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c-axis oriented ZnO formed in a rotating magnetic field with various rotation speeds

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Abstract

A rotating magnetic field was used to fabricate *c*-axis oriented zinc oxide. The influence of rotating speed on orientation structure was also examined. The aligned axes had the largest diamagnetic susceptibility, which axis was difficult to align with a static magnetic field. In *c*-axis oriented ZnO, the degree of orientation (Lotgering factor) in the green compact ranged from 0.2 to 0.5 along *c*-axis. The Lotgering factor increased with rotating speed. For all samples with the rotating magnetic field, the degrees of orientation increased up to above 0.9 after sintering at 1573 K.

Keywords: Shaping; Microstructure-prefiring; ZnO

1. Introduction

Orientation of crystals of microstructures in ceramics is effective for drastically improving their properties.[1–7] The use of a high magnetic field with a super conducting magnet has been reported for alignment crystal grains.[7] The feature of the use of magnetic field is to align crystal grains with no physical contact. The fabrication of oriented materials with weak diamagnetic susceptibilities has been reported for metals, polymers, and ceramics.[7–11] Particle orientation is even possible for substances such as alumina,[12,13] zinc oxide,[14] bismuth titanate,[15,16] and other materials,[17,18] that have very low magnetic susceptibilities ($<|10^{-7}|$) in a high magnetic field of 10 Tesla (10 T).

Magnetically anisotropic particles are usually oriented in the direction of the lowest energy in a static magnetic field. The axis with the largest diamagnetic susceptibility (χ_3) is oriented normal to the magnetic field, but the direction of this axis is random within the plane normal to the magnetic field. As a result, the axis with the smallest diamagnetic susceptibility (χ_1 or χ_2) tends to be aligned along the magnetic field. For Al_2O_3 ceramics, the *a*-axis, which has the largest diamagnetic susceptibility ($\chi_a < \chi_c < 0$), is oriented randomly within the plane perpendicular to the magnetic field, and thus the *c*-axis (χ_c) is aligned along the magnetic field (Fig. 1(a)).

For ZnO, the *a*-axis or *a*, *b*-axes ($h\,0\,0$), ($h\,k\,0$) were aligned along the field in a static magnetic field. The *c*-axis ($0\,0\,l$) is oriented randomly within the plane perpendicular to the field (Fig. 1(b)).[14] However, polycrystalline ZnO ceramic oriented along the *c*-axis is expected to show excellent piezoelectronic properties. A new method is required for uniaxially orienting the *c*-axis, which has the largest diamagnetic susceptibility.

Recently, we reported a fabrication of *c*-axis oriented ZnO with a rotating magnet field.[19] The method to align axis with the largest diamagnetic susceptibility is to use a time-dependent magnetic field, which is a rotating magnetic field reported by Kimura.[20] In the rotating magnetic field, some magnetic fields applied horizontally to particles in the slurry (or rotating particles in the slurry horizontally in a static magnetic field as shown in Fig. 2). The axis with the largest diamagnetic susceptibility should be aligned in the direction of the axis of rotation, as shown in Fig. 1(c). This is the most stable direction energetically for the particles. In the case of the ZnO system, the *c*-axis of the particles should be oriented in the vertical direction. The most stable direction energetically is limited to the direction vertical to the rotating magnetic field.

The objectives of this study were to examine the influence of some experimental parameters of rotating magnetic field including the rotating speed on the orientation structure.

2. Experimental procedure

Powders of zinc oxide (Toho Zinc Co., Ltd.) were used as raw materials. The average particle size was nominally 0.2 μm,

