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

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Abstract

Low temperature sintering of PZT ceramics without additives was investigated using a fine powder obtained by the ordinary 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 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 ordinary 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 poly vinyl butyral (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 min under an electric field of 2.5–4.5 MV/mm in silicon oil. The bulk densities of the specimens were determined by Archimedean principle.

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The dielectric constant was estimated from the value of the capacitance measured at 1 kHz. The electromechanical coupling factor was calculated by the resonance–antiresonance method using an impedance analyzer.

3. Results and discussion

Fig. 1(a) and (b) show the scanning electron microscope (SEM) micrograph of the starting powder and the powder milled for 48 h, 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 48 h grinding. Their BET values are measured to be 1.8 m^2/g and 4.8 m^2/g, respectively, also indicating that a fine pulverization is attained.

Fig. 2(a)–(c) show the SEM micrograph of the ceramic sintered at 1000 °C, 1100 °C, and 1200 °C, respectively, using the ground powder. As seen, the grain size increases with increasing of the sintering temperature. Fig. 3 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 a gradual decrease of the density with increasing of sintering temperature. This is probably due to a lead oxide evaporation from the surface of the sample during high temperature sintering.

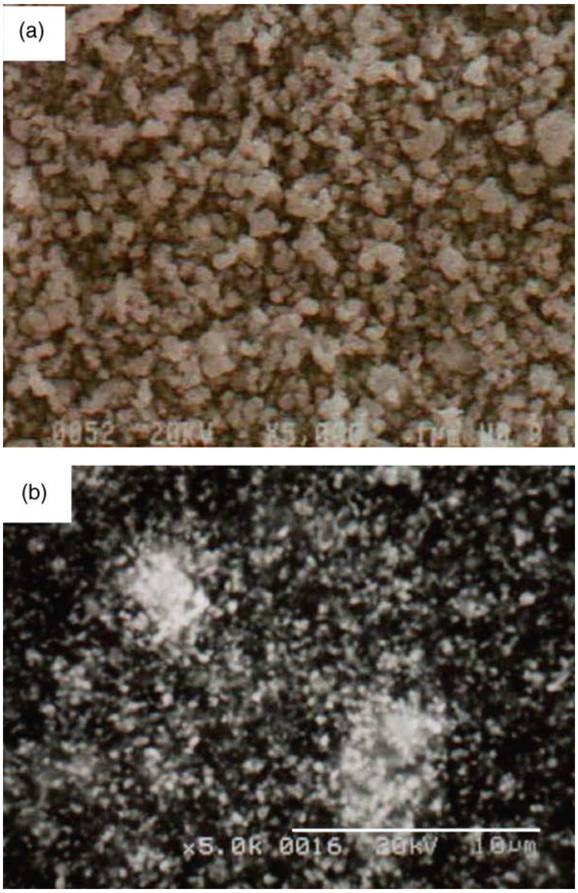

Fig. 1. SEM micrographs of (a) the starting powder and (b) the powder milled for 48 h.

