JOURNALOF

Ceramic Processing Research

# Growth mechanisms and characteristics of ZnWO<sub>4</sub> single crystals grown by the Czochralski method

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Single crystals of ZnWO<sub>4</sub> were grown successfully in the [100], [010] and [001] directions using the Czochralski method. Seed crystals of ZnWO<sub>4</sub> were obtained from single crystal growth using platinum wires from the melt by capillary action. The effect of the growth parameters, such as the rotation speed, pulling rate and diameter of the grown crystals, were examined. The ZnWO<sub>4</sub> crystals had a cleavage plane of (010). The dislocation density on the (010) plane at the center of the crystal was lower than near the edge. The higher dislocation density at the edge of the crystals was attributed to the thermal gradient in the growing crystals. The etch pit arrangement revealed the (100) slip plane to be most active during crystal growth. The formation of cracks in the grown crystals during the cooling process was prevented by annealing. The hardness, thermal expansion coefficients and dielectric constants of the crystals were evaluated.

Key words: Single crystal growth, Czochralski method, ZnWO<sub>4</sub>, scintillator materials.

#### Introduction

ZnWO<sub>4</sub> is a technologically important material with a monoclinic wolframite-type structure in the space group P2/c. There are two formula units per primitive cell with lattice parameters of a = 4.69263 Å, b = 5.72129 Å, c = 4.92805 Å and  $\beta = 90.6321^{\circ}$  [1]. In recent years, ZnWO<sub>4</sub> has attracted considerable attention for potential applications as a scintillator, maser, luminescent material and photocatalyst [2-7]. The physical, chemical and photochemical properties of ZnWO<sub>4</sub> are dependent on the manufacturing method. To enhance the applications of ZnWO<sub>4</sub>, several processes have been developed over the last decade and can be classified. ZnWO<sub>4</sub> is prepared by a range of processes, such as a solid-state reaction method [8], a co-precipitation method [9], from a molten salt [10], by combustion [11], a mechano-chemical method [12], a sol-gel method [13], from a hydrothermal reaction [14-16] and wet chemical solution methods [17, 18].

For high quality applications, ZnWO<sub>4</sub> single crystals are generally grown by the Czochralski method [7, 19-21]. However, the problems associated with the crystal growth mechanisms and the crystal quality of ZnWO<sub>4</sub> are phenomenological in nature because of the complicated growth parameters of the interface between the solid and liquid. Stability with the growth parameters of ZnWO<sub>4</sub> single crystals are still a challenge for commercial applications. Therefore, for improved applications, a more detailed study of the growth mechanisms and characteristics of ZnWO<sub>4</sub> single crystals by the Czochralski method are needed.

In this study, single crystals of  $ZnWO_4$  in the [100], [010] and [001] directions were grown successfully by the Czochralski method. The growth conditions in the [100], [010] and [001] directions were examined in terms of the rotation speed, pulling rate and diameter of the grown crystals. Subsequently, the physical properties of the grown crystals were evaluated in terms of hardness, thermal expansion coefficient and dielectric constants.

#### Experimental

The growth equipment for the Czochralski method was fabricated using a furnace assembly. The ZnWO<sub>4</sub> melts were prepared from polycrystalline ZnWO<sub>4</sub>, placed in a platinum crucible. The platinum crucible was heated in a furnace fabricated with SiC resistive heating elements, and the temperature was monitored and regulated using a controller and thyrister from Eurotherm Co. The single crystals were pulled along the crystallographic axes with a diameter of 0-3.5 cm at a pulling rate of 0-100 mm/h and a rotation speed of 0-68 rpm. The temperatures were controlled precisely with measurements on the surface of the ZnWO<sub>4</sub> melts between 1230-1235 °C during growth. The polycrystalline ZnWO<sub>4</sub> was prepared from stoichiometric amounts of the mole ratio of 1:1 for zinc oxide and tungsten trioxide. The mixed powders was pressed and calcined at 800, 900, 1000 and 1100 °C for various times. The phase in the powders after calcination was identified by X-ray diffraction (XRD,  $CuK_{\alpha}$ , 40 kV, 30 mA, Rigaku, Japan) at a scan rate of 3° minute<sup>-1</sup>. The polycrystalline ZnWO<sub>4</sub> calcined at 900 °C for 12 h was identified using the reported crystallographic data for ZnWO<sub>4</sub> (JCPDS Code 15-0774).