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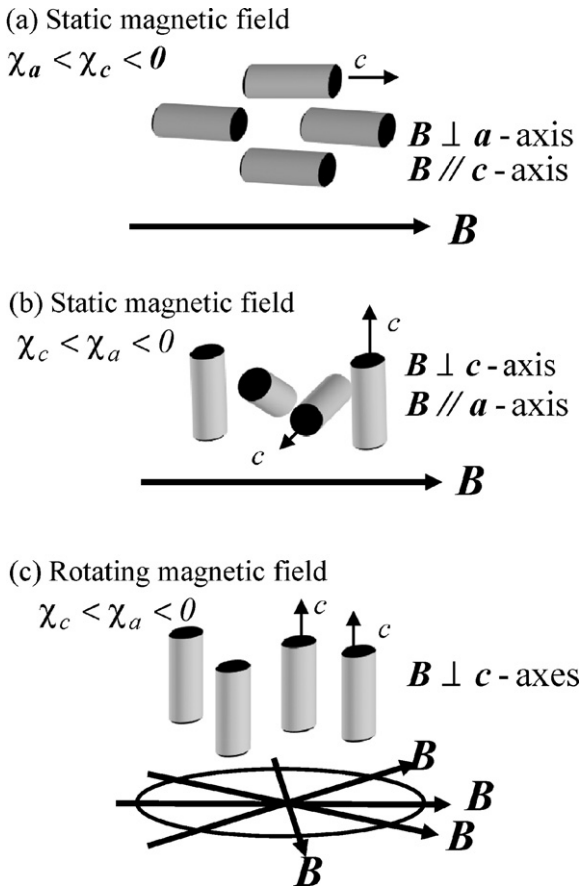

Fig. 1. Schematic illustration of a particle in a slurry in a static or a rotating magnetic field. (a) static magnetic field, $\chi_a < \chi_c < 0$, (b) static magnetic field, $\chi_c < \chi_a < 0$, (c) rotating magnetic field, $\chi_c < \chi_a < 0$.

and the specific surface area, measured by the BET method, was 4.2 m^2/g. The raw powder was placed in a ball mill with distilled deionized water, a dispersant, and alumina balls, and mixed for 24 h to prepare a slurry with a solids loading of 30 vol.%. The slurry (5×10^{-6} m^3) was placed in a shallow container made of Teflon and this was placed horizontally in a superconducting magnet (bore: 100 mm Ø, TM-10VH10, Toshiba, Japan). The container was rotated at 0–60 rpm in the horizontal magnetic field (10 T) for 1 day at room temperature until the slurry was completely dried (Fig. 2). For reference, slurries were also dried in the absence of a magnetic field. After the dried green compacts taken from the magnet field, they were heated at 5 °C/min to 1300 °C and held at that temperature for 1 h before cooling to room temperature. The orientations of particles in the green and sintered bodies were determined by X-ray diffraction analysis using the Lotgering method.[21] The sintered density was measured by the Archimedes method with distilled water as the immersion liquid. The specimen was polished and thermally etched at 1200 °C for 1 h to examine the microstructure with a scanning electron microscope (SEM).

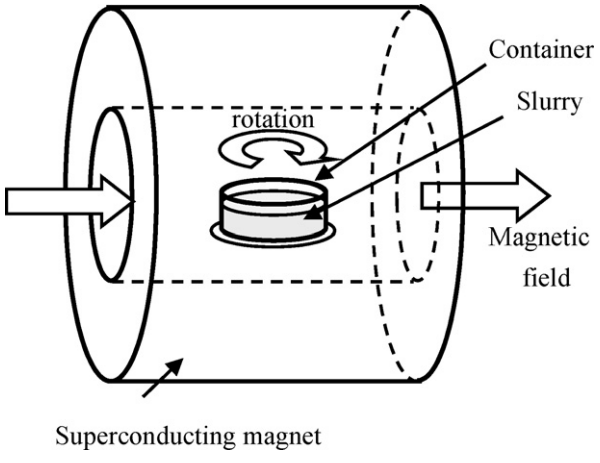

Fig. 2. Schematic illustration of rotating a container containing slurry in a static magnetic field.

3. Results and discussion

3.1. Fabrication of c-axis oriented ZnO

Fig. 3 shows an SEM micrograph of the ZnO powder used in this study. The particles have plate-like shapes. The particle size varies from 0.1 to 1 μm. Smaller particles have a shape with nearly equal axes, but larger particles tend to have a platelet shape.

Fig. 4 shows X-ray diffraction patterns taken for the sintered specimen prepared in a rotating magnetic field, which rotating speed 60rpm. The planes of analysis are in the directions perpendicular and parallel to the applied rotating magnetic field. *c*-axis oriented ZnO ceramics was fabricated. The strong diffraction peaks in the plane normal to the magnetic field are those associated with the c-planes of the crystal, such as (0 0 2) and (0 0 4) (Fig. 4(a)). On the other hand, the analysis in the plane parallel to the applied field (Fig. 4(b)) showed diffraction peaks associated with the *a*, *b*-plane of the crystal, such as (1 0 0) and (1 1 0), but not those associated with the *c*-axis.

