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# PLZT ceramics from mechanically alloyed powder and their anomalous photovoltaic effect

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Piezoelectric ceramics that interchange electrical and mechanical energies have found increasing applications, such as electronic devices in printers, cameras and computers [1]. Among the piezoelectric ceramics, lanthanum-modified lead zirconia titanate (PLZT) ceramics are known as photostrictive piezoelectric ceramics, as they show deformation when illuminated [2]. Photostrictive actuators are wirelessly and remotely controllable, satisfying the recent tendency toward miniaturization and integration of electronic components. Compared with electrically driven piezoelectric actuators, photo-driven actuators have more attractive applications in the fields of microelectromechanical system (MEMS), optical communication and space technology. However, more work is needed to further increase the photo-induced strain to meet the requirements for the above applications.

It is generally recognized that PLZT ceramics exhibit a photostrictive effect because of the superposition of a photovoltaic effect and reversible piezoelectricity; light illumination generates a high electric voltage, known as the anomalous photovoltaic (APV) effect, resulting in displacement due to the coupled effect of reversible piezoelectricity [2]. Glass [3] and Brody [4] have shown theoretically that the APV effect can be enhanced by grain size refinement. In the present study, fine-grained PLZT ceramics that show an enhanced photovoltaic effect were successfully fabricated by pressureless sintering of oxide powders treated by mechanical alloying (MA). Mechanical alloying (MA) is a relatively new process first proposed by Benjamin [5], and it has been successfully employed to synthesize amorphous metal and intermetallic powders [6]. Recently, it was revealed that MA is also applicable to the synthesis of complex oxide powders from the constitutional oxides [7–9], and that MA-derived powder can be sintered at low temperature, resulting in effective refinement of microstructure in its sintered compact [10].

In the present study, the starting materials were commercially available $\beta$-PbO powder (average particle size: 3 $\mu$m, Wako Pure Chemical Industry, Ltd., Japan), $La_2O_3$ powder (average particle size: 3 $\mu$m, Kojundo Laboratory Co., Ltd., Japan), $ZrO_2$ powder (crystallite size: 22 nm, Tosoh Co., Ltd., Japan) and $TiO_2$ powder (average particle size: 1 $\mu$m, Wako Pure Chemical Industry, Ltd., Japan). These powders were mixed according to the weight ratio determined by the nominal composition of $(Pb_{0.97}La_{0.03})(Zr_{0.52}Ti_{0.48})O_3$, which was previously reported to be an optimal composition in the photorestrictive PLZT system [11]. The mixed powders were put into a $ZrO_2$-3 mass%$Y_2O_3$ (YTZ) ceramic jar with an inner diameter of 100 mm and a volume of 500 mL, with YTZ balls of 10 mm in diameter; and the weight ratio of powder to balls was 1:50. The MA was conducted using a planetary high-energy ball mill (Fritsch pulverisette 6) in an air atmosphere at a rotational speed of 300 rpm for various times. After the powder mixture was milled for the predetermined period, about 100 ml of ethanol solution was added to the jar and additional milling for 24 h at a low rotational speed (200 rpm) was conducted. The additional wet milling was conducted in the present study to pulverize strong agglomerates formed due to the high MA impact energy.

The milled powders were dried in air and then compacted under a pressure of 100 MPa by die pressing and cold isostatic pressing under 200 MPa. The powder compacts were sintered in an oxygen atmosphere in an $Al_2O_3$ crucible that contained a small amount of $PbZrO_3$ powder to produce an excess-PbO atmosphere. Several sintering conditions were chosen to prepare PLZT ceramics with various grain sizes.

X-ray diffractometry (XRD) with Cu-$K_\alpha$ radiation and scanning electron microscopy (SEM) were used for phase identification and microstructure characterization of the sintered bodies. For the SEM observation, polished surfaces of the sintered samples were heated at 1000 °C for 1 h to clearly show the grain boundaries by thermal etching. The average grain size was measured by the line intercept method using an image analyzer with an optical microscope.

