

# Preparation and characterization of ZnWO<sub>4</sub> nanocrystallines and single crystals

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**Abstract** ZnWO<sub>4</sub> nanocrystallines were prepared from polymeric complex method using microwave irradiation. The average nanocrystalline sizes were 18~25 nm showing an ordinary tendency to increase with the temperatures from 400 to 600°C. Bulk type single crystals of ZnWO<sub>4</sub> were grown successfully in the [100], [010] and [001] directions using the Czochralski method. The effect of the growth parameters, such as the rotation speed, pulling rate and diameter of the grown crystals, were examined. The hardness, thermal expansion coefficients and dielectric constants of the crystals were evaluated.

**Key words** Preparation, Characterization, ZnWO<sub>4</sub>, Crystal growth, CZ method

## 1. 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  $a = 4.69263 \text{ \AA}$ ,  $b = 5.72129 \text{ \AA}$ ,  $c = 4.92805 \text{ \AA}$  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> were 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 the solid-state reaction method [8], co-precipitation method [9], molten salt [10], combustion [11], mechano-chemical [12] sol-gel [13], hydrothermal reaction [14-16].

To obtain pure nanocrystalline of ZnWO<sub>4</sub>, polymerized complex method was employed. Microwave irradiation as a heating method has found and developed a number of applications in chemistry and ceramic processing. Compared with the usual method, microwave synthesis has the advantages of very short reaction time, small particle size, narrow particle size distribution, and high purity method in preparing nanocrystalline samples.

For high quality applications, ZnWO<sub>4</sub> single crystals

are generally grown by the Czochralski method [7, 17-19]. 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. The 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, the pure ZnWO<sub>4</sub> nanocrystallines were prepared from polymeric complex precursor using microwave. The ZnWO<sub>4</sub> nanocrystallines were evaluated for the crystallization process, thermal decomposition and morphology. Bulk type single crystals of ZnWO<sub>4</sub> 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 for hardness, thermal expansion coefficient and dielectric constants.

## 2. Experimental Procedure

Zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), Junsei Chemical Co. LTD., Japan), tungstic acid (H<sub>2</sub>WO<sub>4</sub>, Acros Organics, USA), were used as metallic cations. De-ionized water (DW) and citric acid (HOC(CO<sub>2</sub>H)(CH<sub>2</sub>CO<sub>2</sub>H)<sub>2</sub>,

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CA, Yukiri Pure Chemical Co, LTD., Japan) were used as polymerization/complex cation agents for the process. The citrate solution was prepared by dissolving appropriate molar ratios of citric acid in de-ionized water. Zinc acetate dehydrate and tungsten acid were dissolved in the molar ratio of total chelate metal cations (TO) and citric acid (TO : CA molar ratio = 1 : 5). By keeping the solution at a temperature of 50°C for 60 min under constant stirring, the solution became more viscous pale-yellow solution. A domestic microwave oven with 650 W power (Samsung Electronic Corp. Korea) was conducted for the polymerizations of the precursors. Heat-treatment of the precursor was performed at various temperatures from 300 to 600°C for 3 h.

The growth equipment for the Czochralski method was fabricated using a furnace assembly. The  $\text{ZnWO}_4$  melts were prepared from polycrystalline  $\text{ZnWO}_4$ , 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 thyristor from Eurotherm Co. The single crystals were pulled along the crystallographic axes with a diameter of 0~3.5 cm at pulling rate of 0~100 mm/h and a rotation speed of 0~68 rpm. The temperatures were controlled precisely with the measurements on the surface of the  $\text{ZnWO}_4$  melts between 1230~1235°C during growth. The polycrystalline  $\text{ZnWO}_4$  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 nanocrystalline after calcination was identified by X-ray diffraction (XRD,  $\text{CuK}\alpha$ , 40 kV, 30 mA, Rigaku, Japan) at a scan rate of 3°/min. The polycrystalline  $\text{ZnWO}_4$  calcined at 900°C for 12 h was identified using the reported crystallographic data for  $\text{ZnWO}_4$  (JCPDS Code 15-0774). Fourier transform infrared spectroscopy (FT-IR, Model IR 550, Magna, Nicolet Company) was used for the interpretation of the thermal-decomposition behavior of the precursors and heat-treated powders in frequency ranges from 400 to 4000  $\text{cm}^{-1}$ . The FT-IR spectra were measured in KBr pellets. The average crystallite size of the heat-treated powders was calculated using the XRD line broadening method through the Scherrer's relationship.

