Enhancement in Piezoelectric Properties of PZT-Based Ceramics by High Energy Ball-Milling Treatment of Solid-State Synthesized Powders

Dae-Uk Kim, Han-Bok Lee, Nguyen Viet Hung, Ky Nam Pham,
Hyoung-Su Han, and Jae-Shin Lee*

School of Materials Science and Engineering, University of Ulsan, Ulsan 680-749, South Korea

(Received September 3, 2010; Revised September 20, 2010; Accepted October 5, 2010)

Abstract The effects of high energy ball-milling (HEBM) on the sintering behavior and piezoelectric properties of 0.1 wt% Li_2CO_3 doped $0.8\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ - $0.2\text{Pb}(\text{Zr}_{0.475}\text{Ti}_{0.525})\text{O}_3$ (PMN-PZT) ceramics were investigated. It was found that HEBM treatment was quite effective to reduce the average particle size down to 300 nm, leading to increased density as well as enhanced piezoelectric properties of a sintered specimen even though prolonged HEBM resulted in unwanted secondary phases that caused a degradation of piezoelectric properties. The dielectric constant (ϵ_r), piezoelectric coupling factor (k_p) and piezoelectric constant d_{33} of 0.1 wt% Li_2CO_3 doped PMN-PZT ceramics prepared via HEBM for 10 h reached 2040, 0.68 and 554 pC/N, respectively.

Keywords : Piezoelectric ceramics, High energy ball milling, Sintering, Microstructure

1. Introduction

Recently high energy ball-milling (HEBM), which is often called as mechanochemical activation, has been investigated to synthesize lead zirconate titanate (PZT) ceramics by several research groups [1-4]. The basic idea was to apply intensive milling in solid state synthesis of PZT and to skip multiple steps of calcination at elevated temperatures and subsequent milling. Brankovic *et al.* [2] reported that PZT ceramics, having a morphotropic phase boundary composition of $\text{Pb}(\text{Zr}_{0.52}\text{Ti}_{0.48})\text{O}_3$ synthesized using HEBM, showed piezoelectric properties comparable to those obtained by conventional solid-state reaction method. The PZT nanopowders, however, required a sintering temperature of 1100°C to attain piezoelectric properties equivalent to conventionally prepared ones. Considering the previous reports, it seems difficult to lower the sintering temperature (T_s) of HEBM derived PZT powders down to 950°C through solid-state sintering, which is practically important for low cost

multilayer ceramic actuators utilizing inexpensive Ag as an internal electrode material instead of expensive Ag-Pd alloys.

Liquid-phase sintering is an attractive way to lower T_s of PZT-based ceramics. Among various approaches, low-melting lithium compounds such as Li_2CO_3 [5, 6] and Li_2O [7] were reported to be quite effective as sintering aids for lowering T_s of PZT-based ceramics below 950°C without degradation of their piezoelectric properties. Therefore it is interesting to apply both HEBM and low melting sintering aids simultaneously to the preparation of PZT-based piezoelectric ceramics. In this work we investigated the effects of HEBM on the sintering behavior, piezoelectric and mechanical properties of $\text{Pb}(\text{Zr}_{0.475}\text{Ti}_{0.525})\text{O}_3$ - $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ (hereinafter abbreviated as PMN-PZT) + 0.1 wt % Li_2CO_3 ceramics.

2. Experiments

Ceramic powder with a composition of 0.8Pb

*Corresponding Author : [Tel : +82-52-259-2286; E-mail : jslee@ulsan.ac.kr]

Table 1. HEBM condition for pulverization of PMN-PZT piezoelectric powder

Batch size	40 g
Ball weight	120 g (BPR=3:1)
Milling media	Zirconia balls with 3 mm (50 wt%), 5 mm (30 wt%), 10 mm (20 wt%) in diameter
Volume of jar	150 ml
Rotation speed of jar	790 rpm
Milling time	0-40 h

$(\text{Zr}_{0.475}\text{Ti}_{0.525})\text{O}_3\text{-}0.2\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ was synthesized using the columbite precursor method. A mixture of MgO , Nb_2O_5 , ZrO_2 and TiO_2 powders was calcined at 1050°C for 4 h to form a columbite phase of $\text{MgNb}_2(\text{Zr}, \text{Ti})\text{O}_8$ and then a stoichiometric amount of PbO was added and calcined again at 900°C for 2 h. The calcined powder was added with 0.1 wt% Li_2CO_3 and then ball-milled for 24 h in ethanol with zirconia balls as milling media. The milled powder was further pulverized in a HEBM equipment under the condition summarized in Table 1. Milled powder was pressed into a disk-shaped pellet with diameter of 18 mm at 100 MPa. The pellets were sintered at 900°C for 2 h in a covered alumina crucible.

