ceramic abbreviated as "PMNT were fabricated for the first time by introducing pore forming agent multi walled carbon nanotubes (MWCNT), the thermal analysis of Nano tube, and the effect of MWCNT ratio on their density, phase analysis, microstructure were investigated. the complete burnout of the MWCNT as pore forming agent was about 850℃. The ideal sintering procedure of PMNT ceramic was arranged in agreement with thermo gravimetric reading of Nano material. XRD test indicated that MWCNT as Nano voids shaping factor did not influence on PMNT ceramic crystallographic structure. The porosity of PMNT ceramic 24% more than that of pure sample while the density difference between dense and porous was very low ~1.53 g/cm^3 at a fixed MWCNT addition.

Keywords: *0.65PMN-0.35PT, Nano Porous ceramic, MWCNT, sintering, FESEM and XRD*

1. Introduction

The groups of materials (PT, PMN, PCN, PZN, PZT, PLZT, etc.) act the bulk of the dense ferroelectric ceramics are produced in the current world to obtain high piezoelectric responses. Plenty of bulk piezoelectric ceramic materials have been prepared from binary systems containing a combination of normal ferroelectric materials like PZT and relaxor in form of Pb (B'B") O_3 to create PZT-PZN [1-2], PZT-PMN [3-8], PZT-PNN [9] and PMN-PT [10] advances ceramics. Although scientists observed one of ceramic materials like PZT, PZT-PMN are joined with a planned porous micro-structure, being a favorable material for sensors, actuators, besides under water and ultrasonic transducers but previously researchers analysis considered the porosity is as a weakness that leads to reducing of the piezoelectric and mechanical ceramic characteristics. On the contrary, the creation of porosity can greatly enhance the properties of ultrasonic appliances, like hydrophones or medical diagnostic devices [11-15]. Fabrication method of micro porous of PZT [16], PZT-PMN [17], PZT-PZN has been studied [18] but preparation procedure in details and chacterization of Nano porous PMN-PT ceramics with MWCNT as pore forming agent have limited researches therefore recent research focus on the incorporation of multi walled carbon Nano tube MWCNT as pore forming agent into PMN-PT ceramic to form composite structures, with an emphasis on fabrication method, sintering procedure and micro-structure.

2. Experimental

2.1. Fabrication method

The materials used in the preparation of PMNT ceramic, purity, sizes and suppliers are listed in Table1. Nano porous PMN-PT ceramics were prepared by mixing 0.65PMN-0.35PT ceramic powder with MWCNT as pore forming agent (PFA) 0.1 weight percentage (wt%) of it was regularly joined to PMNT ceramic powder via zirconia ball grinding using ethanol as grinding agent. Ceramic powder with MWCNT were compressed with Φ 15 mm -2.5 mm disk shape by template and thereafter firing in 1200 ℃ at 1.5 h. A bulk PMNT ceramic was also made for comparison, the thermo-gravimetric analysis of MWCNT is used to design the sintering procedure. The complete burnout of this CNT was about 850℃ according to DSC analysis.

Table 1: The materials Specifications used in this study

Materials	Purity	Sizes	Manufacturer
PMNT ceramic powder	99.95%	<1 μm	MSE supplies
MWCNT	98%	Diameter 12-30 nm Nano tube Length about 0.5 to 2 mm,	Merck co.

2.2. Experimental procedure

2.2.1. Dry density and porosity measurement

The dense and porous of PMNT ceramic densities were measured with a Sartorius-CP324S densitometer working based on Archimedes' principle. Besides, the overall porosity was determined by:

$$P = 100\left(1 - \frac{\rho^*}{\rho}\right) \quad (1)$$

Where, ρ* is the porous sample density calculated by means of the Archimedes technique.

2.2.2. X.R.D

The phase creation manner of the PMNT ceramic is showed by an XRD technique (STOE, Model STADI P, year 2000) with cu Kα radiation a step scan of 0.015° from 5 to 120° (Germany, 2000), the crystallographic structure was carried to review composition of bulk PMNT ceramic and Nano structure ceramic with MWCNT as pore forming agent.

