Synthesis of PLZT Ceramics by the Coprecipitation Method and the Effects of Grinding on Synthesis and Sintering Behavior of Powders

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共沈法による PLZT の合成と微粉碎処理の影響

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PLZT((Pb, La)(Zr, Ti)O₃) ceramics was synthesized by the coprecipitation method using nitrates and ammonia. Dehydration was promoted by replacement with butanol and ethanol to prevent the aggregation of primary particles. Precursor gel consisted of well dispersed particles less than 10 nm was obtained by replacement with butanol. A powder treated in butanol and calcined at 500°C for 2 h was sintered to full density at 1150°C for 6 h. Transparency of sintered body was related to its porosity. The sintered body obtained at 1200°C for 20 h showed the transmittance of 20%. Mechanochemical effects on the synthesis and pulverization of PLZT ceramics were also examined. Grinding of the precursor gel powder promoted mechanochemical reaction. Grinding of calcined powders caused the decrease in the crystallinity. Sinterability was reduced by grinding, but annealing of calcined and ground powder recovered the original sinterability.

Key-words : PLZT, Coprecipitation, Gel, Transparency, Grinding, Mechanochemical effect, Sinterability

1. Introduction

PLZT ceramics has been studied for the application to electro-optic devices such as optical shutters, displays and so on.¹⁾ It must have the high transparency and electro-optic birefringence.²⁾

The preparation of fine powder is a key to obtain dense sintered body which is expected to have high transparency.

The chemical coprecipitation and the alkoxide method have been used for the synthesis of ultrafine powders required for enhancing the sinterability in normal sintering.³⁾⁻⁵⁾ Tsurumi et al.⁶⁾ evaluated the relation between the agglomeration of powder and its sinterability, and reported that the weak agglomeration of particles by replacing water with acetone and the addition of electrolytes enhanced the sinterability. In the previous work, we succeeded the synthesis of ultrafine PbTiO₃ powder by the chemical coprecipitation and replacement using butanol.⁷⁾

On the other hand, grinding of precursor or crystal-

lized powder affects the character of powder which relates closely to the sinterability. We have investigated the grinding effects on the sinterability of multi-component oxide ceramics such as cordierite.⁸⁾

In this paper, the synthesis of PLZT fine powder by the coprecipitation followed by the butanol replacement, and grinding of precursor gel and calcined powder were investigated.

2. Experimental

The chemical composition of PLZT was set to (Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})_{0.98}O₃. TiCl₄ was used as source of TiO₂. A certain amount of TiCl₄ was mixed with Zr-oxychloride solution. Zr, Ti-hydroxide was coprecipitated by ammonium water above pH 9. This coprecipitated hydroxide was washed by distilled water to eliminate Cl ion and dissolved in nitric acid. Certain amounts of La₂O₃ and Pb(NO₃)₂ were dissolved into nitric acidic water and mixed with Zr, Ti-solution. Finally, (Zr, Ti, Pb, La) (OH)_x coprecipitation was obtained by adding ammonium water. This coprecipitate was washed to eliminate nitric acid and ammonium ion, and was mixed with *n*-butanol. The mixture was dehydrated by azeotropic distillation at 110°C (abbreviated to BuOH-replaced). On the other hand, the coprecipitated gel was filtered and then washed by ethanol at room temperature to eliminate water in the gel as the simple replacement process (abbreviated to EtOH-replaced). The gel was dried at 150°C and turned into the precursor gel.

The precursor gel was calcined at 500°C for 2 h and crystallized to PLZT with the intermediate phase (PbO). This calcined powder was formed as a compact by cold isostatic pressing of 200 MPa and sintered at 1100-1300°C for 6-20 h with PbZrO₃ powder in oxygen flow.

On the other hand, the precursor gel and calcined powder were ground before sintering for 12 h, 36 h, or 216 h in the case of the precursor gel, and 50 h, 100 h or 200 h in the case of the calcined powder, respectively. Powders were ground in anhydrous

ethanol with a media agitating mill of which pot, shaft and media (2 mm ϕ diameter) were made of zirconia. The rotation speed of shaft was 230 r.p.m..

Crystalline phases of powder and sintered body were examined by the X-ray diffraction method. Morphologies of powder and microstructure of sintered body were observed by SEM and TEM. The chemical composition of powder was measured by the analytical electron microscopy (AEM) using EDS micro-region analysis (diameter of about 80 nm). Bulk density and porosity of sintered bodies were measured by the Archimedes method on the assumption of the theoretical density of 7.87 g/cm³ for PLZT and pore area measured in SEM photographs. Transparency of sintered body was measured by a spectrophotometer in the range of wave length for 340–650 nm.

