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# Fabrication of *c*-axis oriented zinc oxide by electrophoretic deposition in a rotating magnetic field

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**Abstract**

The fabrication of *c*-axis oriented zinc oxide was attempted by electrophoretic deposition (EPD) in a rotating magnetic field. The EPD was conducted in a small container which was placed on a turntable arranged in a superconducting magnet. The suspension was rotated at 0–90 rpm in a 12 T magnetic field during the deposition. The deposits were dried and then sintered at 1400 °C for 2 h. The degree of the *c*-axis orientation was evaluated by the Lotgering factor calculated from the X-ray diffraction data.


*Keywords:* ZnO; Suspensions; X-ray methods; Magnetic field

## 1. Introduction

Texturing is currently of much interest as one of the promising techniques to improve the physical and chemical properties of ceramics for both structural and functional applications. Textured bulk ceramics have been produced by a variety of techniques, such as tape casting,[1–3] hot forging or deformation,[4–6] eutectic solidification,[7] and templated or seeded grain growth.[8–10] Recently, we developed a promising processing technique to fabricate polycrystalline bulk ceramics and ceramic thick films with a preferred crystalline orientation by electrophoretic deposition (EPD) in a strong magnetic field.[11–18] Ceramic particles dispersed in a liquid are aligned in the magnetic field due to their magnetic anisotropy and then deposited on a substrate in a dc electric field.

Zinc oxide has a hexagonal crystal structure and the magnetic susceptibility of the *c*-axis $\chi_c$ is smaller than those of the *a*- and *b*-axes. Therefore, when a single-crystalline zinc oxide particle is placed in a high static magnetic field, the *c*-axis [0 0 1] of the particle is aligned perpendicular to the applied magnetic field; the *c*-axis is randomly oriented within the plane which is perpendicular to the magnetic field. However, the *c*-axis orientation is more significant for zinc oxide because the electric conductivity and piezoelectric constant along the *c*-axis are high.

The uni-axial alignment of the smallest diamagnetic susceptibility axis is impossible in a static magnetic field, but it can be achieved in a rotating magnetic field.[19,20] The reason for this is explained using the schematic shown in Fig. 1. When a magnetic field is applied to a crystal in the *x*-direction, the *c*-axis of the crystal rotates to be in the *y*–*z* plane since it is the most stable condition that minimizes the system energy. On the other hand, when a magnetic field is applied to the crystal in the *y*-direction, the *c*-axis of the crystal rotates to be in the *z*–*x* plane. Therefore, if the direction of the applied magnetic field is altered in the *x*–*y* plane over time, it is expected that the *c*-axis of the crystal finally aligns parallel to the *z*-axis, which is the only stable position for the *c*-axis in the rotating magnetic field.[21,22] In actuality, it is impossible to rotate a strong superconducting magnet; however, a similar effect is expected by rotating the sample in the *x*–*y* plane in a static magnetic field in order to alter the applied field direction. The *c*-axis oriented bulk ceramics of hydroxyapatite,[21] aluminum nitride[23] and zinc oxide[24–26] have recently been fabricated by slip-casting or gel-casting. Compared to these shaping techniques, the EPD process is very versatile since it offers easy control of the thickness and morphology of a deposited film through simple adjustment of the deposition time and applied potential. Our strategy is to prepare *c*-axis oriented zinc oxide free-standing films and bulk compacts by EPD in a rotating magnetic field; the rotating magnetic field is used to align the *c*-axis of the ZnO particles suspended in a liquid, and the electric field is then applied to carry the oriented parti-

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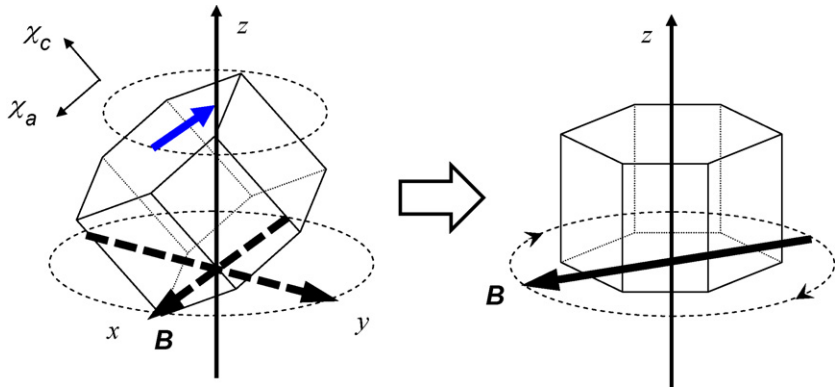


Fig. 1. Schematic drawing showing the *c*-axis alignment of a hexagonal crystal with the relation $\chi_c < \chi_{a,b}$ by altering the direction of applied static magnetic field.

cles along the electric field lines and consolidate them on a substrate.