2.2.3. Thermal Test

Differential Scanning calorimetry (DSC) test was applied to find the MWCNT phase conversion temperature. The ideal sintering method was applied in accordance with the CNT thermo-gravimetric examination like earlier researches [19-22].

2.2.4. Scanning Electron Microscopy (SEM)

Crystalline structure as well as morphology, of bulk PMNT ceramic and Nano composite with MWCNT as pore forming agent were examined by SEM. (Model MIRA, TESCAN, IRQST Zeiss company Germany 2005).

3. Results and discussion

3.1. Dry density and porosity

With the addition of 0.1 wt. % of MWCNT as pore forming agent to PMNT ceramic powder after sintering process the results indicate that the porosity of Nano porous PMNT ceramic was increased nearly 24% more than of unmixed specimen while the density difference between dense and porous was very low ~1.53 g/cm^3. Many previous works on PZT and PMN-PZT have reported a similar behavior [19-26]. The samples obtained are summarized in Table 2.

Table 2: Parameters of Nano porous PMNT ceramic and dense PMNT ceramic

Parameters	Nano porous PMNT ceramics	Dens PMNT ceramics
Density (g/cm^3)	7.7	7.82
Porosity (%)	6.2	4.7

3.2. X.R.D

The XRD models of unmixed and mixed specimen (PMNT and MWCNT as PFA) are presented in Figure 1. It is noticeable that only Perovskite framework was watched for two specimens with no other form identified, indicating that MWCNT as Nano size voids forming media did not affect the PMNT ceramic phase.

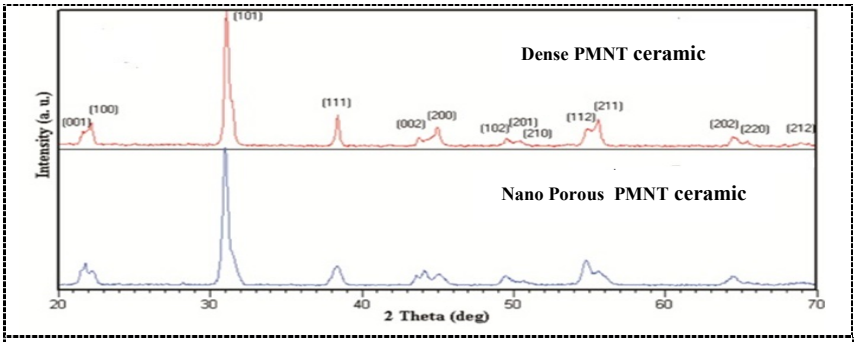

Fig. 1: The XRD models of dense and porous PMNT ceramics

3.3. MWCNT thermal analysis results and sintering method of Nano porous PMNT ceramic

The results of TG, and DTG tests of MWCNT shows that the complete burnout of the MWCNT as pore forming agent was about 850℃ as shown in Figures 2 and 3 respectively, the perfect sintering method was arranged in agreement with the thermo-gravimetric examination of MWCNT as shown in Figure 4, therefore the heating procedure of MWCNT was determined to start with heating range of 1 ℃/min till to 850 ℃ to assure the complete burnout of the MWCNT followed by 2℃/m up to1200 ℃ which represent the ideal sintering temperature of PMNT bulk ceramic during the sintering of porous samples, the samples were placed in covered alumina crucibles containing PZTCN powder to decrease the evaporation of PbO.