3. Results and discussion

3.1 Characterization of PLZT powder and their sinterability

X-ray diffraction patterns of as-dried precursor gel powders and calcined powders are shown in Fig. 1. Precursor gels are in amorphous state (BuOH-replaced) and weak peaks of $\text{Pb}(\text{NO}_3)_2$ exist (EtOH-replaced). BuOH-replaced powder showed the possibility of the conversion from hydroxide to oxide which was suggested by DTA-TG analysis of the gel. No endothermic peak with weight loss during dehydration was observed in the BuOH-replaced gel, which was observed in non-replaced gel. After calcination, PLZT peaks are recognized with broad PbO peaks as the intermediate phase in BuOH-replaced powder and EtOH-replaced powder. Sintered bodies obtained from these powders consist of the single phase of PLZT (Fig. 1(C)).

Fig. 1. X-ray diffraction patterns of as-dried and calcined (at 500°C for 2 h) powders of BuOH-replaced (A) and EtOH-replaced (B), and sintered bodies (C).

Morphology of each powder shows difference in BuOH-replaced and EtOH-replaced powders (Fig. 2). Precursor gels in both cases exhibit a slight difference in the particle size and the state of aggregation. The BuOH-replaced powder is more finer and dispersed. Calcined powder of the EtOH-replaced gel shows the hard aggregation whereas the weak aggregation was observed in the case of BuOH-replaced gels. Butanol plays a role in dispersing the primary particles through replacement and dehydration process. The dehydration was promoted by azeotropic distillation, which was possible in the case of butanol use. So the aggregation of resulting powder was suppressed.

TEM observation supports this result (Fig. 3). Precursor gel powders consist of aggregation of primary particles with less than 10 nm (BuOH-replaced) and in the range of 10 nm to 20 nm (EtOH-replaced) in primary particle size. After calcination, the particle size increases to 10–30 nm in

Fig. 2. SEM photographs of powders as-dried (a), calcined at 500°C for 2 h (c) of BuOH-replaced, and as-dried (b), calcined at 500°C for 2 h (d) of EtOH-replaced.

Fig. 3. TEM photographs of as-dried (a) and calcined (c) powders of BuOH-replaced, and as-dried (b) and calcined (d) powders of EtOH-replaced.

both cases and tightly aggregate each other in the EtOH-replaced powder. Composition of each powder is shown in Fig. 4. The BuOH-replaced powder shows the uniform distribution of elements in precursor gel, whereas EtOH-replaced powder shows the significantly heterogeneous distribution of elements. After calcining, both powders reveal the homogeneous distribution of elements, which indicate the occurrence of the atomic diffusion through heat treatment.

The sinterabilities of BuOH-replaced and EtOH-replaced powders are significantly different. A compacted body sintered to nearly the theoretical density at 1150°C for 6 h in the case of BuOH-replaced, whereas the EtOH-replaced powder required to sinter above 1200°C. This result agrees with the result by Tsurumi et al., who revealed the relationship between the aggregation of raw powder and sintered density. BuOH-replaced powder was improved in aggregation state and particle size. The relationship between porosity of each sintered body and sintering temperature is in accord with that of relative density (Fig. 5). But small amount of pore remains in the sintered body which was densified to nearly theoretical density.

The transparency of sintered bodies sintered by using BuOH-replaced and EtOH-replaced powders are shown in Fig. 6. Higher temperature and prolonged sintering time are effective to reach higher transparency, but the obtained value (about 20%) is low.

Fig. 4. Composition of each part of powders as-dried of BuOH-replaced (A), of EtOH-replaced (B) and calcined of both cases (C). Composition is indicated as a molar ratio in (Pb+La)-Zr-Ti triangle diagram.

Fig. 5. Relationship between porosity and sintering temperature for sintered bodies of BuOH-replaced and EtOH-replaced. Sintering time was 6 h for each sintering temperature.

Fig. 6. Relationship between transparency and wavelength for each sintered bodies (thickness 0.5 mm); BuOH-replaced for (a) sintered at 1200°C for 20 h, (b) sintered at 1200°C for 6 h, (c) sintered at 1150°C for 6 h and (d) EtOH-replaced for sintered at 1300°C for 6 h.

Fig. 7. Sintered body of BuOH-replaced and sintered at 1200°C for 20 h (thickness 0.5 mm) (a) and SEM photograph of polished and chemical etched surface (b).

er than that of previous works by the hot pressing and other methods. The light scattering behavior may be one of reasons explaining this result. Sintered body obtained from EtOH-replaced powder showed the lower transmittance value which reflects the low sinterability. Microstructure of sintered body sintered at 1200°C for 20 h by using BuOH-replaced powder consists of grains of about 5 μm in average size with the highest transparency (Fig. 7). Sintering at 1150°C for 6 h resulted in the decrease of grain size to less than 3 μm in densified sintered body. So, the improvement of powder characters in particle size and aggregation could enhance the sintering behavior of powder.

