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Effects of high energy ball-milling on the sintering behavior and piezoelectric properties of PZT-based ceramics

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Abstract

PZT-PMN-PFN powders were synthesized by the columbite precursor method and then treated with high energy ball-milling (HEBM). The milling process reduced the average particle size from 500 to 100 nm. The sintering behavior and piezoelectric properties of the ceramics with the sintering aid 0.1 wt.% Li_2CO_3 were explored. Compared with conventional ball-milling, HEBM suppressed the formation of unwanted pyrochlore phases and furthermore resulted in finer grained microstructures with better piezoelectric properties. The planar electromechanical coupling factor (k_p) and piezoelectric constant (d_{33}) of a specimen sintered at 850 °C were 0.64 and 511 pC/N, respectively.

Keywords: A. Milling; A. Powders: solid-state reaction; C. Piezoelectric properties; D. PZT

1. Introduction

High energy ball-milling (HEBM), which is also known as mechanochemical activation, has been investigated for the synthesis of lead zirconate titanate (PZT) ceramics [1–4]. The basic idea was to apply intensive milling in the solid-state synthesis of PZT and to skip the 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 $Pb(Zr_{0.52}Ti_{0.48})O_3$ synthesized using HEBM, showed piezoelectric properties comparable to those obtained by the conventional solid-state reaction method. Kong et al. [3,4] also prepared the PZT ceramics from mixtures of PbO and HEBM-derived $(Zr_xT_{1-x})O_2$ nanosized powders via reaction sintering. The PZT nanopowders, however, required a sintering temperature of 1100 °C to attain piezoelectric properties equivalent to the conventionally prepared ones. Considering the previous reports, it seems difficult to lower the sintering temperature (T_s) of the HEBM-derived PZT powders below 950 °C through solid-state sintering. Achieving a lower T_s is practically important for the realization of low cost multilayer ceramic actuators which utilize inexpensive Ag as an internal electrode material rather than expensive Ag–Pd alloys.

Liquid-phase sintering is an attractive way to lower the T_s of PZT-based ceramics. Among the various approaches, low-melting lithium compounds including Li_2CO_3 [5], Li_2O [6,7], and $LiBiO_2$ [8] were reported to be quite effective sintering aids which lowered the T_s of the PZT-based ceramics below 950 °C without any degradation of their piezoelectric properties. Therefore, a utilization of both HEBM and low-melting sintering aids simultaneously to the preparation of PZT-based piezoelectric ceramics may result in a lower T_s. In this work we investigated the effects HEBM on the sintering behavior, piezoelectric and mechanical properties of PMN-PFN-PZT + 0.1 wt.% Li_2CO_3 ceramics. The HEBM method was compared with conventional ball-milling in the preparation of the piezoelectric ceramic powders.

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2. Experimental procedure

Ceramic powders with a composition of $Pb(Zr_{0.475}Ti_{0.525})O_3$–$Pb(Mg_{1/3}Nb_{2/3})O_3$–$Pb(Fe_{1/2}Nb_{1/2})O_3$ (hereinafter abbreviated as PFMNZT) were 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 the columbite phase of $(FeMg)Nb_2(ZrTi)O_8$ and then a stoichiometric amount of PbO was added and calcined again at 900 °C for 2 h. Before milling the calcined powders, 0.1 wt.% Li_2CO_3 was added as a sintering aid. Two milling methods were employed in the present study for comparison; conventional ball-milling (CBM) and HEBM. The milling conditions are summarized in Table 1. The milled powders were pressed into a disk-shaped pellet with diameter of 18 mm at 100 MPa. The pellets were sintered at 850–950 °C for 2 h in a covered alumina crucible.

The sintered specimen was polished to a thickness of 0.8 mm. Silver paste was applied on both sides of the specimen as electrodes and fired at 700 °C for 10 min. For electrical measurements, 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).