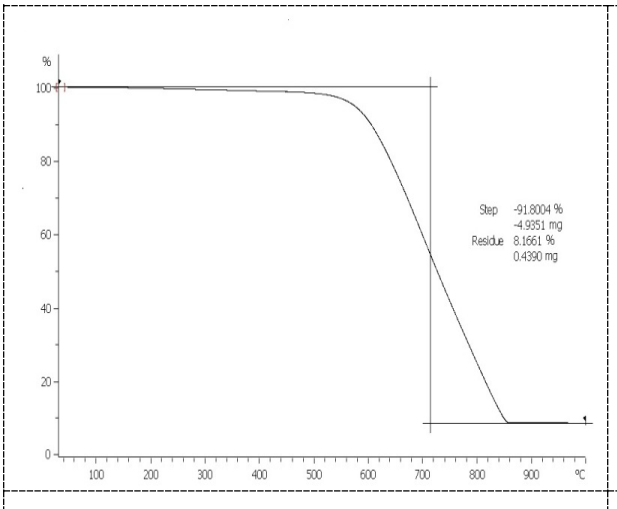

Fig. 2: MWCNT TG curve at heating range 10℃/min in air

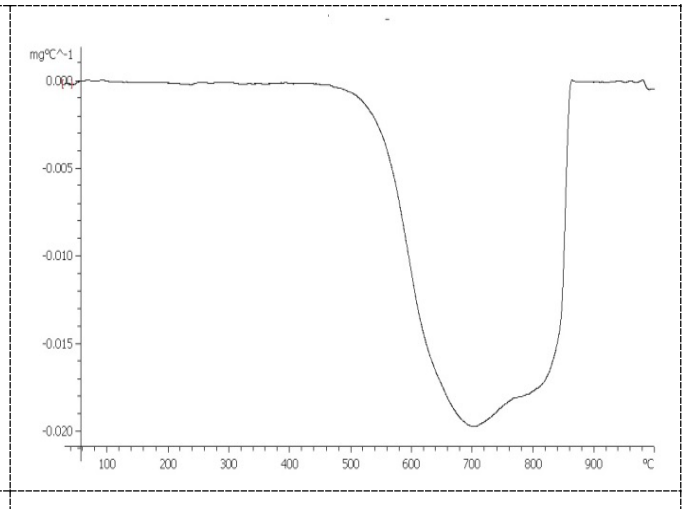

Fig. 3: MWCNT DTG curve at heating range 10℃/min in air

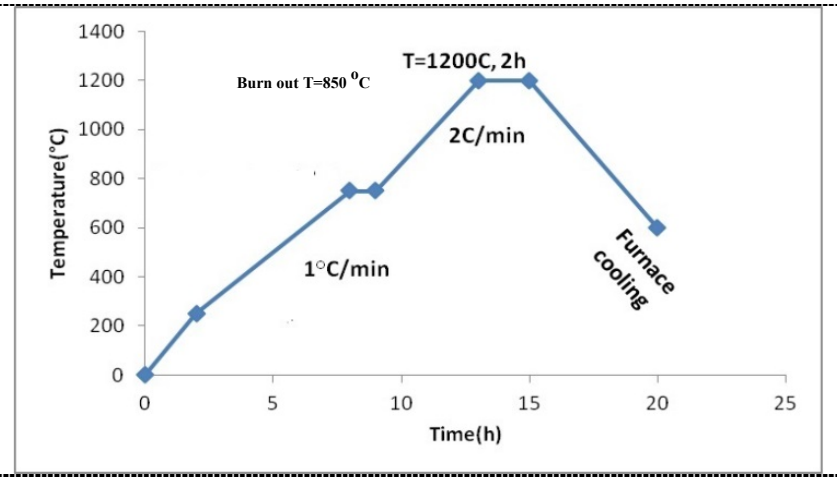

Fig. 4: A typical sintering procedure of PMNT ceramic with MWCNT as PFA

3.4. Scanning Electron Microscopy (SEM)

Figures 5 and 6 photographs are shown morphology of MWCNT with different magnification. Figure 6 appears MWCNT with diameter of approximately 15 nm, while Figures 7 and 8 are showing morphologies of starting materials, PMNT ceramic powder and ceramic powder with MWCNT respectively (before pressing and sintering process), it is clear in d image that the small diameter of MWCNT make it difficult to obtain a good mixture of the two phases prior to pressing and sintering procedure. Figures 9 and 10 shows section of PMNT ceramic after sintering with addition of MWCNTs as pore forming agent at low and high magnification respectively. The resultant pores are mostly Nano pores with range about 18-28 nm were created in ceramic specimen after sintering process, the hole volume and cavity shape are linked to the volume and form of the MWCNT used.

