Low temperature sintering of PZT ceramics without additives via an ordinal ceramic route

Hiroshi Maiwa
Department of Materials Science and Engineering, Shonan Institute of Technology, 1-1-25 Tsujido-Nishikaigan, Fujisawa, Kanagawa 251-8511, Japan
Osamu Kimura
Collaborative Research Center, Ashikaga Institute of Technology, 268-1 Omaecho, Ashikaga, Tochigi 326-8558, Japan
Kazuo Shoji
Department of Electrical and Electronic Engineering, Ashikaga Institute of Technology, 268-1 Omaecho, Ashikaga, Tochigi 326-8558, Japan
Hiroshi Ochiai
Labo Co.Ltd. 2754-1 Hayakawa, Ayase, Kanagawa 252-1123, Japan

Low temperature sintering of PZT ceramics without additives was investigated using a fine powder obtained by the ordinal ball milling process. The starting commercial PZT ceramic powder with the composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ of average grain size of 0.5 μm is effectively ground in a ball mill using zirconia balls of 3 mm in diameter in isopropyl alcohol containing an organic surfactant. Its particle size reaches less than 0.2 μm after 48 h grinding. It is dried, added with a PVB binder, pressed, and sintered in air for 2 h from 950°C to 1200 °C. The bulk density and dielectric constant of the PZT ceramics sintered at 1000 °C reach 7.85 g/cm^3 and 1566, respectively, sufficiently high for industrial applications. PZT ceramics sintered at 1000 °C and those sintered at 1100 °C exhibited the electromechanical coupling factors (kp) of 60% and 69%, respectively.

KEYWORDS
Sintering, Piezoelectric properties, PZT, Actuators,

1. Introduction

$Pb(Zr,Ti)O_3$, (PZT) is known to have excellent piezoelectric properties. In general, PZT ceramics is sintered above 1200°C.(1) Low temperature sintering of PZT ceramics has been required for co-firing with electrode metals having low melting points. In addition, it is desired for suppression of energy consumption accompanied by high temperature sintering and environmental pollution caused by volatilization of lead oxides from PZT ceramics. Hitherto, it has been reported that fine powders obtained via chemical routes such as a sol-gel process reveal good sinterability.(2) They are, however, expensive and unsuitable for mass-production due to the complicated processes required for the chemical processes. Some studies have been reported on the low temperature sintering of PZT by using sintering aids;(3,4) however, their electrical and electromechanical properties might be degraded by addition of sintering aids. This paper describes low temperature sintering of PZT ceramics without additives using a fine powder obtained by the ordinal ball milling process.

2. Experimental

The starting powder is the commercial PZT ceramic powder with the composition of $Pb(Zr_{0.52}Ti_{0.48})O_3$ (Sakai Chemicals PZT-LQ) of average grain size of 0.5 μm. It is effectively ground in a ball mill using zirconia balls of 3 mm in diameter in isopropyl alcohol containing an organic surfactant (Kusumoto Chemicals. Ltd.). It is dried, added with 1% of PVB binder, pressed in a die at a pressure of 80 MPa and sintered in air for 2 h from 950°C to 1200 °C. It is noted that sintering aids were not added. Sintered samples were polished, then electroded using silver paste. The specimens were poled at 100°C for 2□minutes under an electric field of 2.5-4.5MV/mm in silicon oil. The bulk densities of the specimens were determined by Archimedean principle. The dielectric constant was estimated from the value of the capacitance measured at 1kHz. The electromechanical coupling factor was calculated by the reasonance-antireasonance method using an impedance analyzer.

3. Results and discussion

Figure 1(a) and (b) show the scanning electron microscope (SEM) micrograph of the starting powder and the powder milled for 48h., respectively. As seen, the particle size of the starting powder is 0.5 μm and that of the ground powder decreases to less than 0.2 μm after 48h grinding. Their BET values are measured to be $1.8m^2/g$ and $4.8m^2/g$, respectively, also indicating that a fine pulverization is attained.

