

Fabrication of ZnO ceramics using ZnO/Al₂O₃ nanocomposite particles prepared by mechanical treatment

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Nanocomposite particles of Al₂O₃-doped ZnO prepared by mechanical treatment were used for fabricating ZnO ceramics. TEM observations revealed that Al₂O₃ nanoparticles uniformly existed on a ZnO particle. The sintering body fabricated using the composite powder prepared by this mechanical treatment process had more uniform and finer microstructures than that fabricated using the powder mixture prepared by conventional wet mixing. The ZnO ceramics prepared by the mechanical treatment exhibited higher electrical conductivity than those prepared by the conventional wet ball milling process.

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1. Introduction

ZnO is a typical n-type semiconductor; many researchers have studied the electrical properties of ZnO ceramics for many years. Because of the advantages offered by the particular properties of ZnO ceramics, they have been used to manufacture varistors,¹⁾ sensors,²⁾ thermoelectric traducers,³⁾ transparent conductive films,⁴⁾ light emitting diodes,⁵⁾ etc. The electrical properties of ZnO ceramics are controlled by adding small additives. For example, it has been reported that Cr₂O₃, CoO, MnO, Bi₂O₃, and Pr₆O₁₁ additives exhibit a nonlinearity of electrical conductivity.^{6,7)} In addition, because Al₂O₃ dissolves in ZnO, the carrier concentration can be controlled (controlled valency); therefore, Al₂O₃-doped ZnO improves electrical conductivity.^{8,9)}

Many researchers have fabricated ZnO ceramics by a solid reaction; here, the powder used for the fabrication is usually mixed by a ball milling technique. The homogeneous dispersion of additives is one of the most important processes in powder processing; this process results in the production of better ZnO ceramics. The homogeneous mixing of additives can be better achieved by using nanoparticles rather than large particles as the raw material. However, the use of the wet milling process with liquid dispersion media such as water and ethanol might lead to reagglomeration of nanoparticles during drying. Consequently, the amount of mixed material obtained might not be sufficient to take advantage of the characteristics of nanoparticles. Therefore, we have focused on the fabrication of ceramics by mechanical treatment, in which nanoparticles are mixed only by the dry mixing process. By using this mechanical treatment process, we can obtain nanocomposite particles; in this process, nanoparticles are bonded to submicron particles by applying an external mechanical force, especially shear force.¹⁰⁾

For example, we have reported the direct bonding of TiO₂ par-

ticles to Si₃N₄ particle by mechanical treatment, and it is possible to fabricate nanoparticle-dispersed Si₃N₄ ceramics.¹¹⁾ It has also been confirmed that the mechanical treatment process improves the properties of ceramics manufactured using other materials.¹²⁾ In this study, we developed Al₂O₃-doped ZnO ceramics using nanocomposite particles composed of γ -Al₂O₃ nanoparticles and ZnO submicron particles prepared by mechanical treatment and investigated the effect of the mixing process on the electrical conductivity of ZnO ceramics.

2. Experimental procedure

2.1 Sample preparation

ZnO powder (grain size: 0.2–0.6 μ m, JIS 1, Hakusui Tech Co., Ltd.) and γ -Al₂O₃ powder (grain size: 7 nm, TM-300, Taimei Chemicals Co., Ltd.) were used in this study. The amount of γ -Al₂O₃ used was 0.1, 1.0, and 3.7 mol%. These powders were pre-mixed for 30 min by dry ball milling. Milling was carried out using Al₂O₃ balls of ϕ 10 mm. The premixed powder was mechanically treated for 10 min using a powder composer (Nobilta NOB-130, Hosokawa Micron Co.) working at 2000 rpm for 10 min to prepare composite powders. In this process, share force is applied to the particles by rotating blades at high speed to form nanocomposite particles in the same way as Ref. 11. For reference, raw material powders of the same compositions were prepared by carrying out wet ball milling in ethanol using Al₂O₃ balls of ϕ 10 mm for 24 h.