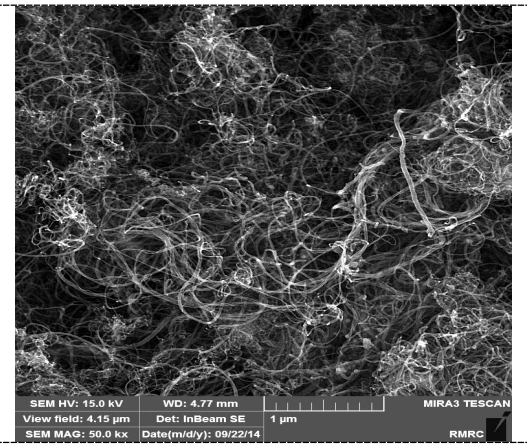

Fig. 5: SEM of MWCNTs with low enlargement

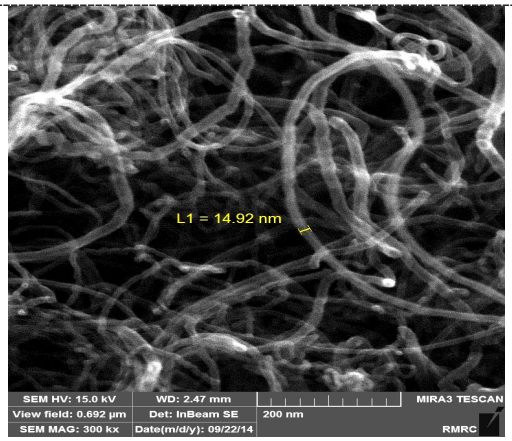

Fig. 6: SEM of MWCNTs with high enlargement

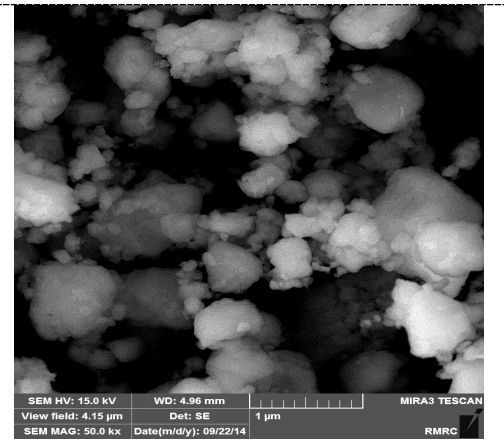

Fig. 7: SEM of PMNT ceramic powder as starting material

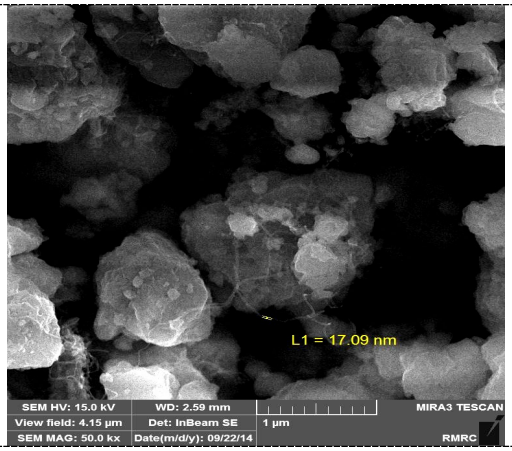

Fig. 8: SEM of PMNT ceramic powder and MWCNT as starting materials

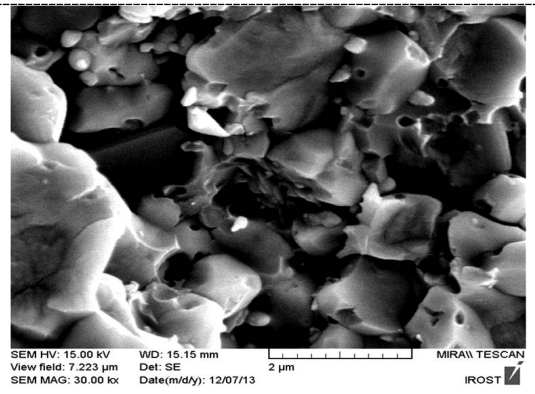

Fig. 9: Section of PMNT ceramic after sintering with addition of MWCNTs as pore forming agent at low magnification