Figure 2 shows the bulk density of PZT ceramics as a function of sintering temperature. The bulk density of the PZT ceramics obtained by sintering the ground powder at 1075°C reached 7.92 g/cm^3. This is 99 % of theoretical density of PZT ceramics (8.002 g/cm^3 for $Pb(Zr_{0.517}Ti_{0.483})O_3$) and is sufficiently high for industrial applications. By using the ground powder, PZT ceramics sintered at 1000°C showed the bulk density of 7.85 g/cm^3, while, without grinding, the bulk density of the PZT sintered at 1000°C was 5.86 g/cm^3. The PZT ceramics exhibited maximum density in the sample sintered at 1075°C, and gradual decrease of the density with increasing of sintering temperature. This is probably due to lead oxides evaporation from the surface of the sample during high temperature sintering.

The dielectric constant and electromechanical coupling factor (kp) of PZT ceramics as a function of sintering temperature are shown in Figures 3 and 4, respectively. In the case of the ceramics from ground powder, the value of kp was over 60 % above 1000°C and reached its maximum of 68% at 1100°C. In the case of PZT ceramics without grinding process, the kp value was only 30% at 1025°C, which is half of that of the sample sintered at 1000°C using the ground powder. The maximum kp value of 68% is obtained at 1150°C. These behaviors correspond well to those of bulk densities, however, the behaviors of dielectric constant and electromechanical coupling factor were observed more temperature dependent than that of the bulk density. This indicates that dielectric constant and kp are more sensitive to the effect of grain growth and lead loss in the sample.

4. Conclusions

Low-temperature sintering of PZT ceramics without additives was attained via improvement of the grinding process. The commercial PZT powder could be effectively ground in a ball mill using zirconia balls of 3 mm in diameter in isopropyl alcohol containing an organic surfactant. Its particle size reached less than 0.2 μm after 48 h grinding. By using these powder, PZT ceramics with bulk density of 7.92 g/cm^3 and electromechanical coupling factors (kp) of 60%, could be obtained at a sintering temperature of 1000°C without using sintering aids. Here, we applied the grinding method to the commercial PZT; however, this process may be applied to other lead-containing perovskite piezoelectric ceramics leading to lower their process temperature. We believe that combination of the grinding method and composition modification or addition of sintering aids can reduce sintering temperature of lead-containing perovskite piezoelectric ceramics, resulting in the improvement of the performance of multilayer actuator and in the reduction of energy consumption and the decrease in pollution caused by lead oxides evaporation.

References

1. Buckner, D. A., and Wilcox, P. D., Effect of Calcining on Sintering of Lead Zirconate-Titanate Ceramics, Am. Ceram. Soc. Bull., 1972, **51**, 218-222.
2. Duran, P. and Moure, C., Sintering at Near Theoretical Density and Properties of PZT Ceramics Chemically Prepared, J. Mater. Sci. 1985, **20**, 827-835.
3. Ogawa, T., Sano, A., Senda, A., and Wakino, K., Jpn. J. Appl. Phys., 1989, **28**, 91-94.
4. Hayashi, T., Inoue, T., and Akiyama, Y., Low-Temperature Sintering and Properties of (Pb,Ba,Sr)(Zr,Ti,Sb)O_3 Piezoelectric Ceramics Using Sintering Aids, Jpn. J. Appl. Phys., 1999, **38**, 5549-5552.

Figure captions

Fig. 1 SEM micrographs of (a) the starting powder and (b) the powder milled for 48h.

Fig. 2 Bulk density of PZT ceramics as a function of sintering temperature.

Fig. 3 Dielectric constant of PZT ceramics as a function of sintering temperature.

Fig. 4 Electromechanical coupling factor (kp) of PZT ceramics as a function of sintering temperature.