In order to fabricate granules, paraffin (4 mass%, melting point: 46–48°C, Junsei Chemical Co., Ltd.), dioctyl phthalate (DOP, 2 mass%, Wako Pure Chemical Industries, Ltd.), and cyclohexane (S grade, Wako Pure Chemical Industries, Ltd.) were added to these mixed powders followed by sieving the powder mixture using a 250 μ m-mesh nylon sieve. They were then molded into cylindrical pellets by uniaxial pressing at 50 MPa followed by cold isostatic pressing at 200 MPa. After the binder was burned out in air at 500°C for 3 h, the green bodies were

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fired at 1400°C in air for 2 h.

2.2 Characterization of composite particles and sintered bodies

The mechanically treated powders were observed using a transmission electron microscope (TEM, JEM-3000F, JEOL Ltd.), and their specific surface area were measured by the BET method using a surface area analyzer (Quantasorb, Quantachrome Instruments, USA). The microstructure of the ZnO ceramics was observed using the TEM. After thermal etching at a temperature of 1250°C, the etched surfaces of the ZnO ceramics were observed by using a scanning electron microscope (SEM, JSM-5200, JEOL Ltd.) and the average grain size was estimated by the linear intercept method.¹³⁾ Their densities were measured by the Archimedes method. The electrical conductivity of the ceramics was measured by the four-terminal method; these samples were cut into cuboids. The electrical conductivity was calculated by using the following equation:

$$\sigma = \frac{1}{\rho} = \frac{I}{E} \cdot \frac{l}{S} \quad (1)$$

where σ is the electrical conductivity, ρ is the electrical resistance, I is the current, E is the voltage, l is the length between the internal electrodes, and S is the cross-sectional area.

3. Results and discussions

3.1 Characterization of composite particles

Figure 1 shows the TEM images of the ZnO–Al₂O₃ powder mixture after the mechanical treatment (Figs. 1(A) and (B)) and wet ball milling (Figs. 1(C) and (D)). Figures. 1(B) and (D) are enlarged TEM photographs. The angular and dark pieces of grains shown in Figs. 1(A) and (C) represent the ZnO grains. Smaller particles existed on the surface of a ZnO particle in Fig. 1(A). Figure 1(B) shows that the size of the smaller particles on the ZnO particles was less than 10 nm, which was the almost similar to that of γ -Al₂O₃ used in this study. Therefore, it appears that the γ -Al₂O₃ nanoparticles were directly bonded to ZnO particles. On the other hand, a big agglomerate formation of γ -Al₂O₃ was observed after wet ball milling (Fig. 1(C)), and it was concluded that γ -Al₂O₃ nanoparticles were not directly bonded to the ZnO particle (Fig. 1(D)).

Figure 2 shows the XRD profiles of the ZnO–Al₂O₃ powder

before and after the mechanical treatment; and the figure also shows the raw materials used. The characterization of the composite powder was carried out by X-ray diffraction using Cu K α radiation. It was observed that the phases present of the composite powder consisted of only ZnO and γ -Al₂O₃, which was the same as the raw materials. Therefore, we inferred that γ -Al₂O₃ bonded to the ZnO grain surface because of the mechanical treatment. Abe et al. reported the formation of SiO₂ inter-nanoparticle bonds and the mechanical process used for fabricating the SiO₂ nanoparticles and SiO₂ fiber composites.¹²⁾ Tatami et al. reported that TiO₂ nanoparticles directly bonded to submicron Si₃N₄ particles because of the mechanical treatment.¹¹⁾ In this experiment, we were also able to establish the phenomenon reported above. Nogi et al. estimated the temperature at the particle interface in shear fields.¹⁴⁾ To apply these results to our study, the temperature of the particle interface must be maintained below 700°C. It is known that sintering shrinkage of ZnO starts at a temperature of approximately 600°C.¹⁵⁾ It should be noted that γ -Al₂O₃ is phase transformed to α -Al₂O₃ with an increase in temperature and grain growth. Therefore, the temperature of the γ -Al₂O₃ and ZnO particles themselves should be very low and only the temperature of the interface between ZnO and γ -Al₂O₃ should be slightly higher due to the shear force.

