Microstructural and Piezoelectric Characteristics of PSN-PMN-PZT Ceramics Produced by Attrition Milling

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For the piezoelectric transformer application, $Pb(Sb_{1/2} Nb_{1/2})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ceramics were produced by attrition milling. Microstructural, dielectric and piezoelectric characteristics of the ceramics were investigated as a function of milling time. The particle size and grain size decreased while dielectric constant, density and mechanical quality factor (Q_m) increased with milling time. Temperature coefficient of resonant frequency (TCf_r) was shifted to positive side with increasing milling time. The attrition milling process proved to be one of the effective routes to produce transformers for high power application.

Keywords : mechanical quality factor,   particle size,   attrition milling,
            temperature stability of resonant frequency, piezoelectric transformer

1. INTRODUCTION

For the piezoelectric ceramics used for piezoelectric transformers, resonators and filters, stable piezoelectric properties including electromechanical coupling coefficient and mechanical quality factor are required. In particular, the temperature coefficient of resonant frequency (TCf_r) close to zero is necessary. For high power application of piezoelectric transformers, however, the material strength is the prerequisite and normally can be achieved by producing microstructure of fine grains and low porosity. Another requirement for such application is high mechanical quality factor, Q_m since the temperature rise is always associated with the transformer at its resonant frequency, leading to the deterioration in piezoelectric properties[1]. For the fabrication of dense piezoelectric ceramics with low porosity, special processing routes such as hot pressing and hot isostatic pressing (HIP) have been tried and in many cases, promising results have been obtained[2]. From the standpoint of mass production, however, the utilization of those methods is not simply

rationalized because of complexity of the processes (especially in HIP) and high production cost. Another route that can be employed for the production of high strength material would be the attrition milling process originally designed for the mechanical alloying of materials with high melting point or reactive materials[3-5]. The attrition milling or high energy ball milling process is well known for its capability of producing fine powder particles under sub-micron scale and now the process is extended to produce nano-scale particles as well[6].

Regarding piezoelectric properties, Takahashi and coworkers [7] reported that $Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ceramics showed moderate electromechanical coupling coefficient, k_p and very high Q_m. In addition, Tapano[8] demonstrated that the grain growth can be effectively suppressed by the presence of $Pb(Sb_{1/2} Nb_{1/2})O_3$. In this study, based on these results, $Pb(Sb_{1/2} Nb_{1/2})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ system ceramics was chosen for the piezoelectric transformer application. As described above, attrition milling process was utilized in order to increase material strength. Micro structural, dielectric and piezoelectric characteristics of $Pb(Sb_{1/2}Nb_{1/2})O_3$-$Pb(Mn_{1/3}Nb_{2/3})O_3$-$Pb(Zr,Ti)O_3$ ceramics were investigated with the variation in attrition milling time.

2. EXPERIMENT

PSN-PMN-PZT ceramics with the following chemical composition were used for fabricating the specimens.

$$0.035Pb(Sb_{1/2}Nb_{1/2})O_3\text{-}0.065Pb(Mn_{1/3}Nb_{2/3})O_3\text{-}$$
$$0.90Pb(Zr_{0.49},Ti_{0.51})O_3\text{+}0.5wt\%PbO \qquad (1)$$
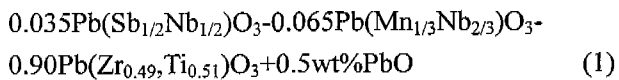
The composition ceramics were produced from reagent grade raw material oxide via a conventional mixed-oxide process. Raw materials of the given composition were acetone-milled for 24 h in a zirconia ball mill. Calcination at 850°C for 2 h was followed. The material was ground by 270 rpm for 1 to 9 h in the attrition mill and dried again. The ball to powder ratio was 3. 5wt% PVA solution was mixed with the material

and sieved through a -#100 mesh. The powders were consolidated using uni-axial pressing at stress of 1 kg/cm^2 and sintered at 1275°C for 2 h in air. The poling treatments of the specimen was performed in a 120°C silicon oil bath at 30 kV/cm for 30 min. Electrical and piezoelectric properties of the specimens with poling treatment were determined by the resonance method [9] using frequency data obtained using an impedance analyzer (HP4194A). The particle size of the calcined powder ground in the attrition mill was measured using Cilas 1064 particle size analyzer. The fracture surface of the sintered specimens was investigated using scanning electron microscopy. Dielectric constant was calculated from the 1 kHz capacitance data measured using LCR meter, ANDO AG 4304. Temperature stability of the resonant frequency was investigated by measuring resonant frequencies of the specimens in the temperature range between –20 and 80°C.