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The microstructure of the etch pits were observed by optical microscopy and scanning electron microscopy (SEM, JSM-35CF, JEOL). The dislocations in the cleaved slices were examined by chemical etching. The etched surfaces were obtained from a boiling 2 molar NaOH solution. The (010) surface was etched in a boiling solution for 4 minutes, whereas the (001) and (100) surfaces were etched for 2 minutes. The orientations of ZnWO<sub>4</sub> single crystals in [100], [010] and [001] directions were identified from Laue back reflection patterns. The hardness, thermal expansion coefficients and dielectric constants of the grown crystals were evaluated.

## **Results and Discussion**

For the Czochralski growth of single crystals with a specific orientation, a seed crystal fixed properly to the pulling rod must be used. Platinum wires were used to obtain seed crystals employing capillary action from the melt. The platinum wires were dipped into the melt and the temperature was adjusted, a small crystal as a nucleus was grown inside the hole of the four platinum wires by capillary action. The temperature of the hole of the platinum wires was lower than the surface of the melt, so that nucleation occurred at a lower temperature. This crystal consisted of two crystals, due to heteronucleation during the dipping procedure at a lower temperature. The rotation speed was fixed to 40 rpm, and the pulling rate was 0-10 mm/h. The maximum diameter was 1.9 mm and the crystal had a red-brown color.

Seed crystals were fabricated with a length and diameter of 2.5 cm and 0.2 cm, respectively, and employed for crystal growth along a crystallographic direction after identifying the crystal orientation by Laue back reflection. The ZnWO<sub>4</sub> single crystals were grown using the typical growth procedure and parameters listed in Table 1. The temperature was controlled between 1230-1235 °C, the rotation speed

**Table 1.** Typical growth procedure and parameters of the ZnWO<sub>4</sub> single crystals grown

Parameter Procedure	Temperature (°C)	Pulling rate (mm/h)	Rotation speed (rpm)
Melting	1235	0	60
Dipping	1233	5	60
Necking	1234	8	60
Crowning	1231	3.5	60
Growing	1230	8-10	60
Tailing	1233	10	60

was fixed to 60 rpm and the pulling rate was between 0-10 mm/h. The grown crystals showed perfect cleavage on the (010) plane, and the thin sections were found to cleave along the (101) plane. The (100) twin appeared to be the most common along the (101) plane.

For Czochralski growth, the crystal rotation speed and diameter were associated with the fluid-flow convection modes in the melt. Table 2 shows the crystal shape, rotation speed and maximum diameter of the single crystals of ZnWO<sub>4</sub> grown. An increase in the crystal diameter results in an increase in the centrifugal force at the crystal periphery, which may bring a change in the fluid-flow convection of the liquid in contact with the growing interface. Table 2 shows the various crystal shapes according to rotation speeds of 15-68 rpm and a maximum diameter of 17-23 mm at a pulling rate of 0-10 mm/h.