The crystal structure was analyzed using an X-ray diffractometer (XRD, RADIII, Rigaku, Japan), and

the surface morphology was examined with a field emission scanning electron microscope (FE-SEM), JEOL, JSM-650FF, Japan. For electrical measurements, a thick film silver electrode was printed on both sides of a specimen and fired at 700°C for 10 min. The specimen was poled in silicon oil at 100°C by applying a *DC* electric field of 3 kV/mm for 30 min. After poling, a Berlincourt d_{33} meter was used to measure the d_{33} constant at 100 Hz. The piezoelectric coupling coefficient (k_p) was evaluated using the resonance method with an impedance analyzer (HP 4194A).

3. Results and Discussion

Fig. 1 shows the scanning electron micrographs of HEBM treated powders for different milling times. Before milling the calcined powder reveals typical aggregates of fine particles as can be seen in Fig. 1 (a). These aggregates indicate that there were solid state reactions between PbO and MgNb_2O_5 , ZrTiO_4 during the second calcination at 850°C . As the milling time increases, it is clearly seen that the brittle particles get fragmented continuously through the grain boundaries, leading to a reduction in particle

Fig. 1. Change in the surface morphology of PMN-PZT powders with HEBM treatment.

Fig. 2. Change in the particle size distribution of PMN-PZT powders by HEBM treatment.

size. The average particle size was decreased from 5.6 μm to 0.3 μm after milling 40 h. Accordingly the BET surface area was increased from 1.0 m^2/g to 2.7 m^2/g . However, prolonged milling over 20 h resulted in agglomeration of fine powders as shown in Fig. 1 (e), which well matches to previous reports [8-12]. This phenomenon is generally explained by the ductile behavior of very fine powders.

Fig. 2 shows the results of particle size analyses on PMN-PZT powders as a function of HEBM treatment time. It is clear that HEBM markedly affects the particle size distribution, which initially reveals a bimodal distribution with two peaks at 0.2 μm and 8 μm , respectively, meaning that the conventional ball-milling resulted in a mixture of fine powder and coarse

aggregates. As the HEBM treatment time increases, the peak for big aggregates significantly decreases with a shift toward a smaller size of 3 μm while maintaining the bimodal distribution. Instead the peak at 0.2 μm gradually increases with HEBM treatment. From these results, it can be concluded that HEBM is quite effective for the size reduction of PMN-PZT ceramic powder.

Li_2CO_3 with a low melting point of 618°C was incorporated into PMN-PZT powders as a sintering aid in this work. The microstructure of 0.1 wt% Li_2CO_3 added PMN-PZT ceramics sintered at 900°C after HEBM treatment is shown in Fig. 3. All specimens demonstrate well densified microstructures while the average grain size decreases from 1.3 μm to 1.0 μm with increasing HEBM treatment time from 0 to 40 h. One possible explanation may be associated with transient liquid-phase sintering that was observed in several systems. Li [13] reported on the transient liquid-phase sintering in PNN-PMN-PZT ceramics with ZnO and Li_2CO_3 . At initial and intermediate stages of sintering, densification and grain growth occur through liquid-phase diffusion, and then the liquid phase at intergranular boundaries gradually dissolves into grains with grain growth. Finer powders prepared with HEBM offer larger solid-liquid interfacial area during sintering, and fur-

Fig. 3. Effect of HEBM treatment time on the microstructure of PMN-PZT PMN-PZT ceramics sintered at 900°C for 2 h in air.

Fig. 4. XRD patterns of 0.1 wt% Li_2CO_3 added PMN-PZT ceramics sintered at 900°C for 2 h in air. The specimens were prepared with HEBM treated powders for different milling durations.

ther enhance the dissolution rate of liquid phase into grains, leading to a smaller grained microstructure in the present study.