Fig. 5 shows X-ray diffraction patterns for sintered specimens prepared with a static magnetic field, and without a magnetic field. The analysis was the same as above. An enhanced peak for the *c*-plane of the crystal was observed in the static magnetic

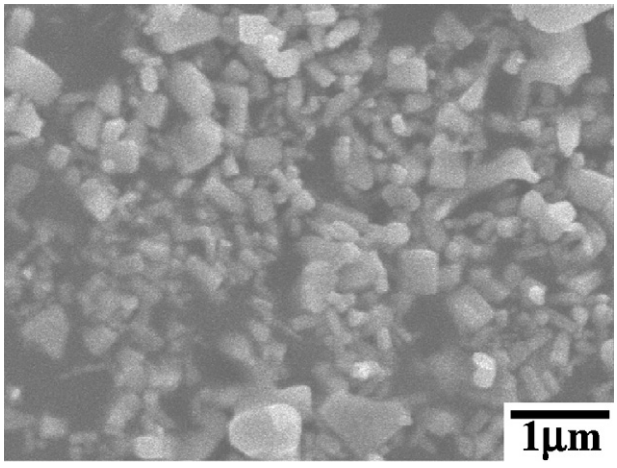

Fig. 3. SEM photograph of ZnO particles.

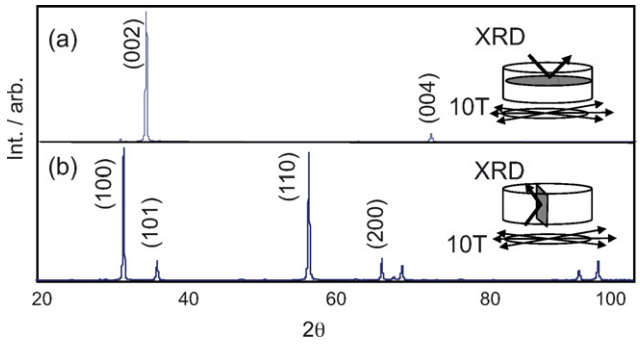

Fig. 4. XRD patterns of sintered ZnO formed by a rotating magnetic field, (a) the plane in the direction parallel to the rotating magnetic field, (b) the plane in the direction normal to the rotating magnetic field.[19]

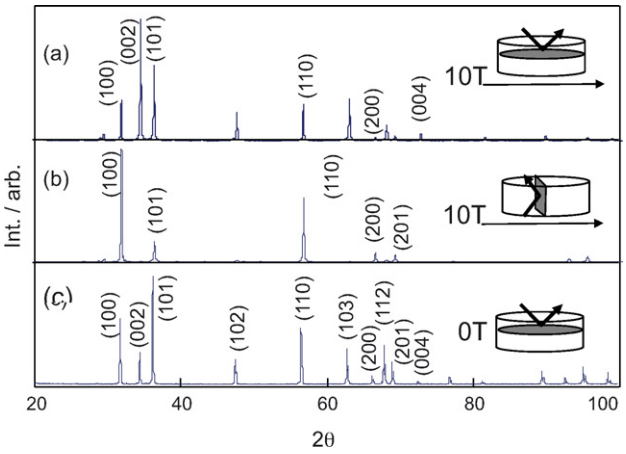

Fig. 5. XRD patterns of sintered ZnO formed with a static magnetic field, (a) the plane in the direction parallel to the magnetic field, (b) the plane in the direction normal to the magnetic field, (c) no magnetic field.[19]

field, but other peaks associated with the *a*, *b*-plane were also observed (Fig. 5(a)). In the face perpendicular to the magnetic field, peaks associated with the *a*, *b*-plane of the crystal, such as (1 0 0) and (1 1 0), were observed (Fig. 5(b)). In the specimen prepared without a magnetic field, strong diffractions were also observed for (1 0 2), (1 0 3), etc., showing that the particles are randomly oriented in this specimen.