### 3. Results and Discussion

Fig. 1 shows XRD results for the phase identification

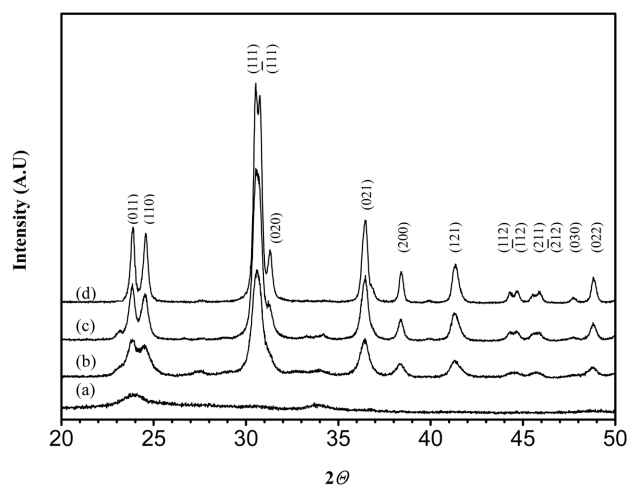


Fig. 1. XRD patterns of the  $\text{ZnWO}_4$  nanopowders heat-treated at (a) 300, (b) 400, (c) 500 and (d) 600°C for 3 h.

of the nanocrystallines heated for 3 h as a function of heating temperature. In Fig. 1(a), the powders at 300°C were amorphous without any crystallized phases. Above 400°C, in Fig. 1(b)~(d) the peaks at  $2\theta = 23.8, 24.6, 30.5, 30.7, 31.3, 36.3$  were  $\text{ZnWO}_4$  (011), (110), (111), (111), (020), (021), respectively. All peaks in Fig. 1(b)~(d) are on basis of the crystallographic data of the known structure of  $\text{ZnWO}_4$  (JCPDS Code 15-0774), suggesting the lattice constants are  $a = 4.69263 \text{ \AA}$ ,  $b = 5.72129 \text{ \AA}$ ,  $c = 4.92805 \text{ \AA}$  and  $\beta = 90.6321^\circ$  [1].

Fig. 2(a)~(e) shows the FT-IR spectra for the precursor and powders heated at 300~600°C. For the precursor (Fig. 2(a)), the bands at 1620, 3445  $\text{cm}^{-1}$  (O-H stretching modes), 1736, 1395  $\text{cm}^{-1}$  (carboxyl group stretching modes), 1278  $\text{cm}^{-1}$  ( $\text{CH}_3$ ) and absorption bands near

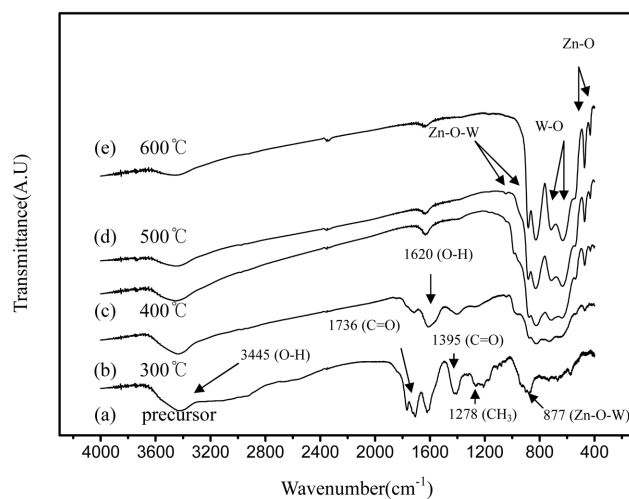


Fig. 2. FT-IR spectra of the  $\text{ZnWO}_4$  (a) precursor and nanopowders heat-treated at (b) 300, (c) 400, (d) 500 and (e) 600°C for 3 h.

