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# Effect of Milling Method on The Particle size of Calcined 0.65PMN-0.35PT Powder

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## Abstract

In this study, stoichiometric 0.65PMN-0.35PT powders have been prepared by columbite method. The perovskite single phase of PMN-PT was successfully synthesized after calcination of the mixed oxide at 900°C/4hr. Due to the particle size of calcined powder has greatly effect on the electrical properties of sintered samples. Therefore, two different milling methods including high energy ball milling (HBM) and conventional ball milling (CBM) were used to grind the calcined powders. The results showed that the particle size distribution of calcined powders from HBM and CBM were 0.17 and 0.19 μm, respectively. As a result, the relative density of the sintered ceramics prepared from both milling methods were up to 94-95%. Consequently, the greatly electrical properties including $d_{33}$ at 523 pC/N and K at 4855 (ceramics from HBM) and $d_{33}$ at 513 pC/N and K at 4675 (ceramics from CBM) were obtained.

**Key words:** Columbite Method, High Energy Ball-Milling, Conventional Ball Milling.

## Introduction

The relaxor ferroelectric, lead magnesium niobate–lead titanate ($(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3$-$xPbTiO_3$, PMN-PT) system has a morphotropic phase boundary (MPB) separating the tetragonal and rhombohedral phases at x=0.3-0.4.(1-2) Due to it has two phases at MPB leading to its high piezoelectric and electromechanical properties which is comparable to or better than those of PZT-5H.(2) Moreover, it showed high E-field induced strains, longitudinal coupling coefficients, temperature stability and high dielectric constants coupled with low electrical loss.(3) These make them as the candidate ceramic material in electronic devices for sensor, capacitor, pyroelectric detector, actuator and transducer applications. In order to form pure complex perovskite PMN-based ceramics without the undesirable pyrochlore phase, a method was suggested in the B-site cations or columbite method in which MgO and $Nb_2O_5$ were first reacted to form $MgNb_2O_6$, and then PbO and $TiO_2$ were reacted with the B-site oxide.(4) It was well known that a crucial parameter for densification of the samples was to control the particle size distribution of the ceramic powder. Many attempts have been studied to obtain nano-sized particles of perovskite phase at room temperature by using high-energy ball milling.(5-8) From this concept, the high-energy ball milling was applied for the calcined powder to reduce the particle size which could promote higher densification of the ceramics at lower sintering temperature. As a result, the improvement of electrical and piezoelectric properties of sintered samples could be obtained. In the present work, the complex perovskite 0.65PMN-0.35PT ceramics from submicron powders synthesized via two different methods including a high-energy ball milling and a conventional ball milling were prepared. The effect of particle size distribution on electrical and piezoelectric properties of ceramics were investigated and discussed.

## Materials and Experimental Procedure

The 0.65PMN-0.35PT piezoelectric material was prepared by columbite method. Powders of magnesium carbonate basic ($(MgCO_3)_4$. Mg $(OH)_2$. $5H_2O$, reagent grade, CARLO ERBA) and niobium oxide ($Nb_2O_5$, 99%, Merck, Germany) were mixed in acetone by ball-milling for 24 hours, then calcined at 1000 °C for 4 hours. Magnesium niobate precursor was then mixed with lead oxide (PbO, 99%, Kanto Chemical, Japan) and titanium dioxide ($TiO_2$, 99%, Riedel-de Haen, Germany). Excess PbO (0.5 wt%) was added to compensate for the lead loss during calcination step. This mixture was ball milled in acetone for 24 hours, then calcined at 900°C for