Fig. 1 shows schematic diagrams of the relationships between the fluid-flowing convection models and interfacial shape at different crystal rotation speeds [22]. Since the interfacial shape coincides with a freezing isotherm, this characteristic feature shows that the appearance of a concave interface is caused by fluid-flow rising from the central hot part of the melt, which is produced by an increase in

Table 2. The crystal shape, rotation speed and maximum diameter of the grown ZnWO<sub>4</sub> single crystals grown

Crystal shape				2 Cm				
Nomination	А	В	С	D	Е	F	G	Н
Rotation speed (rpm)	15, 26	16	39	55	68	54, 40	46	63
Max. diameter (mm)	21	16	23	35	12	20	17	23



Fig. 1. Schematic diagram of the relationships between fluid-flowing convection models and interfacial shape at different crystal rotation speeds. When the crystal rotation speed is relatively low (a), the natural convection going downwards just beneath the interface of  $ZnWO_4$  becomes convex below 55 rpm. When the crystal rotation speed is relatively high (b), forced convection going up towards the ZnWO<sub>4</sub> interface becomes concave above 63 rpm.

the crystal rotation speed. When the crystal rotation speed was relatively low (Fig. 1(a)), natural convection occuring just beneath the interface is predominant. The solid-liquid interfacial shape of the crystal growth of  $ZnWO_4$  became convex below 55 rpm. Forced convection stronger than natural convection was produced when the crystal rotation speed is high in Fig. 1(b). The forced convection is caused by a stream of hot liquid inside the melt going up towards the interface. The solid-liquid interfacial shape of the crystal growth of  $ZnWO_4$  becomes concave towards the melt above 63 rpm. The fluid-flow modes help establish the freezing isotherm indicated by the line curves, allowing a convex or concave interface shape.

The important parameters to consider in fluid-flow are the Prandtle number  $\sigma$  and Rayleigh number  $R_a$ , which are expressed by the following equations [22]:

$$\sigma = \eta c_{\rm p}/k = \upsilon/k,\tag{1}$$

$$\mathbf{R}_{a} = \mathbf{L}^{3} \beta \mathbf{g} (\mathbf{T}_{1} - \mathbf{T}_{2}) / \upsilon k, \tag{2}$$

where  $\eta$  is the viscosity,  $c_p$  is the latent heat at a constant pressure, k is the thermal diffusivity,  $\upsilon$  is the kinetmatic viscosity, L is the dimension of the system under consideration (crucible diameter in the present case),  $\beta$  is the thermal expansion coefficient for liquid, g is gravity, and  $(T_1 - T_2) = \Delta T$  is the temperature difference in a system.

The natural convection caused by the temperature difference in the liquid is normally given by a dimensionless parameter, Grashof number  $G_r$ , which corresponds to the ratio of the viscosity to levitation due to thermal expansion of a liquid:

$$R_{\rm a} = \sigma \ G_{\rm r} \tag{3}$$

On the other hand, the forced convection associated with crystal rotation is given by the dimensionless parameter, Reynolds number  $R_e$ , which is expressed as:

$$R_{\rm e} = LV/\upsilon = d/2 \cdot \pi \ wd/\upsilon, \tag{4}$$

where d is the crystal diameter and w is the crystal rotation speed.

By normalizing the two measures of  $G_r$  and  $R_e$  with respect to the viscosity:

$$d = (4g\beta TR^3 \pi^{-2})^{1/4} / w^{1/2},$$
(5)

was obtained because fluid-flow interacts through drag. Eq. (5) shows the relationship between the crystal diameter and crystal rotation speed, which makes the interface flat. It provides a linear relationship between d and  $w^{-1/2}$ , which means that the natural and forced convections are balanced, giving rise to a flat interface. Therefore, gas-bubble entrapment depends on fluid-flow convection modes. In this study, the pulling rate was regulated between 0-10 mm/h. The rotation speed and diameters were regulated under consideration of fluid-flow convection of a liquid in contact with the growing interface. The gas-bubble entrapments were observed from the viewpoint of fluid-flow modes in the melt in connection with the shape of the growing solid-liquid interface. Gas-bubble entrapment can be avoided by adjusting the crystal rotation speed to make a flat or slightly concave interfacial shape to the melt. The formation of cracks in the grown crystals during the cooling process could be prevented by annealing at 800 °C for 10 h.