Fig. 6 shows micrographs of the microstructure of the sintered ZnO ceramics. Observed directions were parallel and perpendicular to the axis of the rotating magnetic field at the forming process. It also shows the microstructure of the sintered body which was formed without the magnetic field. In the sintered specimen derived from body formed in the rotating magnetic field, the structures vary significantly with direction as shown in Fig. 6(a) and (b), whereas the specimen from the green body formed without magnetic field show the same structure (Fig. 6(c) and (d)). In Fig. 6(a), the particles are elongated in the direction normal to the axis of the rotating magnet field, and they measure about 20 μm by 5–10 μm. The particles have a near equiaxial shape with a dimension of 20 μm when observed from the other direction (Fig. 6(b)). The microstructure suggests that the particles are oriented and the growth of *c*-faces occurs preferentially during sintering. The grains appear large when viewed from the direction of the *c*-axis. ZnO particles have a tendency to form a hexagonal shape, with the *c*-plane comprising the largest face of the grain. The relative density after sintering is high, and is 98% of the theoretical value.

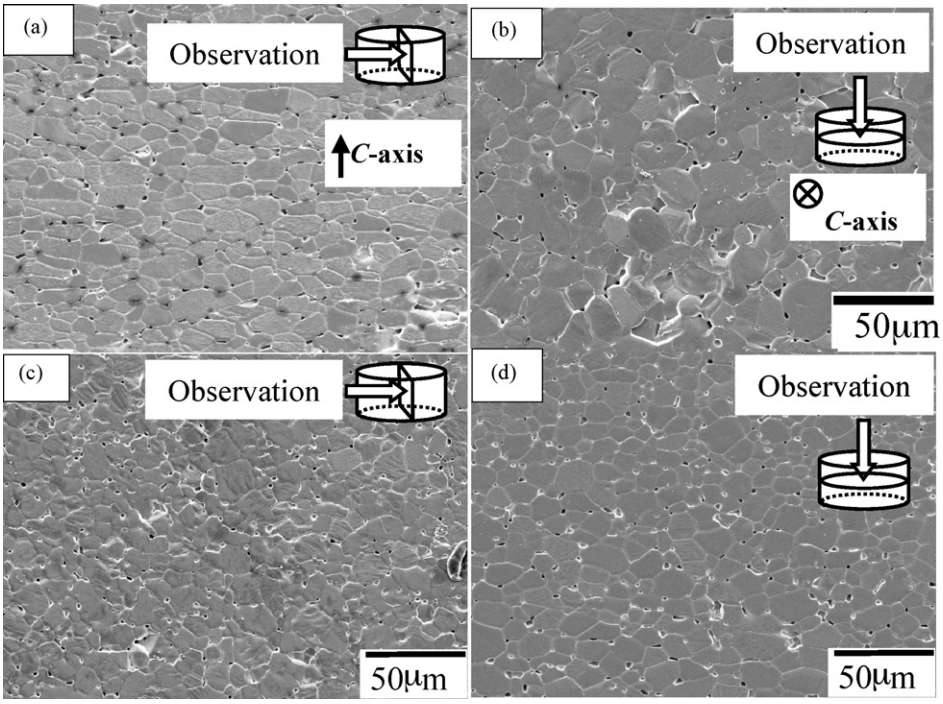

Fig. 6. The microstructure of the sintered ZnO ceramics observed from the directions parallel (a) and perpendicular (b) to the axis of the rotating magnetic field. The microstructure of ZnO formed without magnetic field, (c and d) microstructure observed from the same directions with (a and b), respectively.

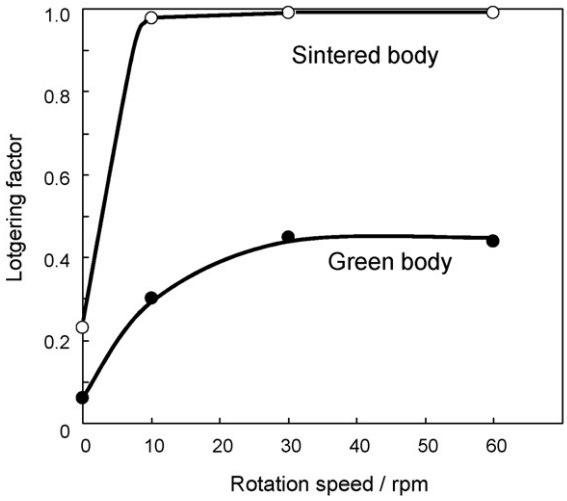

Fig. 7. The influence of rotation speed on Lotgering factor of green and sintered body.