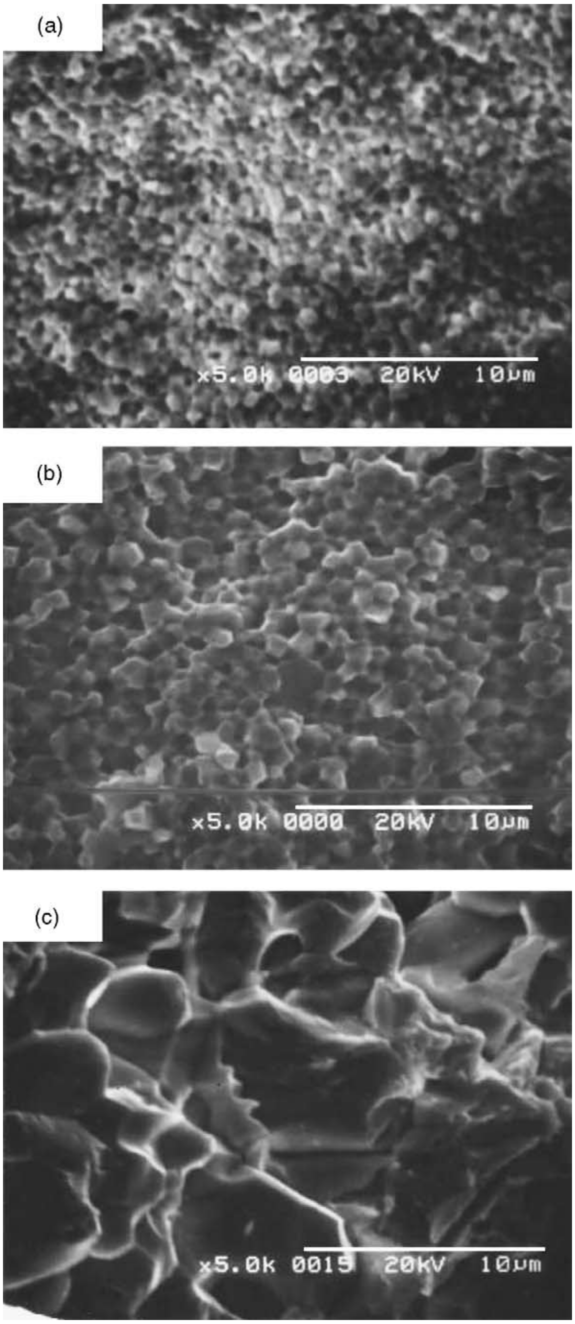

Fig. 2. SEM micrographs of PZT ceramics sintered at (a) 1000 °C, (b) 1100 °C and (c) 1200 °C, respectively.

The dielectric constant and electromechanical coupling factor (kp) of PZT ceramics as a function of sintering temperature are shown in Figs. 4 and 5, respectively. In the case of the

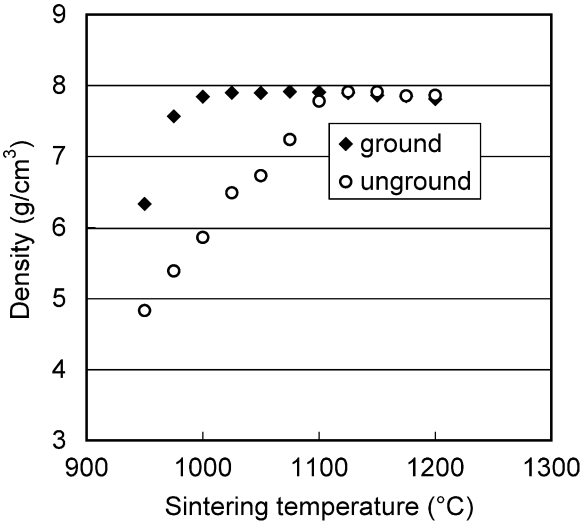

Fig. 3. Bulk density of PZT ceramics as a function of sintering temperature.

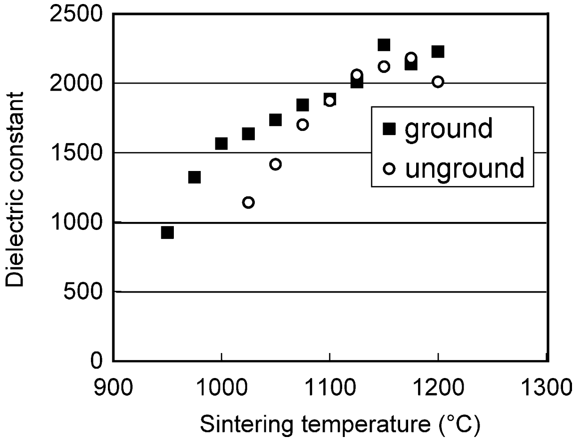

Fig. 4. Dielectric constant of PZT ceramics as a function of sintering temperature.

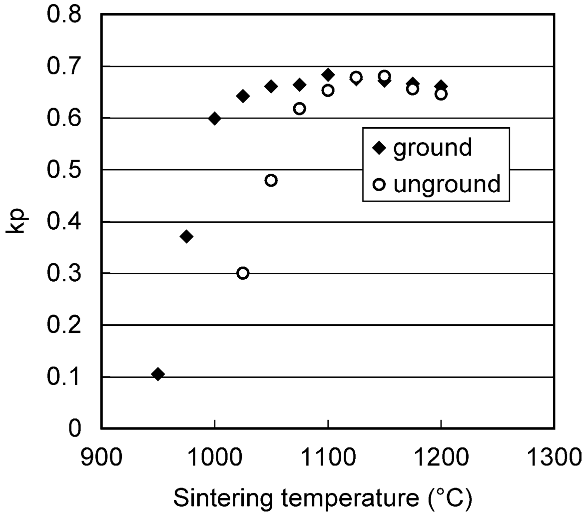

Fig. 5. Electromechanical coupling factor (kp) of PZT ceramics as a function of sintering temperature.

ceramics from ground powder, the value of kp was over 60% above 1000 °C and reached its maximum of 69% 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 have 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 a lead oxide evaporation.

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