3. RESULTS AND DISCUSSION

Fig. 1 (a) shows the particle size as a function of attrition milling time. The figure indicates that the particle size drastically decreases from average 3.55μm of calcined powder state down to average 0.39μm after 6 h attrition milling. The particle size distribution also shows the increase of smaller particles with increasing attrition milling time as shown in Fig.1(b). In contrast, for the powders milled over 7 h, the particle size increased with the milling time. However, it may not be interpreted as proportional relation between particle size and milling time. Rather, it is more likely that the precise measurement of particle size was shadowed primarily because of the agglomeration of fine particles, resulting in apparent increase of particle size.

Fig. 2 shows the fracture surface of the sintered specimens processed for different milling time. As the variation in particle size, the grain size of the specimens decreased with the milling time. However, the grain size of the specimens milled over 7 h was measured to be larger than that of other samples. Such variation in grain size can be attributed to higher driving force for grain growth caused by the increase in specific surface area of fine particles. This implies that the particle size
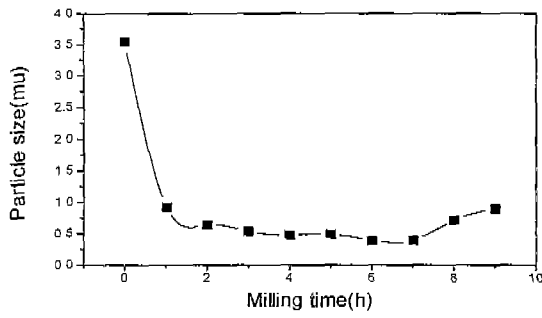
(a) Particle size with milling time
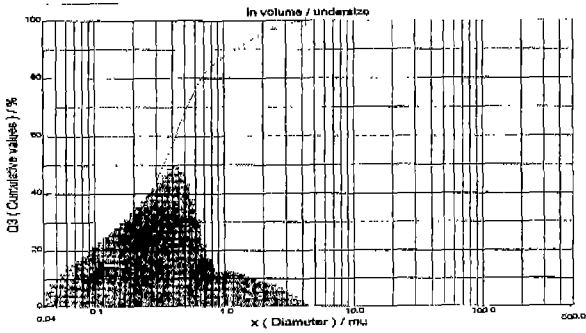
(b-1) Particle size distribution at 3 h milling time
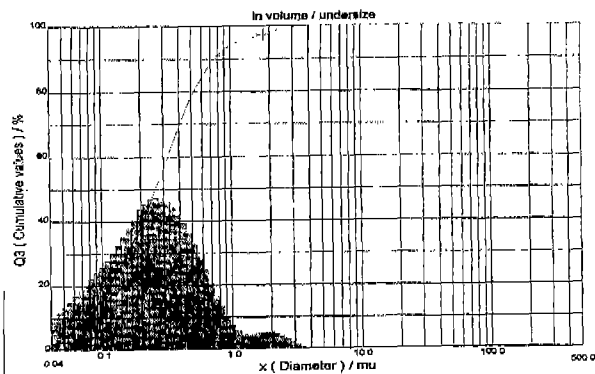
(b-2) Particle size distribution at 6h milling time

Fig. 1. Variation in particle size of calcined powder.

continuously decreases as milling time (up to 9 hours of milling in this case) because the sintering temperature for the specimens was same each other. In addition, for the specimens of S7, S8 and S9, it may be regarded that the sintering temperature of 1275°C was higher than the optimum temperature to obtain fine grains.

Fig. 3 shows X-ray diffraction patterns of the specimens with different milling time. As can be seen, the relative intensity ratio of I(200)/I(002) decreased

(a) 2h   (b) 4h
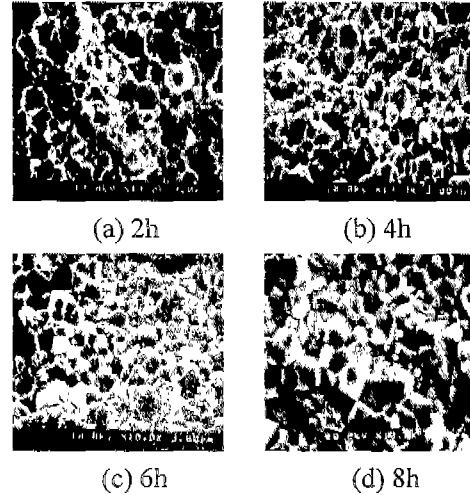
(c) 6h   (d) 8h

Fig. 2. Scanning electron micrographs of the specimens.

with increasing milling time. This is due to the gradual increase in tetragonality. As far as the strength of the material is concerned, the density was measured as an indirect parameter to evaluate mechanical strength.