Table 1 lists the specific surface area of the ZnO–Al₂O₃ powder measured by using the BET method after the mechanical treatment. For reference, the specific surface area of the raw materials ZnO and Al₂O₃ is also listed in the table. The specific surface areas of ZnO and γ -Al₂O₃ were 4.2 m²/g and 196 m²/g, respectively. When 3.7 mol% Al₂O₃-doped ZnO was used, the specific surface area was 12.1 m²/g before the mechanical treatment and 10.3 m²/g after the mechanical treatment. When 1.0 mol% and 0.1 mol% of Al₂O₃ were added, the specific surface area changed from 6.7 m²/g to 5.5 m²/g and from 4.6 m²/g to 4.2 m²/g, respectively. The above decrease in the specific surface areas were assumed to be because of the formation of a bonding area between ZnO particles and γ -Al₂O₃ during the mechanical treatment.

The specific surface area S_0 before the mechanical treatment

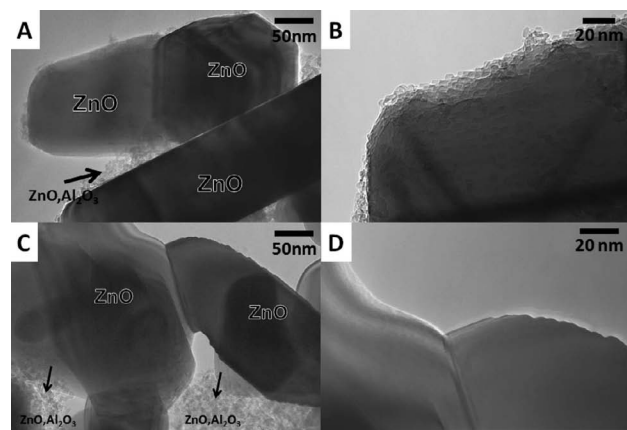


Fig. 1. TEM images of powder mixture (3.7 mol% Al₂O₃-doped ZnO). (A) Powder mixture after mechanical treatment, (B) Enlarged view of powder mixture after mechanical treatment, (C) Ball milling powder, (D) Enlarged view of ball milling powder.

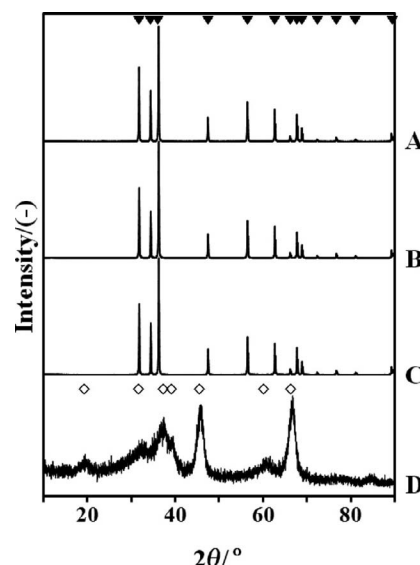


Fig. 2. XRD pattern of powders of (A) Mixing powder before mechanical treatment, (B) After treatment, (C) ZnO powder and (D) γ -Al₂O₃ powder. ▼ : ZnO, ◇ : γ -Al₂O₃.

Table 1. Change in the Specific Surface Area for Each Sample

Sample	Specific surface (m ² /g)		Estimated bonding
γ -Al ₂ O ₃	196		
ZnO	4.2		
	Premixing	Mechanical treatment	
3.7 mol%Al ₂ O ₃	12.1	10.3	9.8
1.0 mol%Al ₂ O ₃	6.7	5.5	5.8
0.1 mol%Al ₂ O ₃	4.6	4.2	4.4

was estimated as follows:

$$S_0 = S_{\text{submicron}}(1-f) + S_{\text{nano}}f \quad (2)$$

where f is the weight fraction of the nanoparticle, $S_{\text{submicron}}$ and S_{nano} are the specific surface areas of the submicron-sized particle and the nanosized particle, respectively. If a cubic-shaped nanoparticle of a phase bonds to the spherical submicron particle, the total surface area should reduce by $2L^2$. When all of the nanoparticles bonded to the submicron particles, the decreasing surface area ΔS per unit of weight was as follows;

$$\begin{aligned} \Delta S &= \frac{2L^2}{6L^2} S_{\text{nano}}f \\ &= \frac{1}{3} S_{\text{nano}}f \end{aligned} \quad (3)$$