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4 hours. To obtain the submicron particle size, the calcined 0.65PMN-0.35PT powders were ground by high energy ball milling (HBM) and conventional ball milling (CBM). The first method was prepared by a 250 ml zirconia vial and alumina balls with 5 mm diameter. The latter was process by using a high density poly-ethylene bottle 250 ml and alumina balls with 5 mm diameter. The milling conditions of both methods were the same as follow. The mixture of starting materials was placed in vial with isopropyl alcohol (IPA) 50 ml. The milling speed was controlled approximately 200 rpm and milling duration at 16 hours. The powders after drying were then mixed with 6 wt% polyethylene glycol (binder) solution and sieved through 135 mesh. After that the green pellets were pressed to the disks of 1.2 cm in diameter and 0.1 cm thickness. All samples were heat treated at 550°C for 1 hour to remove the binder and sintered at 1200°C for 2 hours. Room temperature X-ray diffraction (XRD-6000, Shimadzu) with Fe source ($\lambda$ = 1.93 Å) was used to identify the phases from the calcined powders and sintered disks. The particle size distributions of calcined powders prepared from HBM and CBM were evaluated by particle size Mastersizer 2000.The densities of the sintered pellets were determined by the Archimedes principle. The microstructures of the fracture and surface of pellet were analyzed by Scanning Electron Microscopy (SEM; JEOL, JSM-6340F). Prior to the electrical measurements, the samples were polished to flat and parallel surfaces then electroded with silver paste by painting. The piezoelectric PMN-PT samples were poled in the silicone oil at 120°C and 25 kV/cm for 5 min. The piezoelectric coefficient ($d_{33}$) was determined with a Berlincourt Piezo $d_{33}$ meter. The dielectric constant (K) and the dissipation factor (tan$\delta$) values were measured at 1 kHz with an impedance analyzer (4192A LF Hewlett Packard) at room temperature.

## Results and Discussions

Figure 1 shows the XRD patterns of the 0.65PMN-0.35PT calcined powders after HBM and CBM methods. The XRD peaks have demonstrated the PMN perovskite structure, which was matched with JCPDS file no. 81-861 and no observation of the secondary phase of pyrochlore. The XRD peaks for both calcined powders after HBM and CBM were sharp and distinctively diffractions, which informed that the complete of PMN-PT crystalline were obtained. The characteristic of particle size distribution of the calcined powders from HBM and CBM methods are demonstrated in Figure 2. Both calcined powders showed different particle size distributions. By means of the powders from HBM had a trimodal size distribution with the majority of particle size at 0.19 µm incorporated with various sizes of 0.63 and 2.19 µm, while the powders from CBM had a monomodal size distribution of the mean particle size approximately 0.17 µm.

It was found that the particle size from both milling methods were similar.

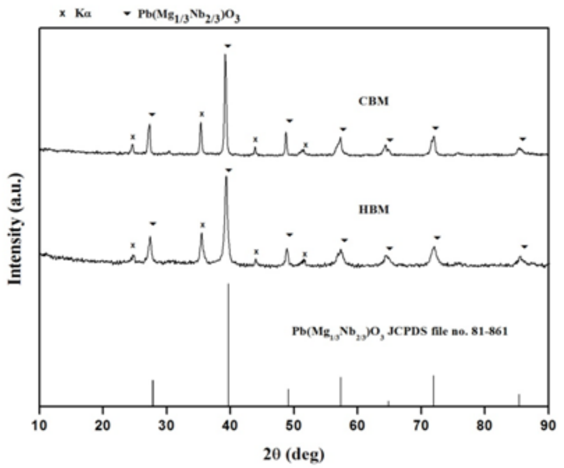

**Figure 1.** XRD patterns of the 0.65PMN-0.35PT calcined powders from HBM and CBM methods.

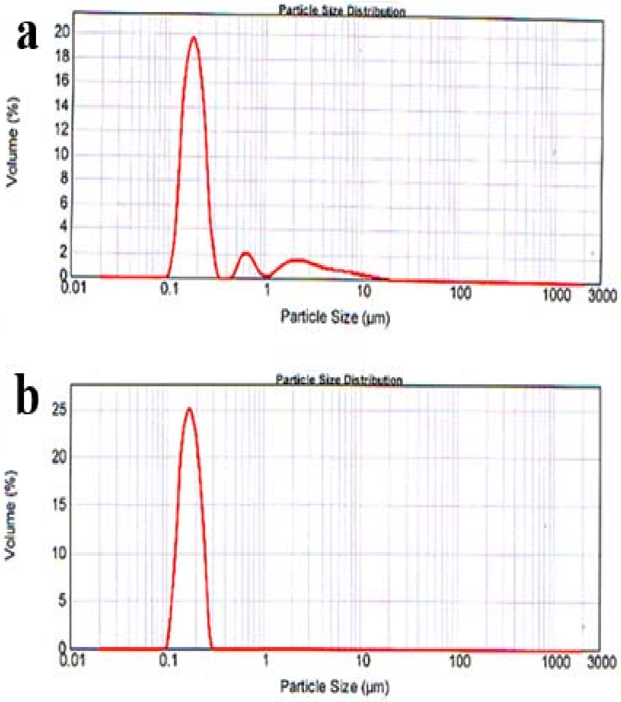

**Figure 2.** The particle size distribution of the calcined powders ground by (a) high energy ball mill (HBM) (b) conventional ball mill (CBM).