Table 1
Comparison of the two milling methods studied in this work

Milling method	Conventional ball-mill	HEBM
Batch size	120 g	40 g
Ball weight	240 g (BPR = 2:1)	120 g (BPR = 3:1)
Milling media	5-mm zirconia balls	Zirconia balls, 3 mm (50 wt.%), 5 mm (30 wt.%), and 10 mm (20 wt.%) in diameter
Milling environment	Ethanol	Air
Jar volume	1000 ml	150 ml
Jar rotation speed	170 rpm	790 rpm
Milling time	24 h	3 h

3. Results and discussion

X-ray diffraction (XRD) analysis confirmed that the PFMNZT powders before and after milling had a perovskite

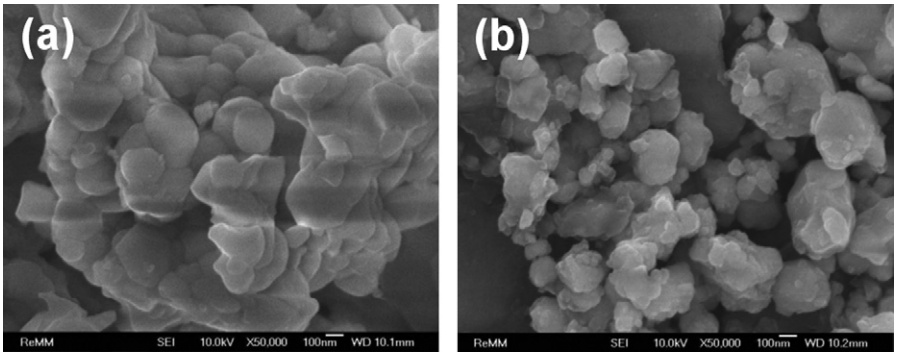

Fig. 1. FE-SEM photographs of PFMNZT powders pulverized using (a) CBM and (b) HEBM.

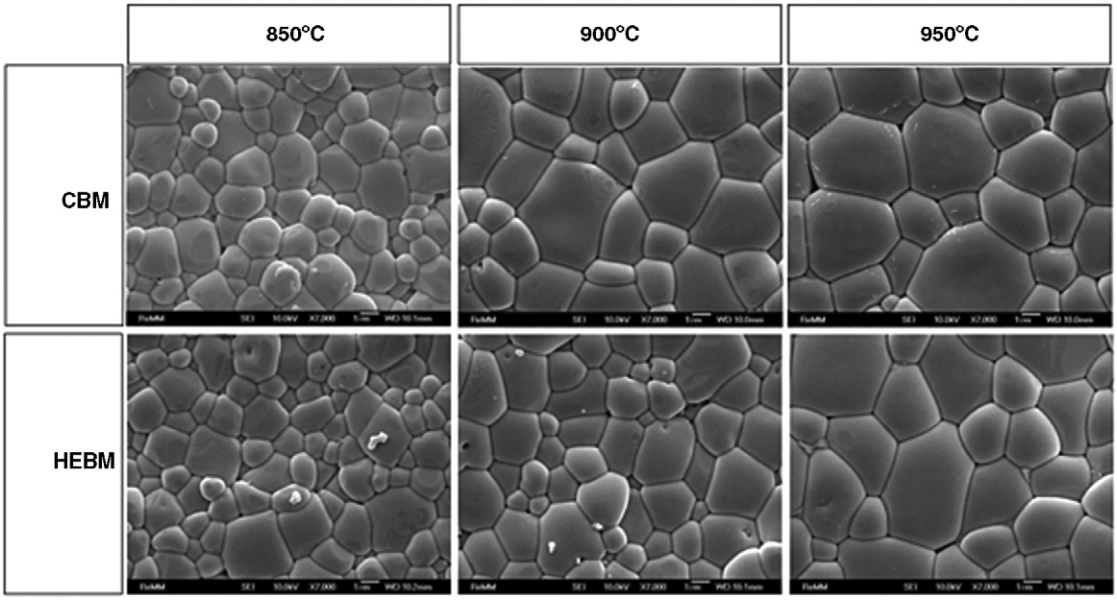

Fig. 2. FE-SEM photographs of the PFMNZT ceramics prepared with either CBM or HEBM. The sintering temperature is indicated on the figure.