Hence, the specific surface area after bonding, S , was estimated as follows;

$$\begin{aligned} S &= S_{\text{submicron}}(1-f) + \frac{2}{3} S_{\text{nano}}f \\ &= S_{\text{submicron}} + \left(\frac{2}{3} S_{\text{nano}} - S_{\text{submicron}} \right) f \end{aligned} \quad (4)$$

The values of the specific surface area after the mechanical treatment calculated in eq. (4) are also listed in Table 1. The calculated values of the specific surface area were in good agreement with the experimental values. Therefore, it was concluded that the specific surface area decreased because of the bonding between the ZnO and γ -Al₂O₃ particles during the mechanical treatment and that almost all of the added γ -Al₂O₃ bonded to the ZnO particles. These results agreed well with those obtained by the TEM analysis.

3.2 Microstructure and electrical property of ZnO ceramics

We fabricated the sintering body by using the prepared composite powder and the powder obtained by wet ball milling of 1.0 mol% Al₂O₃-doped ZnO. The relative densities of the sintering body for the composite powder and the powder obtained by wet ball milling were 98.9% and 99.2%, respectively. From the phase analysis by X-ray diffraction, it was found that the main phase was ZnO and the secondary phase was ZnAl₂O₄ (Fig. 3). The SEM images in Fig. 4 show the microstructure of the sintering body. The dark particles represent ZnO, and the small bright particles represent ZnAl₂O₄. It appeared that the particle size of ZnO prepared from the wet ball milled powder was slightly larger than that of the ZnO prepared from the mechanically treated powder. We measured the grain size of the sintering body by the intercept method.¹³⁾ The average grain size, D , was calculated according to the following equation;

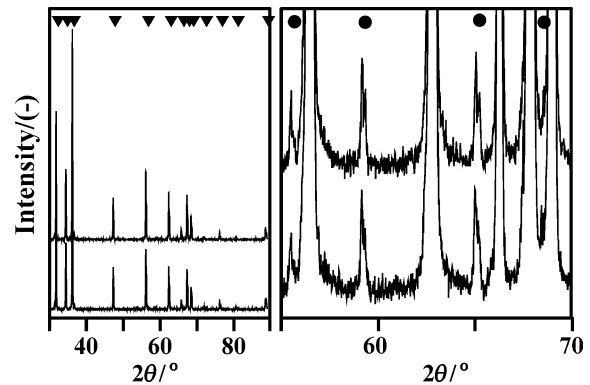


Fig. 3. XRD pattern of 1.0 mol% Al₂O₃-doped ZnO ceramics. ▼ : ZnO, ● : ZnAl₂O₄.

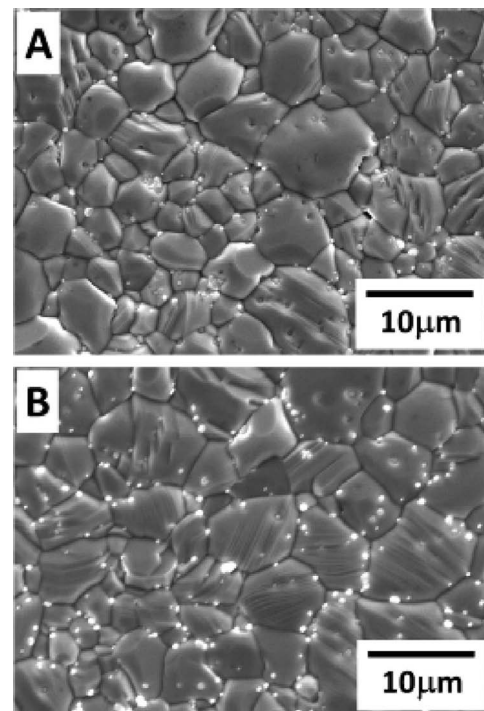


Fig. 4. SEM image of 1.0 mol% Al₂O₃-doped ZnO ceramics. (A) Mechanical treatment, (B) Wet ball milling.