The XRD patterns of the sintered 0.65PMN-0.35PT ceramics from HBM and CBM were displayed in Figure 3. The patterns exhibited the (110)-strongest reflections matched with perovskite structure of JCPDS file no. 81-861. Moreover, the splitting of (200) and (002) peaks was observed for both samples (2θ approximately 57°) which indicated the tetragonal structure of the sintered ceramics.

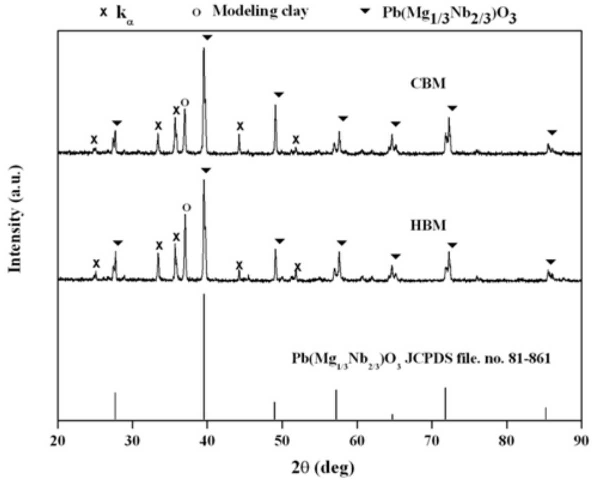

**Figure 3.** XRD patterns of the 0.65PMN-0.35PT ceramics (1200°C/2 hours) from HBM and CBM.

The surface and fracture SEM micrographs of 0.65PMN-0.35PT ceramics from HBM (Figures 4 a-b) and CBM (Figures 4 c-d) are shown. Mean grain sizes of ceramics from HBM were in range of 10-30 μm and the ceramics from CBM were in range of 8-40 μm. The various grain shapes including small round, large square and triangle shaped-grain of both samples were observed. In addition, both sintered samples showed abnormal grain growth. This type of grains in PMN-PT was activated by grain boundary mobility due to the existence of PbO-rich liquid phase during long thermal treatment.(9-10) In our case, the abnormal grain growth may occur from PbO-rich from the excess PbO in the mixture and form the Pb-source ($PbZrO_3$) during sintering. PbO rich condition was also evident from the fracture behavior of the grain in which both sintered ceramics showed inter- and trans-granular fracture characteristics. According to the inter-granular fracture appeared from the covering of PbO-rich layer on the grain causing the weakness at the grain boundaries. On the other hand, some grains have not been covered by PbO layer, the fracture illustrated intra-granular type as observed by other studies.(11)