Fig. 2 shows the grown single crystals of  $ZnWO_4$  in the [100], [010] and [001] directions, which correspond to



**Fig. 2.** The grown single crystals of  $ZnWO_4$  in (a) [100], (b) [010] and (c) [001], which correspond to Table 4 (A), (B) and (C) with the growth direction, rotation speed and diameter. The formation of cracks in the grown crystals in the [001] direction during the cooling process could be prevented by annealing at 800 °C for 10 h.

Table 3 (A), (B), (C) with the growth direction, rotation speed and diameter. As listed in Table 3, the rotation speed was between 40-54 rpm with a diameter of 20 mm for the [100] direction in Fig. 2(a), whereas it was 46 rpm with a diameter of 17 mm for the [101] direction in Fig. 2(b) and 63 rpm with a diameter 23 mm for the [001] direction in Fig. 2(c). The formation of cracking in the grown crystals in [001] direction during the cooling process can be prevented by annealing at 800 °C for 10 h.

Fig. 3 shows the crystal structure of the ZnWO<sub>4</sub>. It is based on a distorted hexagonal close packing of O atoms with Zn and W atoms, each occupying one-fourth of the octahedral interstices. The presence of two non-equivalent oxygen atoms is responsible for the pairs of Zn-O and W-O bonds with different lengths. Therefore, both Zn and W atoms are surrounded by six oxygen atoms, forming a distorted octahedral coordination. Each chain of the ZnO<sub>6</sub> octahedra is corner-linked, and the chains of WO<sub>6</sub> octahedra are edge-linked, which are also parallel to [001]. The ZnO<sub>6</sub> and WO<sub>6</sub> octahedra consist of three pairs of cation-oxygen bonds with Zn and W atoms being displaced from the center of their octahedra by approximately 0.29 and 0.32 Å,

Table 3. Growth conditions of the grown  $ZnWO_4$  single crystals of (A) [100], (B) [010] and (C) [001]

Crystals Conditions	А	В	С	
Direction	[100]	[010]	[001]	
Rotation (rpm)	54, 40	46	63	
Weight (g)	85.9	47.0	90.7	
Annealing effect	no	800 °C, 10 h	800 °C, 10 h	
Remark	crack	bubble	no crack no bubble	

\*The crystal data of A, B, C are corresponding to the crystal in Fig. 2(a), (b), (c).



**Fig. 3.** The crystal structure of the  $ZnWO_4$ . Each chain of the  $ZnO_6$  octahedra is corner-linked, and the chains of the  $WO_6$  octahedra are edge-linked, which are also parallel to [001].



**Fig. 4.** The unit cell of  $ZnWO_4$  projected on the (001) and (100) planes. For the (100) planes, oxygen atoms are halfway between the reflecting planes, and are located in the region of the maximum field amplitude of the anomalously transmitted standing wave. However, for the (001) planes, oxygen atoms are displaced from the position of maximum field amplitude. Hence, they absorb less than the (100) reflection.

respectively, along the [010] direction [9]. Since two like atoms in a unit cell are related by a center of symmetry, they are off center in the opposite sense in a manner characteristic of an antiferroelectric.

Fig. 4 shows the unit cell of  $ZnWO_4$  projected on the (001) and (100) planes. For the (100) planes the oxygen atoms are halfway between the reflecting planes, and are located in the region of maximum field amplitude of the anomalously transmitted standing wave. Therefore, oxygen atoms absorb the transmitted wave. However, for (001) planes, oxygen atoms are displaced from the position of the maximum field amplitude, which means that they absorb less than the (100) reflection. Therefore, the intensity of the (001) reflection. This difference in intensity is due to the different locations of the oxygen atoms relative to the position of the maximum field amplitude in the two reflections.