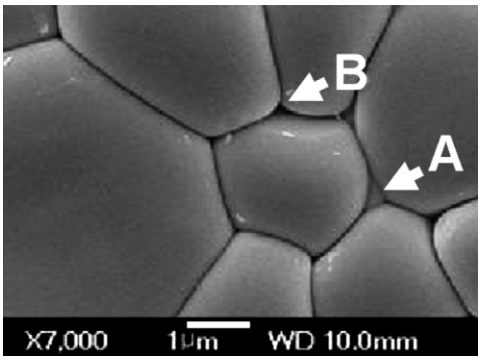

Fig. 3. FE-SEM micrograph of the PFMNZT + Li_2CO_3 ceramics sintered at 950 °C.

structure regardless of the milling method used in this work, either CBM or HEBM. However, the as-milled powders revealed remarkably different microstructures between the two milling approaches as shown in Fig. 1. Fig. 1a shows that aggregates of small grains were observed after CBM, while particles were effectively crushed after HEBM as represented in Fig. 1b.

The PFMNZT ceramics require a sintering temperature (T_s) of over 1100 °C for sufficient densification through solid-state sintering. For this reason, low-melting Li_2CO_3 was incorporated into the PFMNZT powders as a sintering aid. Fig. 2 shows the surface microstructure of the PFMNZT + 0.1 wt.% Li_2CO_3 ceramics sintered at a temperature range of 850–950 °C for 2 h. All specimens showed dense microstructures with a relative density of 95.4–98.5%. The average grain size increased with T_s. Interestingly, the CBM-derived powders resulted in larger grains after sintering than did the HEBM-derived ones. The smaller grained microstructure associated with HEBM could be explained with transient liquid-phase sintering in the PFMNZT + Li_2CO_3 ceramics.

Recently Li [9] reported on the transient liquid-phase sintering in PNN-PMN-PZT ceramics using ZnO and Li_2CO_3. At the initial and intermediate stages of sintering, densification and grain growth occur through liquid-phase diffusion, and then the liquid phase at the intergranular boundaries gradually dissolves into the grains with grain growth. By careful observation of the SEM micrograph given in Fig. 3, evidence of liquid-phase sintering can be found. At grain corners, the ''A-region'' in the figure, a trapped secondary phase is observed. In addition, round-shaped grain corners like the ''B-region'' strongly support liquid-phase sintering [10,11]. XRD analysis also confirmed the existence of a low-melting compound, identified as Li_2PbO_2, in our specimens.

Fig. 4 represents the X-ray diffraction patterns of the PFMNZT ceramics sintered with Li_2CO_3. Besides the perovskite phase, secondary phases including low-melting Li_2PbO_2 [12] and unwanted pyrochore phases [13–15] were observed, and their peak intensity decreased with T_s. It should be pointed out that HEBM resulted in a smaller amount of secondary phases than CBM. This may be associated with the difference in the particle size before sintering, which depended on the milling method. Finer powders prepared with HEBM offer a larger solid–liquid interfacial area during sintering, and further enhance the dissolution rate of the Li_2PbO_2 phase into the grains leading to a lower concentration of the intergranular secondary phases after sintering. The amount of pyrochlore phases in the specimens also decreased with T_s. It was reported that the pyrochlore phase becomes more stable than the perovskite phase at lower temperatures [14,15].

The piezoelectric and mechanical properties of the PFMNZT + 0.1 wt.% Li_2CO_3 ceramics were measured and summarized in Table 2. The physical constants of a PZT ceramic specimen with a rhombohedral–tetragonal morphotropic phase boundary are also listed for comparison. The piezoelectric constants k_p and d_{33} of low-fired PFMNZT