Table 1  
Average crystallite size of ZnWO<sub>4</sub> nanocrystallines as a function of heating temperature

Temperature (°C)	Average crystallite size (nm)
300	18
400	20
500	23
600	25

877 cm<sup>-1</sup> (W-O-Zn stretching mode) seem to define the relatively dehydrated (Zn-W)-citrate polymeric complex. Heat-treatment at 300°C in Fig. 2(b) leads to a significant change in its infrared spectra. A decrease of the band at 1736, 1395 and 1620 cm<sup>-1</sup> is produced, while the bands at 1278 cm<sup>-1</sup> disappear. At 400°C in Fig. 2(c), the bands of the carbonyl group disappear, while new absorption bands appear between 400 and 900 cm<sup>-1</sup>. In Fig. 2(c)~(e), the bending and stretching vibrations of Zn-O (473, 532 cm<sup>-1</sup>), W-O (633, 710 cm<sup>-1</sup>) and Zn-O-W bond (834, 877 cm<sup>-1</sup>) could be identified to the synthesized ZnWO<sub>4</sub>.

Table 1 shows the average crystallite sizes for the heat-treated nanopowders calculated by XRD line broadening method. The average crystallite size of the heat-treated nanopowders was calculated using the X-ray diffractometry line broadening method through the following Scherrer's equation.

$$D = K\lambda/(\beta\cos\theta), \quad (1)$$

where D is the crystallite size,  $\lambda$  is wavelength of the radiation ( $\lambda = 1.5418 \text{ \AA}$ ),  $\theta$  is the Bragg's angle,  $\beta$  is the full width at half maximum (radian) and K is constant

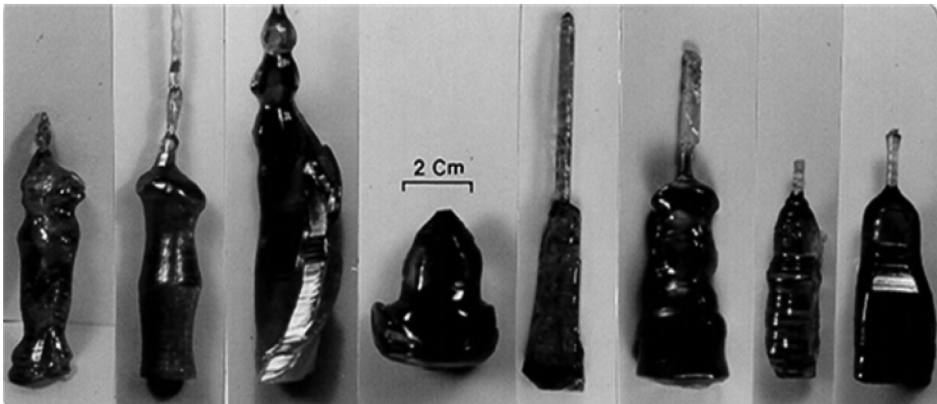
(0.9). The calculated average crystallite sizes in Table 1 were 18, 20, 23 and 25 nm for the heat-treated nanopowders at 300, 400, 500 and 600°C, respectively.

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 the 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 the crystallographic direction after identifying the crystal orientation by Laue back reflection. 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 grown single crystals of ZnWO<sub>4</sub>. An increase in the crystal diameter results in an increase in the centrifugal force at the crystal periphery, which may bring a change in fluid-flow convection of the liquid in contact with the growing interface.