## 2. Experimental

Commercial zinc oxide powder (Toho Zinc Co., Ltd., 0.25 μm average particle size, purity >99.84%) with the hexagonal wurtzite structure was used in this study. An SEM photograph of the powder is shown in Fig. 2. Most particles have a shape with nearly equal axes, but some larger particles have a platelet shape. The major impurities were Pb (5 ppm), Cd (1 ppm) and Fe (1 ppm). The ZnO powder was dispersed in ethanol, and a deflocculated stable suspension with a 2 vol% solid loading was prepared. Butoxyethyl acid phosphate $(C_4H_9OC_2H_4O)_nP(O)(OH)_{3-n}$ $n = 1, 2$ (JP-506H, Johoku Chem. Co., Ltd., Japan) and polyethyleneimine (M.W. = 10,000, Wako Pure Chem. Ind. Ltd., Japan) were used as dispersing agents as to the particles were positively charged.[27] The EPD was conducted in a small container which was placed on a turntable arranged in a cryogen-free superconducting magnet with a room temperature bore of 100 mm (JMTD-12T100NC5, JASTEC, Inc.). The direction of the migration of the particles was downwards since only a slight deposit was obtained when the migration was upwards. The schematics of the experimental setup in the superconducting magnet are shown in Fig. 3. To vertically orient the *c*-axis of the zinc oxide, a magnetic field must be applied to the zinc oxide particles from the horizontal direction while rotating the particles in the horizontal plane. In this experiment, ethanol as a dispersion medium also works as a transmission fluid which converts the rotational motion of a vial into the rotation of the particles. Palladium sheets with a working area of 15 mm × 15 mm were used as the electrodes. The applied voltage and the distance between the electrodes were 50 V and 15 mm, respectively. The turntable was rotated at a speed of 6–90 rpm using a stepper motor which was situated away from the magnet so as not to be affected by the magnetic field. A strong magnetic field of 12 T was maintained while applying a constant voltage of 50 V to the suspension during the EPD at room temperature. To check the influence of the gravitational sedimentation on the orientation, the consolidation by slip casting was also conducted in and out of the magnetic field using the same suspension. All the green deposits were dried, separated from the substrate, and then heat-treated at 1400 °C for 2 h in air out of the magnetic field. The orientation of the zinc oxide crystallites was evaluated by X-ray diffraction (XRD).

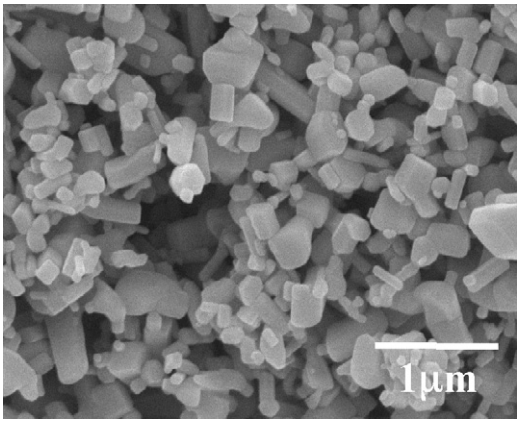


Fig. 2. SEM photograph of the ZnO powder.

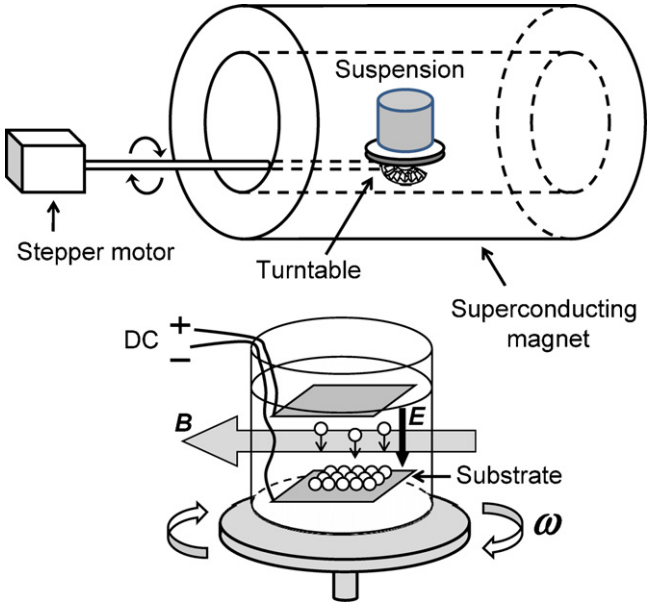


Fig. 3. Schematic drawing showing the experimental setup of the EPD in a rotating high magnetic field.