The variation in density illustrated in Fig. 4 is easily predicted on the basis of the particle size variation shown in Fig. 1. The highest density of 7.92 g/cm^3 was obtained from the specimen S7 consolidated with the powders of 039μm. Presumably, lower sintered densities of the specimens, S7 and S8 may be a result of particle agglomeration that inhibits compact filling of powders leaving larger fraction of inter-particle voids.
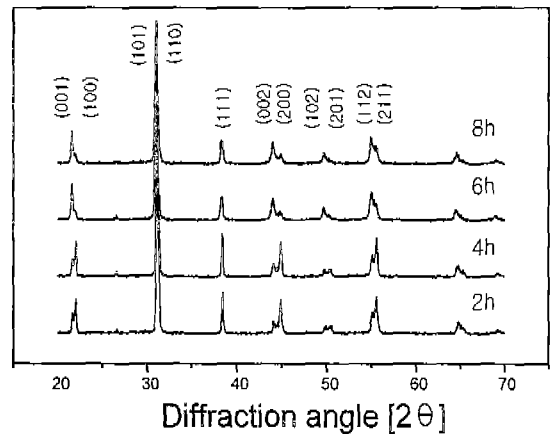

Fig. 3. X-ray diffraction patterns of the specimens with different milling time.
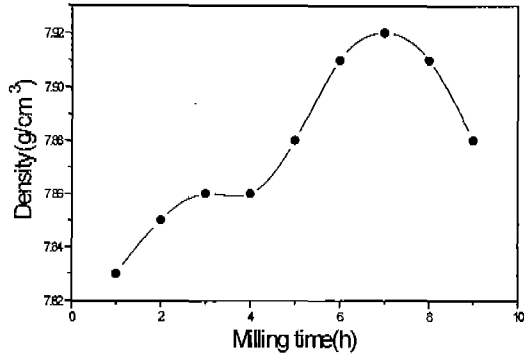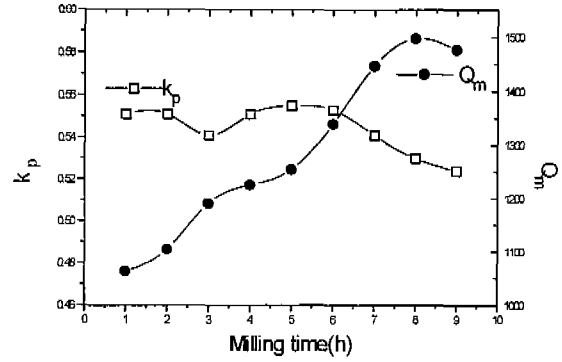
Fig. 4. Density as a function of milling time.

Fig. 6. Electromechanical coupling coefficient and mechanical quality factor with the variation of milling time.
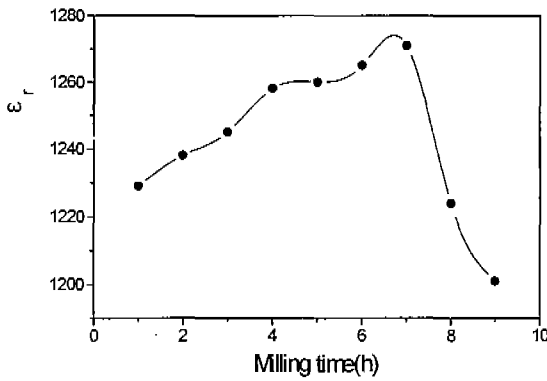
Table 1. Dielectric and piezoelectric properties of PSN-PMN-PZT ceramics.

Fig. 5. Variation in dielectric constant.

Sample No	Milling time[h]	ε r	Density [g/cm³]	Grain size [um]	k_p	Qm	TCFr [ppm/°C]
S1	1	1,229	7.83	1.49	0.551	1,063	38
S2	2	1,238	7.85	1.39	0.551	1,104	68
S3	3	1,245	7.86	1.38	0.540	1,190	62
S4	4	1,261	7.86	1.28	0.551	1,225	57
S5	5	1,260	7.88	1.12	0.555	1,254	63
S6	6	1,265	7.91	1.12	0.553	1,339	79
S7	7	1,271	7.92	1.13	0.541	1,446	83
S8	8	1,224	7.91	1.19	0.530	1,497	87
S9	9	1,201	7.88	1.21	0.524	1,476	95