Fig. 3 shows schematic diagrams of the relationships

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

Crystal shape								
Nomination	A	B	C	D	E	F	G	H
Rotation speed (rpm)	15, 26	16	39	55	68	54, 40	46	63
Max. diameter (mm)	21	16	23	35	12	20	17	23

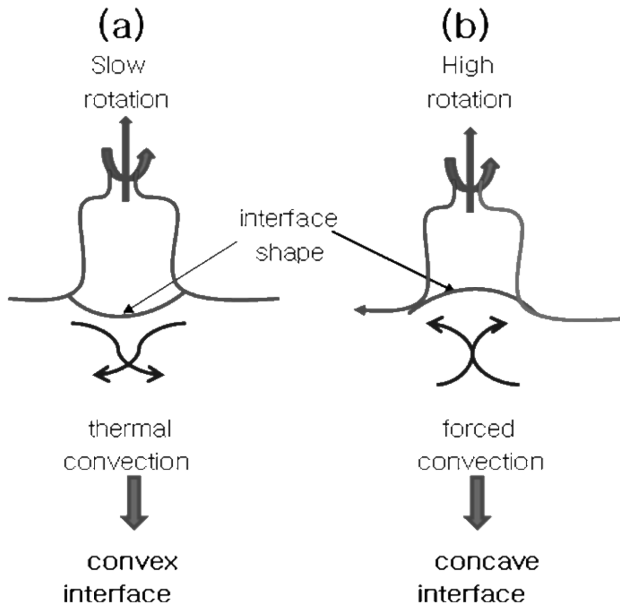


Fig. 3. Schematic diagram of the relationships between fluid-flowing convection models and interface shape at different crystal rotation speeds.

between the fluid-flowing convection models and interface shape at different crystal rotation speeds. Since interface 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 the crystal rotation speed. When the crystal rotation speed was relatively low (Fig. 3(a)), natural convection going just beneath the interface is predominant. The solid-liquid interface shape of the crystal growth of  $\text{ZnWO}_4$  became convex below 55 rpm. Forced convection stronger than natural convection was produced when the crystal rotation speed is high in Fig. 3(b). The forced convection is caused by a stream of hot liquid inside the melt going up toward the interface. The solid-liquid interface shape of the crystal growth of  $\text{ZnWO}_4$  becomes concave toward 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:

$$\sigma = \eta c_p / k = \nu / k, \quad (2)$$

$$R_a = L^3 \beta g (T_1 - T_2) / \nu k, \quad (3)$$

where  $\eta$  is the viscosity,  $c_p$  is the latent heat at a constant pressure,  $k$  is the thermal diffusivity,  $\nu$  is the kinet-

matic 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 a 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:

$$R_a = \sigma G_r \quad (4)$$

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

$$R_c = LV/\nu = d/2 \cdot \pi w d / \nu, \quad (5)$$

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

By normalizing the two measures of  $G_r$  and  $R_c$  with respect to the viscosity,

$$d = (4g\beta TR^3 \pi^{-2})^{1/4} / w^{1/2}, \quad (6)$$

was obtained because fluid-flow interacts through drag. Eq. (6) 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-bubbles 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 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 interface 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.

The physical properties of the crystals were evaluated in Table 3. 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  $7.9 \times 10^{-6}/^\circ\text{C}$  for the [100], [010] and [001] growth directions, respectively.

Table 3  
Hardness, dielectric constant, thermal expansion constant of the grown ZnWO<sub>4</sub> single crystals

Property direction	Hardness (kg/mm <sup>2</sup> )	Dielectric constant	Thermal expansion coefficient (10 <sup>-6</sup> /°C)
[100]	434	68	9.2
[010]	473	49	8.3
[001]	471	57	7.8

#### 4. Conclusions

ZnWO<sub>4</sub> nanocrystallines were prepared from polymeric complex precursor using microwave irradiation. The average crystalline sizes were 18~25 nm showing an ordinary tendency to increase with the temperatures from 400 to 600°C. Single crystals of ZnWO<sub>4</sub> were grown successfully in the [100], [010] and [001] directions by the Czochralski method. 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 dielectric constant of the [100] direction was 68 compared to 49 in the [010] direction and 57 in the [001] direction. The thermal expansion coefficients were 9.2, 8.8 and 7.9 × 10<sup>-6</sup>/°C for the [100], [010], [001] directions, respectively.

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