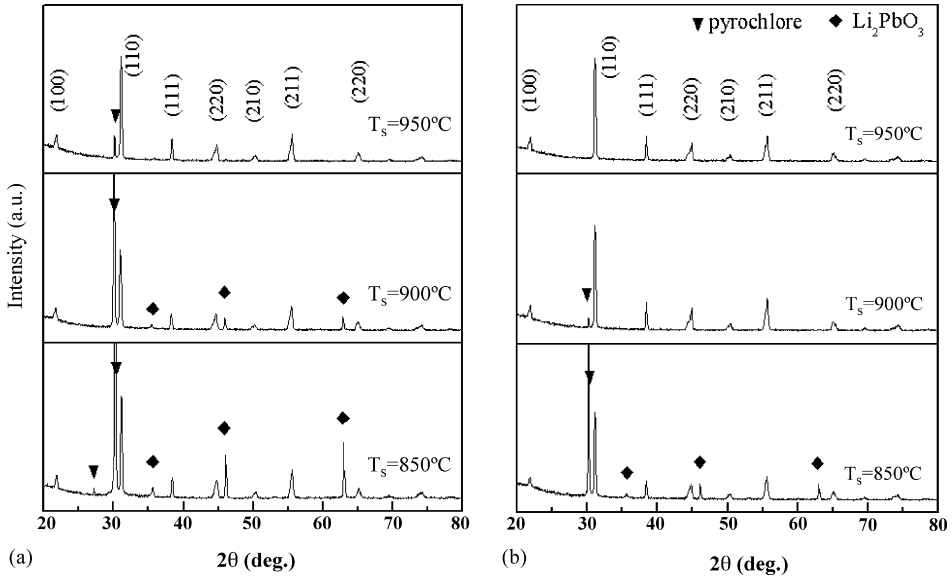

Fig. 4. X-ray diffraction patterns of PFMNZT ceramics sintered at different temperatures. Before sintering, the ceramic powders were treated with (a) CBM and (b) HEBM.

Table 2
The piezoelectric and mechanical properties of the PFMNZT ceramics

Composition (milling method)	T_s (°C)	Sintered density (g/cm^3)	Average grain size (μm)	k_p	d_{33} (pC/N)	H_v (kgf/mm^2)	K_{IC} (MPa m$^{1/2}$)
PZT ceramics (CBM)	1200	7.72	5.4	0.39	243	418	1.20
PFMNZT (CBM)	950	7.95	3.3	0.67	575	437	0.69
	900	7.96	3.0	0.64	521	443	0.64
	850	7.81	1.8	0.61	490	418	0.74
PFMNZT (HEBM)	950	7.97	3.1	0.68	594	454	0.65
	900	7.99	2.2	0.67	563	458	0.76
	850	8.01	1.7	0.64	511	469	0.67

ceramics are in the ranges of 0.61–0.68 and 490–594 pC/N, respectively, which were much higher than those of the high-fired PZT ceramics. With respect to increasing T_s, the k_p and d_{33} of the PFMNZT ceramics increased; this was probably due to the combined effects of an increased grain size and a decreased concentration of the pyrochlore phases at elevated temperature as shown in Figs. 2 and 4, respectively. It should be noted that smaller grained samples prepared by HEBM showed higher piezoelectric constants than those prepared by CBM. This can be attributed to the fact that HEBM suppressed the formation of the detrimental pyrochlore phases that existed in a significant amount of the specimens prepared by CBM.

The hardness (H_v) and fracture toughness (K_{IC}) were measured using the indentation method [16] and are listed in Table 2. The H_v of the low-fired PFMNZT ceramics was in the range of 418–469 kgf/mm^2, which was higher than that of the high-fired PZT ceramics. However, the low-fired PFMNZT ceramics showed a lower K_{IC} than the PZT because of higher hardness. HEBM also resulted in higher H_v values than the CBM for the low-fired PFMNZT ceramics.

4. Conclusions

The effects of HEBM on the sintering behavior and the physical properties of low-fired PFMNZT ceramics were investigated. It was found that HEBM, planetary ball-milling, was quite effective at reducing the particle size down to 100 nm for PFMNZT powders synthesized by the solid-state reaction method. HEBM led to microstructures of low-fired PZT-based ceramics that were smaller grained than CBM, which resulted in improvements in their piezoelectric and mechanical properties. By using both HEBM and Li_2CO_3 as a low-melting sintering aid, the planar piezoelectric coupling coefficient (k_p) and piezoelectric constant (d_{33}) of PFMNZT ceramics sintered at 850 °C for 2 h were 0.64 and 511 pC/N, respectively. These results are very promising for the development of low-cost, high performant multilayer ceramic actuators.

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