Fig. 5 shows the variation of dielectric constant(ε_r). Up to 7h, the dielectric constant is proportional to the milling time. The trend is reversed after 7 hour milling as the density variation discussed above. The finer powders produced by the attrition milling result in gradual increase in density of compact, while removing

voids deteriorating piezoelectric and dielectric constants. On the other hand, decrease in ε_r can be related to
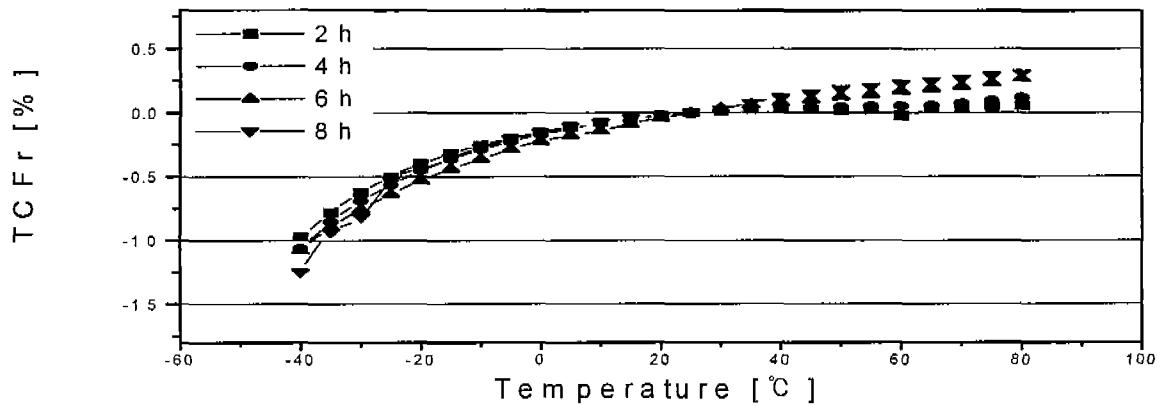

Fig. 7. Temperature coefficient of resonant frequency TCFr in ppm/°C at different attrition milling time.

Table   2. Comparison between 24h ball milling (A) and 7 h attrition milling (B) methods.

Sample No.	ε_r	Density [g/Cm³]	K_P	Q_m	Grain size[μm]	-20℃ ~80℃ [TCFr] (ppm/℃)
A	1217	7.73	0.540	941	1.48	37
B	1271	7.92	0.541	1446	1.13	83

exceeded amount of PbO vaporization from the material. This is also an indicative that the sintering temperature of 1275°C used in this study was too high to control PbO vaporization for the specimens, S8 and S9.

Fig.   6 shows k_p and Q_m. The highest k_p and Q_m were measured from the specimens S5 and S8, respectively. The variation of these parameters deviate from the normal relation that Q_m and k_p are proportional to the density. However, it may be regarded that the variation in Q_m follows such trend since the density difference between S7 and S8 was small. With regard to k_p, more investigation will be made.

The   Fig.   7 shows   the temperature coefficient of resonant frequency in the range of –20 and 80℃.   The coefficients were calculated based on the following equation.

$$TCf_r = [f_r(T℃) - f_r(25℃)] / [f_r(25℃)] \times 100(\%) \quad (2)$$

Where, $f_r(T℃)$ and $f_r(25℃)$ are the resonant frequencies at temperature of T and 25°C, respectively. As shown in the figure, the TCf_r was shifted to positive side as increasing milling time. This is due to the increase in tetragonality caused by the over-firing of the specimens of S7, S8 and S9. This suggests that lowering sintering temperature below 1275°C result in improvement of TCf_r stability. More investigation on the optimum sintering temperature for fine particles will be followed. All of the experimental data presented in the previous figures are summarized in Table 1.

In order to see the effects of the attrition milling on the properties concerned, the microstructural and piezpelectric properties are compared in Table 2.   The

data listed in the table are from another investigation on ball milling for 24 h in our laboratory and specimen S7 in this study. As can be seen, significant improvement in density, Q_m and grain size was achieved from the samples processed by attrition milling. Again, TCf_r close to zero is expected by reducing sintering temperature for the fine powders produced via attrition milling.

4. CONCLUSIONS

Microstructural,   dielectric   and   piezoelectric characteristics of $Pb(Sb_{1/2} Nb_{1/2})O_3$ - $Pb(Mn_{1/3} Nb_{2/3})O_3$ - $Pb(Zr,Ti)O_3$ ceramics produced by attrition milling were investigated. The results obtained from the experiment are as follows:

1. The particle size and grain size decreased as increasing milling time.
2. In general, ε_r, density and Q_m increased with milling time. The highest Q_m of 1,497 was obtained from the specimen milled for 8h.
3. The TCf_r was shifted to positive side with increasing milling time. TCf_r close to zero is expected by reducing sintering temperature.
4. The attrition milling process proved to be one of the effective routes to produce ceramics for transformer application.

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