The dislocation density of ZnWO<sub>4</sub> was obtained from the etch pits on the surfaces of the grown crystals. Fig. 5 shows the etch pattern of the (010) plane of a grown ZnWO<sub>4</sub> single crystal. The dislocation density at the center of the crystal was lower than at the edge of the crystal. The features of the dislocations of the (010) plane were propagated along the [001] direction. The etch pit arrangement shows that slip occurred along the (100) plane, particularly near the edge of the crystal. It is possible that a dislocation of this type grew or slipped on either the (010) or (100) slip planes. The fact that these straight dislocations terminate abruptly near the center of the crystal would suggest that extensive cross slip had occurred in the crystal. This can happen without cross slip because the polished crystal surface is flat only on a gross scale, and dislocations lying in



**Fig. 5.** Etch pattern of the (010) plane of a grown  $ZnWO_4$  single crystal. The dislocation density at the center of the crystal is lower than at the edge of the crystal. The features of the dislocations of the (010) plane are propagated along the [001] direction. The etch pit arrangement shows that slip occurred on the (100) plane, particularly near the edge of the crystal.

the (010) plane can intersect this surface.

When slip in the (100) plane is concentrated in a slip band, as indicated by the presence of etch pits on the adjacent section in Fig. 5, an image appears in all anomalous transmission reflections. This probably occurs because the strain fields of the dislocations superpose and the edge components of these dislocations are slightly visible in any plane not perpendicular to them. The etch pits were similar for all crystals grown in the [001], [010], [100] directions. When a crystal is grown in the [001] direction, as is usual for maser applications, the (100) and (010) slip planes are parallel to the growth direction. Existing dislocations, either in the seed or generated in the crystal, can slip, intersect the solid-liquid interface, and then continue to propagate by growth. These arrays coincide with the low-angle grain boundaries, whose tilt could be observed under a microscope.

The crystallographic orientation of ZnWO<sub>4</sub> crystal could considered. ZnWO<sub>4</sub> has a monoclinic wolframite structure in the space group P2/c. There are two formula units per primitive cell with the lattice parameters a = 4.69263 Å, b = 5.72129 Å, c = 4.92805 Å and  $\beta$  = 90.6321°. Cleavage gives a (010) crystal face, and etching gives rise to etch pits aligned parallel to the (100) slip plane in the [001] direction. The optic plane in ZnWO<sub>4</sub> is perpendicular to the (010) cleavage plane. The lattice parameter of b (5.72129 Å) is longer than that of a (4.69263 Å) and c (4.92805 Å). Hence, the cleavage surface propagates on the (010) plane.

The physical properties of the crystals were evaluated. The hardness of the grown crystals was similar in each direction (434, 473 and 471 kg/mm<sup>2</sup> in the [100], [101] and [001], respectively). The dielectric constant of the [100] direction was 68 compared to 49 and 57 in the [010] and [001] directions. The thermal expansion coefficients were 9.2, 8.8 and  $7.9 \times 10^{-6}$ /°C for the [100], [010] and [001] growth directions, respectively.

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## Conclusions

Single crystals of ZnWO<sub>4</sub> were grown successfully in the [100], [010] and [001] directions by the Czochralski method. The seed crystals of ZnWO<sub>4</sub> were obtained from single crystal growth on platinum wires due to capillary action from the melt. The rotation speed was controlled between 40-54 rpm with a diameter of 20 mm for the [100] direction, whereas the speed was 46 rpm with a diameter of 17 mm for the [101] direction and 63 rpm with a diameter 23 mm for the [001] direction. The ZnWO<sub>4</sub> crystals had a cleavage plane of (010). The dislocation density on the (010) plane at the center of the crystal was lower than that near the edge. The higher dislocation density at the edge of the crystals was attributed to the thermal gradients of the growing crystals. The etch pit arrangement shows that the (100) slip plane appeared to be most active during crystal growth. The formation of cracks in the grown crystals during the cooling process was prevented by annealing at 800 °C for 10 h.

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#### Acknowledgement

This study was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Education, Science and Technology (2010-0023911).

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