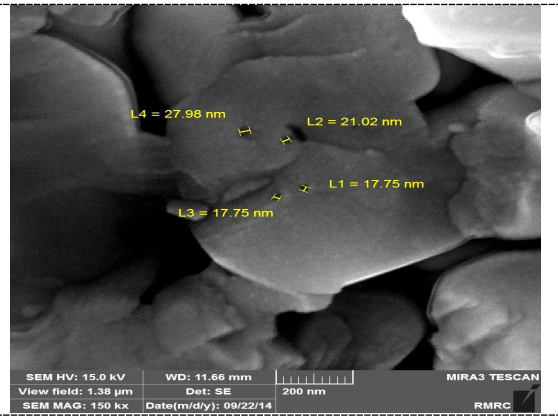

Fig. 10: Section of PMNT ceramic after sintering with addition of MWCNTs as pore forming agent at high magnification

4. Conclusion

Inter-granular Nano porous PMNT ceramics were designed with MWCNT as voids formers with Nano size the porosity of Nano porous PMNT ceramic was increased nearly 24% more than unmixed specimen with the increment 0.1 wt.% of MWCNT. XRD test detected only Perovskite structure for dense and porous PMNT ceramics with no other crystallographic structure. The perfect sintering method was determined in agreement with Tg and DTG tests of MWCNT the results of thermal analysis of MWCNT shows that the complete burnout of pore forming agent was about 850 ℃ therefore the initial heating rate was 1 ℃/min up to 850 ℃ to assure the complete burnout of the MWCNT from the sample. The resultant pores are mostly Nano pores with range about 18-28 nm were shaped in ceramic afterward sintering process and the hole volume and cavity form are concerned with dimensions and shape of the MWCNT used.

References

[1] M.K. Zhu, P.X. Lu, Y.D. Hou, X.M. Song, H. Wang, and H. Yan," Analysis of Phase Coexistence in Fe2O3-Doped 0.2PZN–0.8PZT Ferroelectric Ceramics by Raman Scattering Spectra," J. Am. Ceram. Soc., 89[12] 3739–3744 (2006).

[2] S.B. Seo, S.H. Lee, C.B. Yoon, G. Park, and H. Y. Kim, "Low Temperature Sintering and Piezoelectric Properties of PZT-PZN ceramics j. Am Ceram. Soc.,94[7]1238- 1243(2004).

[3] A.V. Shil'nikov, A. V. Sopit, A. I. Burkhanov and A. G. Luchaninov," The Dielectric Response of Electrostrictive (1-x) PMN-xPZT Ceramics," J. of the European Ceramic Society,19[6-7]1295-1297(1999).

[4] K. Joe, J.Y. Park, "PZT-PMN Ceramics for Large Displacement Piezoelectric Devices," J. Transactions of Electrical and Electronic Materials, 5 [2]76-80(2004).

[5] J.C. Shaw, K.S. Liu and I.N. Lin, "Dielectric Behavior of Morphotropic Phase Boundary for PMN-PZT Ceramics," 29 [7] 981-986 (1993).

[6] Y. Abe, T. Yanagisawa, K. Kakogawa and Y. Sasaki," Piezoelectric and Dielectric Properties of Solid Solution of PZT-PMN System Prepared by Wet-dry Combination Method," Solid State Communications, 113 6 331-334 (1999).

[7] P. Moetakef, A. Nemati," Synthesis of Pyrochlore Free PMN–PZT Ceramics via a Seeding Method," Sensors and Actuators A, [141]463–470(2008).

[8] I. Kim, H. Joo, S. Jeong, M. Kim and J. Song, "Micro Power Generation of a PMN-PZT Triple-morph Cantilever for Electric Harvesting Devices," Journal of the Korean Physical Society, Vol. 56, No. 1, 370-373(2010).

[9] C. h. Nam, H. Y. Park, T. Seo, J.H. Choi, M.R. Joung and S. Nahm," Low-Temperature Sintering and Piezoelectric Properties of 0.65Pb (Zr1-xTix) O3–0.35Pb (Ni0.33Nb0.67) O3 Ceramics," J. Am. Ceram. Soc., 94[10] 3442–3448 (2011).

[10] Piezoelectric PMN-PT ceramics from mechano-chemically activated precursors M. Algueró a, C. Alemany a, B. Jiménez a, J. Holc b, M. Kosec b, L. Pardo a Journal of the European Ceramic Society Volume 24, Issue 6, 2004, Pages 937-940 https://doi.org/10.1016/S0955-2219(03)00598-3.