## 3. Results and discussion

When the consolidation was performed by slip casting without applying the magnetic field, the relative intensities of the XRD peaks were consistent with the standard XRD data of a randomly oriented polycrystalline structure. It was confirmed that the influence of the gravitational sedimentation on the orientation can be ignored; however, the influence of the electric field on the orientation was detected. Fig. 4 shows the XRD patterns of the ZnO films prepared by the EPD with no application of a magnetic field without rotating the turntable [0 T, 0 rpm], under a magnetic field at 12 T without rotation [12 T, 0 rpm], and under 12 T with rotation at 60 rpm [12 T, 60 rpm]. When the consolidation was performed by the EPD at [0 T, 0 rpm], the intensity of the (0 0 2) reflection becomes lower than that of the standard data, and the intensity of the (1 1 0) reflection becomes higher than the standard as shown in Fig. 4. This result shows that the *c*-axis of the ZnO tends to orient perpendicular to the electric field during the EPD. This tendency was reproducible and detected when the applied voltage was higher than 10 V; however, the degree of orientation was almost similar among the samples prepared at 10–200 V. The reason for this phenomenon is still unclear, but it may be related to the anisotropic surface charging of the ZnO crystals. Though the raw ZnO powder includes some particles with a platelet shape, the basal plane tends to align not parallel, but perpendicular to a substrate during the deposition without a magnetic field; therefore, the influence of the hydrodynamic force acting on the orientation of the particles seems to be negligible. When the EPD is performed at [12 T, 0 rpm], the intensity of the (0 0 2) diffraction becomes slightly stronger; however, it still shows a random orientation. An obvious orientation is observed when the turntable is rotated. When the EPD is performed at [12 T, 60 rpm], the intensity of the (0 0 2) diffraction becomes the strongest, and it clearly shows that the *c*-axis of the ZnO is vertically oriented. To confirm the *c*-axis orientation, XRD patterns were taken of both the top and side surfaces of a thick (~3 mm) bulk prepared by EPD for a longer time. This result is shown in Fig. 5. The diffraction peaks of the

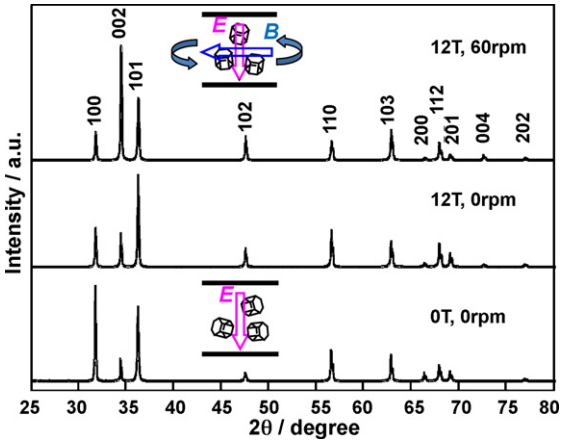


Fig. 4. XRD patterns of ZnO films prepared by EPD with no application of magnetic field and no rotation of the turntable [0 T, 0 rpm], under a magnetic field at 12 T without rotation [12 T, 0 rpm], and under 12 T with rotation at 60 rpm [12 T, 60 rpm].

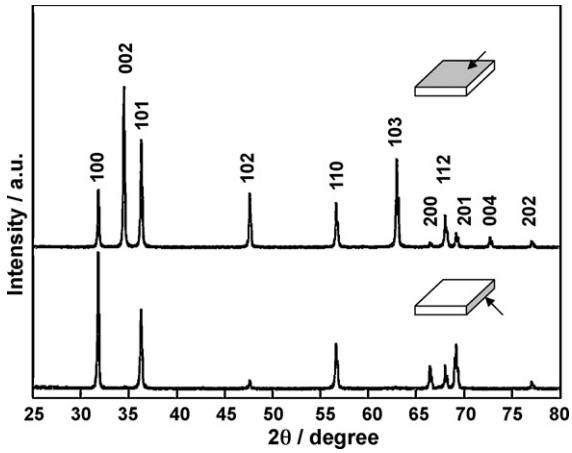


Fig. 5. XRD patterns of the top and side planes of a bulk ZnO prepared by EPD under 12 T with rotation at 60 rpm [12 T, 60 rpm].

(0 0 2) and (0 0 4) planes, which are parallel to the basal plane of the unit cell, are not detected, and the peaks of the (1 0 3) and (1 0 2) planes are very weak in the diffraction pattern from the side surface. The results in Fig. 4 show that the application of a rotating magnetic field effectively orientates the *c*-axis.