3.2 Grinding effects on synthesis and sinterability of PLZT

Figure 8(A) shows X-ray diffraction patterns of the precursor gel powder of no-grinding and ground for 4 h to 216 h. A starting powder was amorphous and the short time (4–12 h) grinding causes crystallization of $\text{Pb}(\text{NO}_3)_2$ as the same case of the EtOH-replaced powder. Through prolonged grinding time, the amount of this phase decreased. This phase was mechanochemically synthesized of Pb with residual NO_3 in precursor gel. Calcination of these ground powders caused the different crystalline phase assemblages. The intermediate phase in powders after heat treatment is assigned as PbO and the relative peak height to PLZT decreases with the increase of

Fig. 8. X-ray diffraction patterns of as-dried and ground precursor gel powders for each grinding time (A), of ground-annealed powders for each grinding time (annealing at 500°C for 2 h) (A') and of calcined-ground powders (B).

Fig. 9. SEM photographs of the precursor gel powders ground for 12 h (a) and of the calcined (at 500°C for 2 h)-ground powder ground for 50 h (b).

$\text{Pb}(\text{NO}_3)_2$ for shorter grinding time (Fig. 8(A')). These results indicated that the segregation in the precursor gel occurred in short time grinding, and reduced during prolonged grinding. Grinding promoted the release of residual NO_3 from gel and the synthesis of segregating phase particularly in its earlier stage. This segregation caused the heterogeneous distribution of elements in powders, but it promoted the synthesis of PLZT. Thus, some kinds of the activation process through heat treatment or the promotion of crystallization of PLZT through the genesis of nitric precursor must be accompanied.

On the other hand, grinding of the calcined powder degrades only the crystallinity of PLZT and PbO (Fig. 8(B)).

Morphology of ground powders (Fig. 9) shows the accelerated aggregation of precursor particles by grinding, whereas no significant effect is recognized on calcined powder. Grinding of the precursor gel promoted the aggregation and a little increase of particle size rather than the reduction of primary particle size.

Grinding of the precursor gel for 12 h caused the heterogeneity of composition on parts of powder. Significant phase separation for Pb component is revealed by the EDS analysis (Fig. 10(A)) and X-ray diffraction patterns (Fig. 8(A)). On the other hand, grinding time of calcined powder causes no effect on the powder composition (Fig. 10(B)).

Figure 11 shows the relationship between bulk density and grinding time for the sintered bodies obtained by the sintering (at 1150°C for 6 h) of the ground powders of precursor gel and calcined powder, and calcined-ground-annealed (at 400°C for 2 h) powder. Grinding of precursor gel and calcined powder results in the degradation of sinterability. In the case of the precursor gel, this degradation was consi-

Fig. 10. Composition of each part of ground powders of precursor gel (A) and calcined-ground powders (B) as the molar ratio in (Pb+La)-Zr-Ti triangle diagram.

Fig. 11. Relationship between bulk density and grinding time for sintered bodies (sintered at 1150°C for 6 h) obtained by gel-ground (A) and calcined-ground (B) (and annealed (C)) processes.

dered to be derived from the heterogeneous distribution of elements or aggregation of particles. The reason of degradation of sinterability on calcined powder was considered to base on the accumulated crys-

tal strain, which sometimes promoted the atom diffusion in the initial stage of sintering and ended up the degradation of final sintered density.⁹⁾ After releasing of the strain by annealing, the powder recovers its sinterability. These sintering behaviors were consistent with the transparency of each sintered body.

4. Conclusions

(1) Ultrafine (less than 10 nm of particle size) powders of PLZT were synthesized by the coprecipitation as the hydroxide and the subsequent dehydration through the azeotropic distillation by butanol replacement.

(2) Butanol replacement had advantages of the particle size reduction, the homogeneous distribution of elements and weak aggregation of particles. Sintered body densified at 1150°C for 6 h and optimum transmittance was 20% (sintered at 1200°C for 20 h). Transparency of the sintered body was affected by the residual pore.

(3) The short time grinding of gel caused the phase separation of Pb by the reaction with residual NO₃ and the heterogeneous distribution of components even in parts of powder. Grinding promoted the aggregation and ended up the degradation of sinterability.

(4) Grinding of calcined powder affected the degrading of sinterability, but it was recovered by annealing of the ground powder.

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