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The as-sintered specimens were cut to a thin disk of 12 mm diameter and 1 mm thick. Silver paste was printed on both surfaces of the disk specimens and baked at 700 °C to form electrodes. Then, the specimens were polarized under an electric field of $2 \times 10^6$ $\mathrm{Vm^{-1}}$ for 1.8 ks in a bath of silicone oil at 120 °C. The piezoelectric and dielectric constants of the disk specimens were measured using an impedance analyzer (Hewlett-Packard: 4129A). Thin square samples with dimensions of $5 \times 5 \times 0.5\ \mathrm{mm^3}$ were prepared from the sintered specimens to measure the photovoltaic property. One $5 \times 5\ \mathrm{mm^2}$ surface was polished to a mirror surface finish using a diamond paste with 1 $\mu$m particles, and two $5 \times 0.5\ \mathrm{mm^2}$ ends were coated with silver paste. Poling was conducted by applying an electrical field to the two silver-paste ends under the same condition as described above.

Photo-induced voltage and current were measured according to the procedure proposed by Uchino *et al.* [11, 12] The photocurrent was measured using a high-input-impedance electrometer (Keithley Model 485) by applying voltages from −500 V to +500 V. During the measurement, UV light with a wavelength of 365 nm and an intensity of 76 $\mathrm{mWcm^{-2}}$ illuminated only the polished surface using a high-pressure mercury lump.

As shown in Fig. 1, the XRD analysis confirmed that a PLZT solid solution powder was synthesized mechanochemically from the constitutent oxides. The diffraction peaks of the starting powders (Fig. 1a) disappeared when subjected to mechanical alloying for 40 h, and consequently some broad peaks corresponding to perovskite phase were detected, as shown in Fig. 1b. The broadening of the XRD peaks of the MA-derived PLZT powder were due to refinement of the particle size and high residual strain induced by MA. The XRD pattern became more sharp and distinctive after sintering, as shown in Fig. 1c, suggesting the formation of a single-phase perovskite structure.

The MA-derived PLZT powder was sintered to high density at relatively low temperatures. As shown in Table I, the sintered density is 7.84 g/cm$^3$ at 1100 °C even without any sintering additives, which is 98% of the theoretical density (nearly 8.0 g/cm$^3$). This sintering temperature is at least 100 °C lower than that for PLZT powder prepared by conventional oxide mixing process. The sintered PLZT ceramics showed dense microstructures with well-developed grain geometry even for the sample sintered at 1100 °C, as can be seen in Fig. 2. The present MA-derived PLZT powder showed high sinterability resulting from its fine particle size or high specific surface area, and MA-induced residual strain might also contribute to the reduction in sintering temperature.

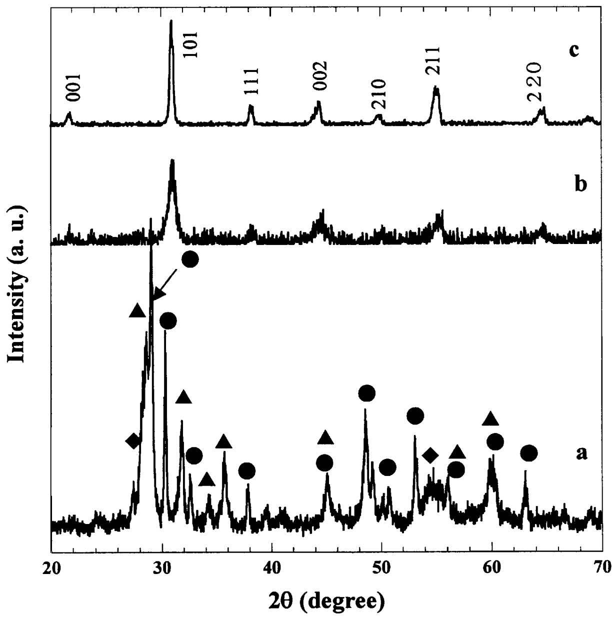

*Figure 1* XRD patterns of (a) starting powders, (b) mechanically alloyed powders and (c) sintered body prepared at 1100 °C for 1 h. The upper numbers are the diffraction indexes of perovskite phase. The symbols indicate the peaks for PbO (circle), $\mathrm{TiO_2}$ (diamond), and $\mathrm{ZrO_2}$ (triangle).