The degree of the *c*-axis orientation of the ZnO ceramics as a function of the rotation rate of the suspension was evaluated from the intensity of the XRD peaks using the Lotgering factor *f* which is defined by the following equations[28]:

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

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

$$\rho_0 = \frac{\sum I_0(0\,0\,l)}{\sum I_0(h\,k\,l)} \tag{3}$$

where $I$ and $I_0$ are the relative intensities of each reflection peak of the $(h\,k\,l)$ planes; $\rho$ is the value calculated from the XRD data measured for our samples and $\rho_0$ is the value calculated from the standard XRD data (ICDD #36-1451). This result is shown

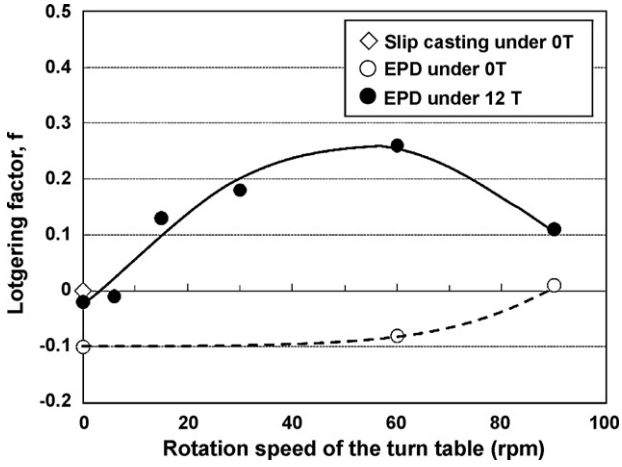


Fig. 6. The degree of the *c*-axis orientation of ZnO films as a function of the rotation speed of the turntable.

in Fig. 6. As stated above, the particles tend to slightly orient due to the applied electric field without applying the magnetic field; however, this effect decreases with an increase in the rotation speed, and the sample deposited at 90 rpm shows a random orientation. If we think the effect of the rotation is to enhance the *c*-axis orientation, we cannot explain the deterioration of the orientation at 90 rpm under the magnetic field. Therefore, it is considered that the generated hydrodynamic flow does not work to improve the orientation of the particles under this experimental condition. An obvious orientation is observed when EPD is performed at 12 T by rotating the turntable. The degree of orientation increased with the rotation rate of the suspension and achieved the highest value at 60 rpm; however, it decreased at 90 rpm probably because the centrifugal force acting on the particle disturbed the alignment of the particles. The degree of orientation $f = 0.26$ at the maximum was not very high.

For the *c*-axis orientation of the particles in a rotating magnetic field, it is preferable that the motion of the liquid is restricted. However, the applied electric field for the sake of electrophoresis of the particles also causes the electro-osmotic flow of the bulk liquid. This flow can disturb the effect of the rotation of the suspension and prevent the orientation of the particles. The surface-charged particles, which migrate in a magnetic field, are also affected by the Lorentz force $\boldsymbol{F} = \boldsymbol{j} \times \boldsymbol{B}$. Therefore, the locus of the particles will become very complicated during the EPD in a capacity-restricted small cell under a rotating magnetic field.

When the suspension was consolidated by slip casting at [12 T, 30 rpm] using the same suspension without applying an electric field, well-oriented ZnO with $f = 0.74$ was obtained. Tanaka et al. has reported that surprisingly well-oriented ZnO with $f = 0.99$ was obtained by drying a suspension in a rotating magnetic field of 10 T followed by sintering at 1300 °C.[24] In our previous studies on the *c*-axis alignment of α-alumina ($\chi_c > \chi_{a,b}$) by EPD in a static magnetic field, there was no difference in the degree of orientation between the samples consolidated by EPD and slip casting. In the case of alumina, the *c*-axis is the axis of easy magnetization. It is not necessary to rotate the suspension to obtain the *c*-axis-oriented alumina; therefore, the electro-osmotic flow of the bulk liquid and the translational motion by the Lorentz force does not disturb the orientation of the particles. Though the *c*-axis alignment of zinc oxide ($\chi_c < \chi_{a,b}$) by the EPD in a rotating magnetic field is not easy, it may be improved using a gelatinous medium to restrict the motion of the liquid.

## 4. Conclusions

The fabrication of *c*-axis oriented zinc oxide was attempted by EPD in a rotating magnetic field of 12 T. It was difficult to obtain ZnO with a high *c*-axis-orientation. The highest degree of orientation with the Lotgering factor of $f = 0.26$ was achieved when the suspension was rotated at 60 rpm.

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