$$D = k \cdot l_c \quad (5)$$

k is 1.5 when the grain shape is assumed to be spherical and l_c is the average intercept length. The grain size of the powder obtained after the mechanical treatment was 5.3 μm , whereas that obtained by wet ball milling was 5.6 μm ; the sintered body fabricated from the mechanically treated powder had a slightly smaller and more uniform grain size than that fabricated from the powder obtained by wet ball milling. Furthermore, the particle size of the secondary ZnAl₂O₄ phase in the ZnO ceramics fabricated by the mechanical treatment process appeared to be considerably smaller and more uniform than that of the secondary ZnAl₂O₄ phase in the ZnO ceramics fabricated by wet ball milling process. It has been reported that the Al₂O₃ added to ZnO restricted the densification and the grain growth of ZnO.¹⁶⁾ Therefore, this homogeneous and fine microstructure in the ZnO ceramics obtained by the mechanical treatment process can be attributed to a uniform dispersion of the nanosized γ -Al₂O₃ particles.

Table 2. Electrical Conductivity of 1.0 mol% Al₂O₃-doped ZnO Ceramics

Process	Electrical Conductivity (S/cm)
Mechanical Treatment	588
Wet Ball Milling	333

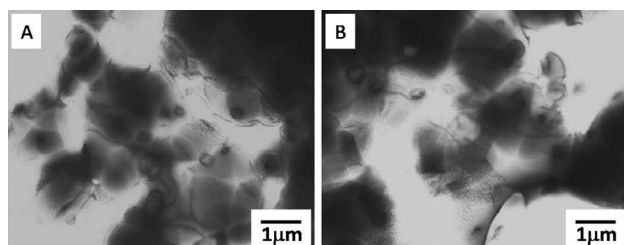
**Fig. 5.** TEM images of 1.0 mol% Al₂O₃-doped ZnO ceramics. (A) Mechanical treatment, (B) Wet ball milling.

Table 2 lists the electrical conductivity values for the sintering body measured by the four-terminal method. The electrical conductivities of the sintered body obtained by wet ball milling and the mechanical treatment process were 333 S/cm and 588 S/cm, respectively. In other words, the electrical conductivity of the composite powder obtained by the mechanical treatment was almost twice that of the powder obtained by wet ball milling. The high electrical conductivity of Al₂O₃-doped ZnO was attributed to the dissolution of Al₂O₃ in ZnO to form electrons as carriers. The grain boundary structure and the segregation of impurity also influenced the electrical conductivity of ZnO ceramics. TEM images revealed that there was no difference between the sintering bodies obtained by the mechanical treatment and wet ball milling (**Fig. 5**). The solubility limit of Al in ZnO is 0.3 mol%, which is smaller than the amount of Al₂O₃ added in this study.¹⁷⁾ The excess amount of Al might be segregated in the grain boundary and might be present as a secondary phase (ZnAl₂O₄).⁹⁾ However, the grain boundary and the secondary phases were not considerably different in the case of the mechanical treatment and ball milling processes except for the size of the secondary phase; this implied that the microstructure had a small effect on the difference in the electrical conductivity observed in this study.

4. Conclusion

We fabricated ZnO/nano-Al₂O₃ composite particles by

mechanical treatment and investigated their electrical property. After the mechanical treatment, γ -Al₂O₃ nanoparticles were directly bonded to the ZnO particles. The ZnO ceramics fabricated by using ZnO/nano-Al₂O₃ composite particles had a uniform and fine microstructure. The ZnO ceramics fabricated by the mechanical treatment process exhibited higher electrical conductivity improved because of the homogeneous dissolution of Al in ZnO; this dissolution was attributed to the homogeneous dispersion of nanosized γ -Al₂O₃ due to using nanocomposite particles.

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