3.2. Influence of rotation speed on orientation structure

The degree of orientation f is calculated by using the following equations:[21]

$$f = \frac{(\rho - \rho_0)}{1 - \rho_0}, \tag{1}$$

and

$$\rho_0 = \frac{\sum I_0(0\,0\,l)}{\sum I_0(h\,k\,l)}, \qquad \rho = \frac{\sum I(0\,0\,l)}{\sum I(h\,k\,l)}, \tag{2}$$

where I and I_0 are the intensities of each reflection peak ($h\,k\,l$) in X-ray diffraction patterns, ρ is the value calculated from the experimental data, and ρ_0 is the value calculated from the ICDD cards. In ideal, multiple horizontal magnetic field is required to align axis with the largest diamagnetic susceptibility.

Fig. 7 shows the Lotgering factor for the c-axis as a function of the rotating speed of green and sintered bodies. Fig. 7 shows the Lotgering factor f increased up to 0.45 with a rotating speed in the green body, and increased up to 0.99 by subsequent sintering. The result of green body suggests the aligned particle were scattered again when the rotation speed was low. The enhancement of Lotgering factor by sintering has been reported in past studies.[19] In the green body, diffraction peaks other than the c-plane still existed. Clearly, the minor group of nonoriented particles were eliminated by growth of oriented particles through densification and grain growth during the subsequent sintering process.

Fig. 8 shows schematic estimated illustrations of the oriented ZnO crystallites prepared in rotating magnetic fields (from 0 to 60 rpm). In the specimen prepared in the rotating magnetic field at 30 and 60 rpm, all particles are oriented with the c-plane of the crystallite in one direction after sintering. Decreasing the rotating speed, the c-plane in the body gradually randomly oriented. The peak corresponding to the a, b-plane observed.

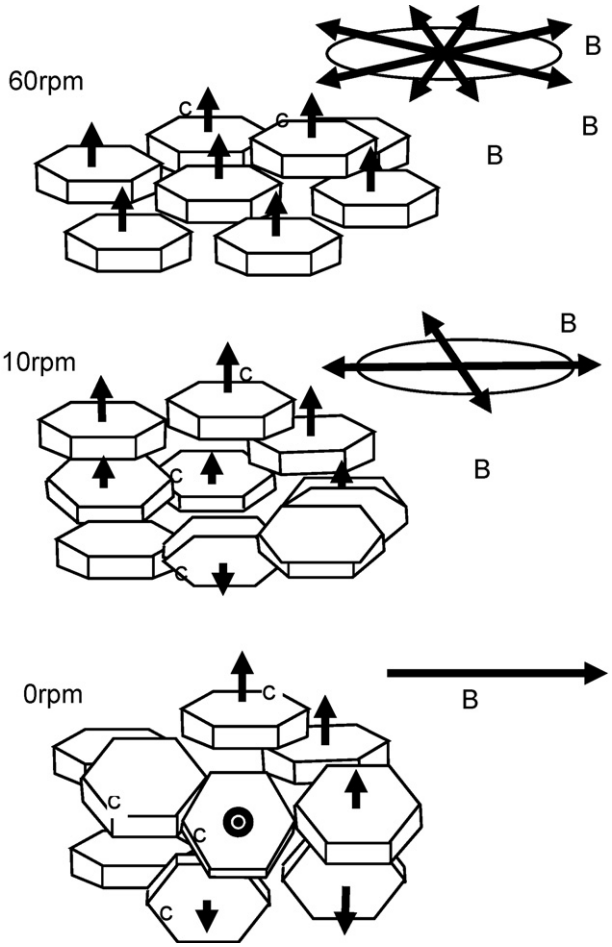

Fig. 8. Schematic estimated illustration of the oriented ZnO crystallites prepared in rotating magnetic fields (from 0 to 60 rpm).

4. Conclusion

c-axis ($0\,0\,l$) oriented ZnO ceramics were fabricated by using a rotating magnetic field and influence of a rotation speed and subsequent sintering treatment were examined on orientation structure. The following conclusions were obtained.

(1) Crystal axis with the largest diamagnetic susceptibility can be oriented in a rotating magnetic field.
(2) The degree of orientation was about 0.45 in the green compact and 0.99 in the sintered body along ($0\,0\,l$) on the Lotgering scale.
(3) Rotating speed affected on the Lotgering factor. The subsequent magnetic field during drying was required for effective alignment.

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