[11] K. Boumcheddaa, M. Hamadia, G. Fantozzi," Properties of a Hydrophone Produced with Porous PZT ceramic, "Journal of the European Ceramic Society, 27 4169–4171(2007).

[12] K. K. Shung, J. M. Cannata , Q. F. Zhou", Piezoelectric Materials for High Frequency Medical Imaging Applications: A review," J. Electro-ceramic 19 139-145 (2004).

[13] W.A. Smith, "The Role of Piezo-Composition in Ultrasonic Transducers," IEEE Proceeding Ultrasonic Symposium (1989).

[14] V. V. Eremkin, V. G. Smotrakov, V. A. Aleshin, and E. S. Tsikhotskii, "Microstructure of Porous Piezo ceramics for Medical Diagnostics," Inorganic Materials, 40 [7] 775–779 (2004).

[15] P. V. Ivanov, V. V. Eremkin, V. G. Smotrakov, and E. S. TsikhotskiiInorganic, "Porous Piezoelectric Ceramics: Materials for Ultrasonic Flaw Detection and Medical Diagnostics Materials," Inorganic Materials, 38 [4] 408–410(2002)

[16] H. Kara, R. Ramesh, R. Stevens and C. R. Bowen ,"Porous PZT Ceramics for Receiving Transducers," IEEE Transactions on Ultrasonic, Ferroelectrics, and Frequency Control, [50] No 3 (2003).

[17] Piezoelectric properties of 3-1 type porous PMN-PZT ceramics doped with strodiumWei Liu , Yu Cao , Jianhong Wang , Yanzhong Wang , Xiaoqin Xi , Jinlong Yang Materials Science and Engineering: B [263], 11-14 (2021)

[18] S.H. Lee, S.H. Jun and H.E. Kim," Fabrication of Porous PZT–PZN Piezoelectric Ceramics with High Hydrostatic Figure of Merits Using Camphene-Based Freeze Casting," J. Am. Ceram. Soc., 90 [9] 2807–2813 (2007).

[19] Z. He and J. Ma, R. Zhang, "Investigation on the microstructure and ferroelectric properties of porous PZT ceramics, "Ceramic international, 30 1353-1356(2004).

[20] J. F. Li, K. Takagi, M. Ono, W. Pan and R. Watanabe," Fabrication and Evaluation of Porous Piezoelectric Ceramics and Porosity-Graded Piezoelectric Actuators J. Am. Ceram. Soc., 86 [7] 1094-98 (2003).

[21] T. Zeng, X. Dong, C. Mao, S. Chen and H. Chen ,"Preparation and properties of porous PMN-PZT ceramics doped with strontium ,"Materials science and engineering B, 135 50-54(2006).

[22] H.L. Zhang, J.F. Li, B. Zhang," Microstructure and electrical properties of porous PZT ceramics derived from different pore-forming agents," Acta Materialia [55] 171–181(2007).

[23] Zhang S.J. High entropy design," A new pathway to promote the piezoelectricity and dielectric energy storage in perovskite oxides,". Microstructures. [3] 20-23(2023).

[24] Li Z.M., Bian L., Yi X.Y., Zhu R.Q., Yuan X.T., Dong S.X. ,"A co-fired multilayer PMNS-PZT ceramic based linear piezoelectric ultrasonic micro-motor with a high-load-density," Appl. Phys. Letters.[120]82-90. 2022 doi: 10.1063/5.0084187

[25] Jan H., Francesco P., Sona H., Vojtech N. ," Sintering aids, their role, and behavior in the production of transparent ceramics," Open Ceram. [7]10-37(2021).

[26] Kim B.S., Ji J.H., Koh J.H. ,"Improved strain and transduction values of low-temperature sintered CuO-doped PZT-PZNN soft piezoelectric materials for energy harvester applications ,"Ceram. Int. [47] 6683–6690 (2021).

[27] Zhang S.K., Guo F.F., Jia B., Zhou H.Q., Dai Z.H., Xi Z.Z. ,"Effect of Li2CO3 on the structure and electrical properties of low-temperature-sintered 15PSN-52PMN-33PT ceramics,". J. Am. Ceram. Soc. ;[33]:2044–2051 (2022)