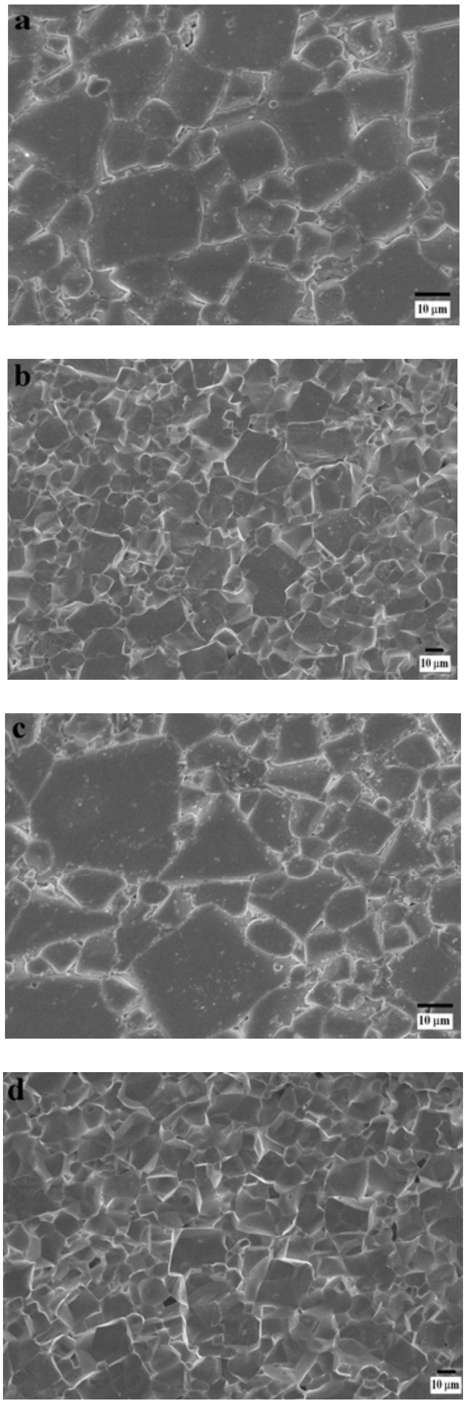

**Figure 4.** SEM micrographs of surface and fracture of the sintered ceramics from the calcined powders of (a-b) HBM (c-d) CBM.

The physical properties of the 0.65PMN-0.35PT ceramics from HBM and CBM methods sintered at 1200°C for 2 hours are displayed in Table 1. The PbO loss of sintered ceramics from HBM showed higher than those of ceramics from CBM. Generally, the PbO loss always occurred in the PMN-PT with excess PbO system.(9, 11-12) Therefore, the amount of excess PbO in PMN-PT had to be limited because the PbO liquid phase at the grain boundaries could contribute to the PbO loss and then generate the porosity. However, the density of sintered ceramics from HBM was slightly higher than sintered ceramics from CBM. This was because the ceramic from HBM had significantly more shrinkage as well as less porosity compared to those ceramics from CBM as seen in Figure 4d and Table 1.

**Table 1**. Physical properties of 0.65PMN-0.35PT ceramics from HBM and CBM sintered at 1200°C for 2 hours.

| Method | PbO loss (%) | Shrinkage (%) | Relative density (%) | Porosity (%) |
|---|---|---|---|---|
| HBM | 0.82 ± 0.07 | 15.08 ± 0.07 | 95.33 | 0.39 |
| CBM | 0.16 ± 0.05 | 11.74 ± 0.05 | 94.35 | 0.63 |

The influence of dielectric and piezoelectric properties on sintered 0.65PMN-0.35PT ceramics prepared from calcined powders milled by HBM and CBM are demonstrated in Table 2. The ceramic from HBM exhibited $d_{33}$ of 523 pC/N and K of 4855 and ceramic from CBM showed $d_{33}$ of 513 pC/N and K of 4675. The electrical properties of both ceramics were not significantly different and showed rather close to other researches ($d_{33}$ was 563 pC/N and K was 3640).(15) It was believed that the large grain size was preferred to high polarizability resulting in higher $d_{33}$ and K in PMN-PT system as observed in previous reports.(13-14)

**Table 2.** Dielectric and piezoelectric properties of 0.65 PMN-0.35PT ceramics from HBM and CBM sintered at 1200°C for 2 hours.

| Method | Piezoelectric property | Dielectric properties[a] | |
|---|---|---|---|
| | $d_{33}$ (pC/N) | K | Tan δ |
| HBM | 523 | 4855 | 0.0085 |
| CBM | 513 | 4675 | 0.0068 |

[a] measured at 1 kHz

## Conclusions

The effects of milling method with high energy ball mill and conventional ball mill on the particle size distribution of calcined 0.65PMN-0.35PT powders were not significantly different. As a result, the electrical properties and microstructure of sintered ceramics were also similar. Higher density, lower porosity and the large grain size facilitated to orientation of the polarizations during poling. Thus, the greatly electrical properties were shown with $d_{33}$ of 523 and 513 pC/N and high K values of 4855 and 4675 for sintered ceramic prepared from HBM and CBM, respectively. These make them suitable for sensor and actuator applications.

## Acknowledgements

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