Fig. 3 shows the photovoltage of the PLZT ceramics as a function of grain size. As the average grain diameter was reduced from 4.1 to 1.1 $\mu$m, the photovoltage was raised from 800 to 2860 V/cm, which is fairly high compared with reported data. For example, the photovoltage of PLZT ceramics fabricated by conventional oxide mixing process is about 700 V/cm, when the average grain diameter is about 2.2 $\mu$m [13]. Poosanaas *et al.* increased the photovoltage of PLZT up to 1600 V/cm by doping with oxides such as 1.0 at% $\mathrm{Nb_2O_5}$ or 0.5 at% $\mathrm{WO_3}$, for which the grain diameter was also reduced to 1.4–1.7 $\mu$m [13]. Compared with their results, it is clear that the photovoltage obtained in the present study is extremely high, and the photovoltage is increased purely due to the reduction of grain size because no other oxides and sintering additives were added to the PLZT powder in the present study. As shown in Fig. 4, the experimental data can be well fitted to the following relationship between photovoltage ($E_{\mathrm{ph}}$) and grain diameter ($d$):

$$E_{\mathrm{ph}} = 0.044 + 3.081/d \qquad (1)$$

This experimental finding is in a good agreement with the theory by Brody [4], which predicts a proportional

TABLE I Density, grain size, piezoelectric and dielectric constants of the PLZT ceramics sintered under various conditions

| Sintering condition | | | | | |
|---|---|---|---|---|---|
| Temperature (°C) | Time (h) | Bulk density (g/cm$^3$) | Average grain diameter ($\mu$m) | Piezoelectric constant, $d_{33}$ ($0^{-12}$ m/V) | Relative dielectric constant ($\varepsilon_{33}\ T/\varepsilon_0$) |
| 1200 | 8 | 7.82 | 4.1 | 295.6 | 788 |
| 1200 | 1 | 7.89 | 2.7 | 330.3 | 916 |
| 1150 | 8 | 7.83 | 2.5 | 380.9 | 1150 |
| 1100 | 8 | 7.84 | 1.1 | 332.8 | 849 |

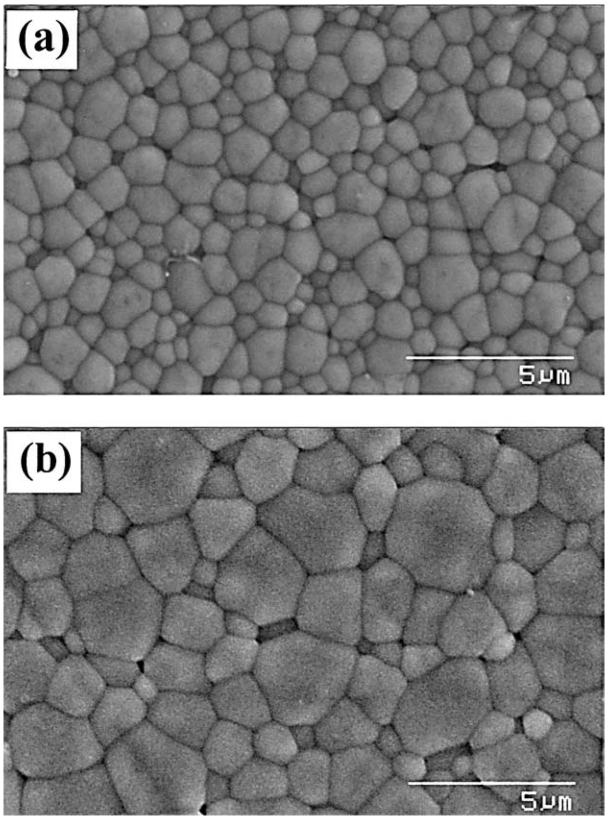

*Figure 2* Representative SEM micrographs of the PLZT ceramics sintered under two selected conditions to produce the smallest and largest grain sizes: (a) at 1100 °C for 8 h and (b) at 1200 °C for 8 h.