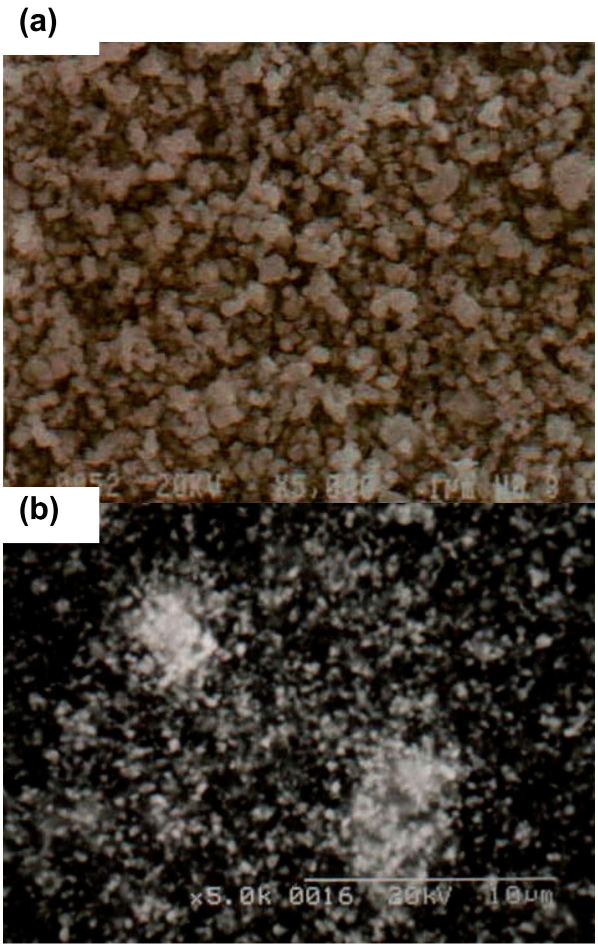

Fig. 1 H.Maiwa et al,

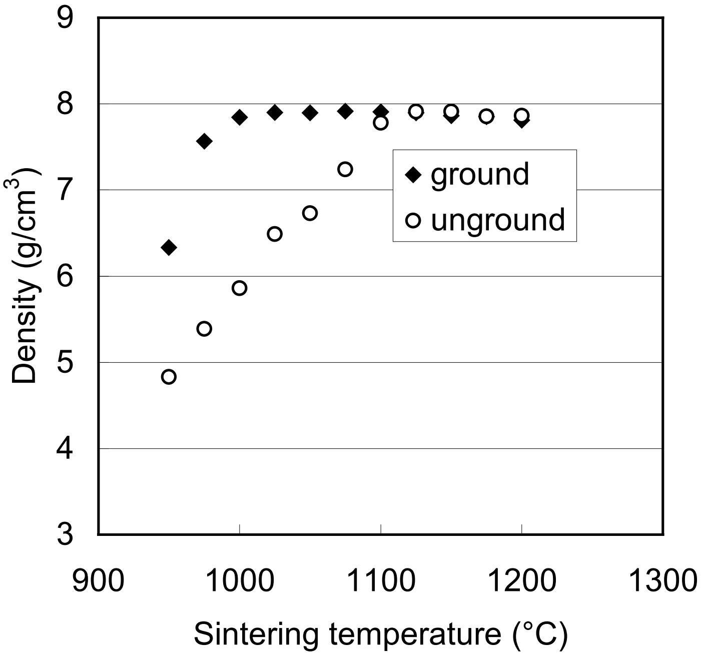

Fig. 2 H. Maiwa et al.