The XRD patterns of 0.1 wt% Li_2CO_3 added PMN-PZT ceramics are displayed in Fig. 4. Secondary phases including low melting Li_2PbO_3 [14] and unwanted pyrochlore phases $\text{Pb}_3\text{Nb}_4\text{O}_{13}$ and $\text{Pb}_2\text{Nb}_2\text{O}_7$ are observed and the peaks of pyrochlore phase are lowered as the milling time increased with ceramics sintered at the same temperature. Finer powders prepared with HEBM offer larger solid-liquid interfacial area during sintering and further enhance the dissolution rate of Li_2PbO_3 phase into grains, resulting in a lower concentration of intergranular secondary phases after sintering.

Fig. 5 represents the planar piezoelectric coupling coefficient k_p and piezoelectric constant d_{33} as a function of HEBM treatment time. The specimen prepared from powders using conventional ball-milling (when HEBM time=0) showed $k_p=0.64$ and $d_{33}=527$ pC/N, respectively. HEBM treatment of calcined powders for 10 h, however, enhances both k_p and d_{33} up to 0.68 and 554 pC/N, respectively. This may be related with the reduction of unwanted secondary phases in HEBM derived specimens as can be seen from XRD patterns in Fig. 4. Further HEBM, in

(a)

(b)

Fig. 5. Effect of HEBM time on (a) piezoelectric coupling coefficient k_p and (b) piezoelectric charge constant d_{33} of PMN-PZT ceramics sintered at 900°C for 2 h.

contrast, degrades the piezoelectric properties probably due to the incorporation of undesirable impurities that are introduced from milling media and jar wall of HEBM equipment [15, 16].

4. Conclusions

In summary, HEBM was found to be effective in reducing particle size of PZT-based ceramics, leading to an enhancement in the piezoelectric properties of PMN-PZT ceramics. Interestingly HEBM resulted in a smaller grained microstructure after sintering than the conventional ball-milling. This fact is prom-

ising for piezoelectric ceramics with high mechanical strength as well as excellent piezoelectric properties because they are generally used under high mechanical stress condition. However, prolonged HEBM treatment brings about a degradation of their piezoelectric properties due to unwanted contamination of impurities from ball milling media and jar.

Acknowledgement

This work was financially supported by the National Research Foundation, Republic of Korea, under the contract No.2010001-4113.

References

- [1] J. Xue, D. Wan, S.E. Lee and J. Wang: J. Am. Cer. Soc., **82** (1999) 1687.
- [2] Z. Brankovic, G. Brankovic, Jovalekic, Y. Maniette, M. Cilense and J. A. Varela: Mat. Sci. Eng. A, **345** (2003) 243.
- [3] J. S. Lee, M. S. Choi, N. V. Hung, Y. S. Kim, I. W. Kim, E. C. Park, S. J. Jeong and J. S. Song: Ceramics Inter., **33** (2007) 1283.
- [4] Y. H. Kim, D. Y. Heo, W. P. Tai and J. S. Lee: J. Korean Ceramic Soc., **45** (2008) 363.
- [5] S. H. Kang, C. W. Ahn, H. J. Lee, I. W. Kim, E. C. Park and J. S. Lee: J. Electroceramics, **21** (2008) 855.
- [6] J. S. Lee, M. S. Choi, H. S. Han, Y. M. Kong, S. J. Kim, I. W. Kim, M. S. Kim and S. J. Jeong: Sensors & Actuators: A. Physical, **154** (2009) 97.
- [7] J. S. Lee, E. C. Park, S. H. Lee, D. S. Lee, Y. J. Lee, J. S. Kim, I. W. Kim and B. M. Jin: Mat. Chem. Phys., **90** (2005) 381.
- [8] C. Suryanarayana: Prog. Mater. Sci., **46** (2001) 1.
- [9] F. Grasset, S. Mornet, J. Etourneau, H. Haneda and J.-L. Bobet: J. Alloys Compounds, **359** (2003) 330.
- [10] M. Sherif El-Eskandarany: J. Alloys Compounds, **279** (1998) 263.
- [11] W. Jo, T. H. Kim, D. Y. Kim and S. K. Pabi: J. Appl. Phys., **102** (2007) 8.
- [12] R. Sachana and J.W. Park: J. Alloys Compounds, **485** (2009) 724.
- [13] L. Li: Key Eng. Mat., **214** (2002) 49.
- [14] PCPDS cards no. 44-1054.
- [15] B. D. Stojanovic, C. Jovalekic, V. Vukotic, A. Z. Simoes and J. A. Varela: Ferroelectrics, **319** (2005) 65.
- [16] L. B. Kong, T. S. Zhang, J. Ma and F. Boey: Prog. Mater. Sci., **53** (2008) 207.