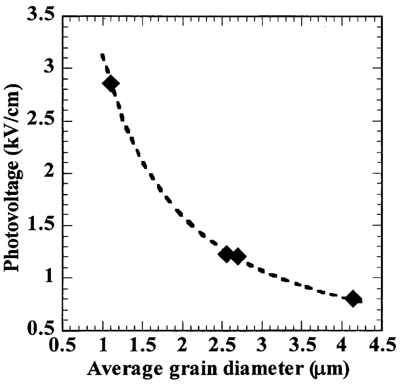

*Figure 3* Change in photovoltage of the PLZT ceramics as a function of average grain size. The symbols are experimental data and the dotted line is the fitted curve.

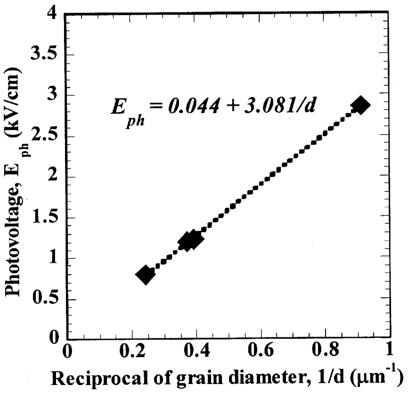

*Figure 4* Linear relationship between photovoltage and reciprocal of grain diameter. Note that the experimental data are well fitted to the dotted line expressed by the equation shown in the figure.

relationship between photovoltage and grain number. For a fixed volume, grain diameter and grain number are inversely proportional.

As summarized in Table I, the piezoelectric and dielectric constants are less dependent on the grain sizes within the investigated range. However, both constants tend to decrease when the average grain diameter is smaller than 2 $\mu$m. This is acceptable because the domain wall movement becomes more restrained near the grain boundary with decreasing grain size. High piezoelectric and low dielectric constants are favorable for the applications of photo-driven actuators.

Photo-induced strain is the product of photovoltage ($E_{\mathrm{ph}}$) and piezoelectric constant ($d_{33}$). By using the above experimental data, it is estimated that the sample with an average grain size of 1.1 $\mu$m can generate a photo-induced strain of approximate $8.5 \times 10^{-5}$, whereas the reported maximum photo-induced strain of PLZT ceramics is about $3.5 \times 10^{-5}$ [13]. Although the present study was focused on the grain size effect, it is believed that the photo-induced strain property can be further improved by optimal compositional design in the PLZT system and doping with other oxides. Additionally, it will be very interesting to investigate the photo-induced strain property when the grain size is further reduced to the submicron range. It is likely that PLZT ceramics with nanometer grains may exhibit significantly high photovoltages. However, piezoelectric constants cannot be kept high if the microstructure is too fine. Therefore, there may exist an optimum microstructural design for the highest photorestrictive strain in the PLZT ceramics.

In conclusion, a single-phase fine-grained PLZT powder was directly synthesized from the constituent oxides at ambient temperature through mechanochemical high-energy milling. The powder can be sintered to give dense PLZT bulk samples with fine-grained microstructures at reduced sintering temperatures. The photovoltage ($E_{\mathrm{ph}}$) of the sintered PLZT ceramics increases in an inverse proportion to grain diameter ($d$), in good agreement with existing theory. The maximum photovoltage is 2800 V/cm at an average grain diameter of 1.1 $\mu$m. Thus, mechanical alloying is an effective method to develop PLZT ceramics with enhanced photorestrictive properties.

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