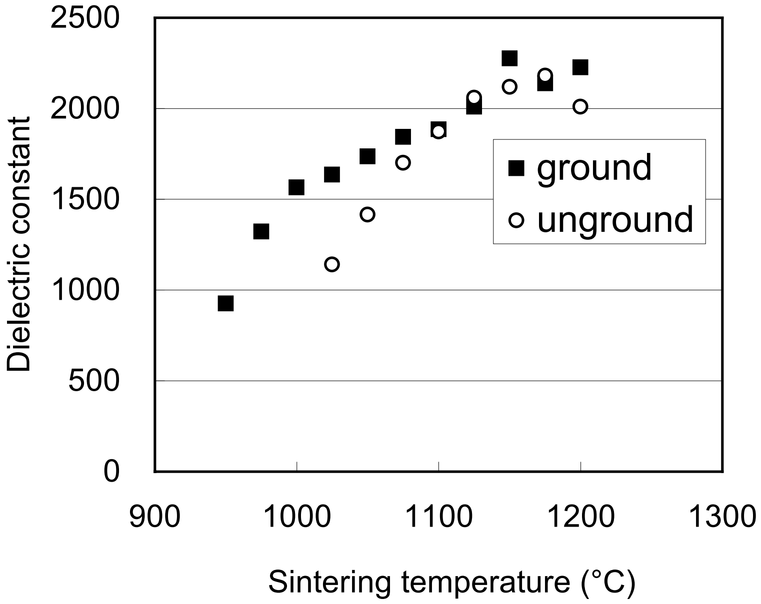

Fig. 3 H. Maiwa et al.

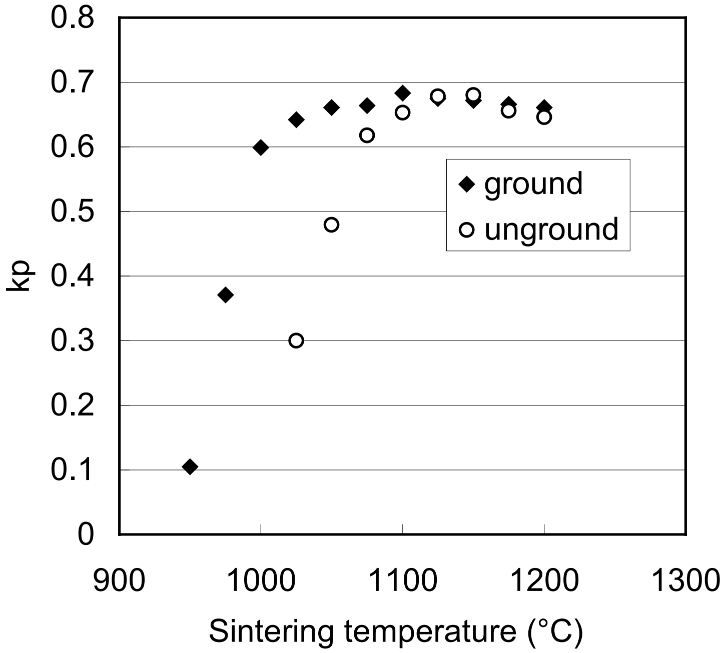

Fig. 4 H. Maiwa et al.

Abstract No.: **157**

Title: Low temperature sintering of PZT ceramics without additives via an ordinal ceramic route

---

Authors: **H. Maiwa, O. Kimura, S. Shoji and H. Ochiai**

Calculation:

Item:	Template:	Calculation:
Title:	60 + 20 x (no. of lines of text in title) + 20 x (no. of lines of authors) + 10 x (no. of lines of address)	230
Abstract:	+ 0.5 x (no. of words in abstract) + 40	111
Main Text:	+ 0.5 x (no. of words) + 20	435
Headings:	+ 20 x (no. of headings (excepted of abstract))	80
Figures:	+ (height figure 1 (in mm when 80 mm wide)+ 20) + (height figure 2 + 20) etc…. (NB: x 2 when table straddles 2 columns)	500
Tables:	+ (height table 1 [4 x no. of lines] + 30) + (height table 1 [4 x no. of lines] + 30) etc…. (NB: x 2 when figure straddles 2 columns)	0
Formulas:	+ 15 x (no. of formula)	
References:	+ 12 x (no. of references)	48
Total:	=	1404
No. of Pages:	**Total = no. of pages/470**	**2.99**