Top-seeded solution crystal growth of Noncentrosymmetric and Polar $\text{Zn}_2\text{TeMoO}_7$ (ZTM)

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Abstract

A top-seeded solution growth (TSSG) method was used to grow large, centimeter size, crystals of $\text{Zn}_2\text{TeMoO}_7$ (ZTM) - a noncentrosymmetric and polar material. A TeO_2 - MoO_3 mixture in combination with the parent compound was used as a flux. The morphologies of the crystals can be controlled by different rotation speeds. Optical spectra indicate that ZTM is transparent up to $5.25\ \mu\text{m}$ with a UV absorption edge of 300 nm. In addition, the refractive index along the optical x , y , and z axes was measured at different wavelengths.

Keywords: Top-seeded solution growth (TSSG), $\text{Zn}_2\text{TeMoO}_7$ crystal, refractive index

Introduction

The single crystal growth of multi-functional materials is necessary in order to fully investigate their physical properties, as well as completely develop structure-property relationships.[1] This is especially true with non-centrosymmetric polar materials. Crystallizing in one of 10 polar crystal classes (1, 2, 3, 4, 6, m, mm2, 3m, 4mm, or 6mm),[2] polar materials may exhibit a range of functional properties including piezoelectricity, ferroelectricity, pyroelectricity, and second-order non-linear optical phenomena.[3-9] Recently, we reported on the synthesis and structure of $\text{Zn}_2\text{TeMoO}_7$, [10] a polar material that exhibits a three-dimensional crystal structure with ZnO_4 , ZnO_6 , MoO_4 , and TeO_3 polyhedra. Our previous work described the origin of the second harmonic generation (SHG) response for ATeMoO_6 ($A = \text{Mg}$, Zn , or Cd ; ZnTM , or CdTM). Using a covalency metric, we were able to account for all contributions - electronic and geometric - that determine the final SHG response.[11] In this paper, we report the large, centimetre size, crystal growth of $\text{Zn}_2\text{TeMoO}_7$ through top-seeded solution growth (TSSG) method. The large single crystals were grown b -axis oriented seeds. In addition to the crystal growth, we also investigate the crystal morphologies with respect to the growth conditions, and determine the refractive indices at a variety of wavelengths.

Background

History of Top-seeded solution growth (TSSG) method

The top-seeded solution growth (TSSG) technique, developed from flux method, was

initially used at Bell Laboratories to grow high quality potassium niobate, KNbO_3 , single crystals.[12] The fundamental difference between TSSG and conventional flux methods is that a crystal seed is involved, and the seed is in contact with the top of the high temperature solution - hence the designation 'top-seeded solution'. At this time, 1957, however, the technique was not called TSSG. A few years later in 1961, Reynolds and Guggenheim developed a two zone temperature difference method.[13] The high temperature zone provides nutrient to the low temperature zone wherein crystallization occurs. The temperature gradient between the two zones was by two baffles inside and outside the crucible. Using this technique, they obtained better quality CoFe_2O_4 single crystals.[13] In 1962, Laudise et. al investigated both TSSG (slow cooling) and the temperature gradient method to grow $\text{Y}_3\text{Fe}_5\text{O}_{12}$ (YIG) single crystals. They discussed the relationship between growth rate and stirring rate well as the crucible parameters.[14] At the same time, Linares investigated the phase diagram of $\text{BaO-B}_2\text{O}_3\text{-Y}_3\text{Fe}_5\text{O}_{12}$ and later attempted to grow YIG using the TSSG technique.[15, 16] He also discussed the influence of pulling rate and rotation speed the crystal quality. Later, Aucoin et. al also utilized the TSSG method to grow hexagonal ferrite crystals using $2\text{BaO}\cdot\text{B}_2\text{O}_3$ as a flux.[17] In 1967, Kestigian YIG single crystal growth by the combined Czochralski-molten salt solvent technique, which in principle is the same as the pulling TSSG method.[18] The phrase 'Top-seeded solution growth' appeared in print for the first time in 1970 when Goodrum demonstrated the growth of tetragonal GeO_2 single crystal.[19] The quality of GeO_2 crystals from pulling and without pulling TSSG methods were compared, better quality crystals were grown using TSSG without pulling. In 1971, Belruss et. al briefly summarized the TSSG method for growing oxide crystals from non-stoichiometric melts.[20] They indicated that the TSSG method is suitable where very high quality crystals are necessary, and controlled size and shape are required. This is in contrast to the usual flux methods as well as Czochralski, floating zone, flame fusion methods. The dislocation density of SrTiO_3 single crystal grown by is $\sim 10^6$ times less compared with the flame fusion method.[20] The major advantage the TSSG method is that crystal growth may be performed at a temperature well the melting point of the material to be crystallized. In summary, the TSSG method is ideal for growing materials in the following categories[21]: (1) Materials that melt incongruently. (2) Materials that undergo a solid state phase transition that results in severe strain or fracture. Crystal growth should occur at a temperature below this transition. (3) Materials that have very high vapor pressure at the melting point. (4) Materials that become non-stoichiometric attributable to the loss of a volatile constituent. (5) Refractory materials that are technically difficult to grow from the because of crucible issues or furnace problems. Belruss et. al also pointed out that the main disadvantage in this method is the low solubility which leads to very low growth rates and solvent inclusions attributable to imperfect temperature control.[20]

Since the 1980's the TSSG method has been used to grow crystals of non-linear (NLO) materials such as KTiPO_4 (KTP) and LiB_3O_5 (LBO), $\beta\text{-BaB}_2\text{O}_4$ (BBO), (BIBO), and $\text{K}_2\text{Al}_2\text{B}_2\text{O}_7$ (KABO),[22-42] as well as high T_c superconductors such as

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$, $\text{YBa}_2\text{Cu}_3\text{O}_{6+d}$, $\text{Y}_{1-x}\text{Ca}_x\text{Ba}_2\text{Cu}_3\text{O}_{7-\delta}$, and $\text{Nd}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_{6+d}$. [43-48] More recently the TSSG method has been used to grow α - and β -phase $\text{BaTeMo}_2\text{O}_9$, $\text{Na}_2\text{TeW}_2\text{O}_9$, $\text{Cs}_2\text{TeMo}_3\text{O}_{12}$, $\text{Na}_2\text{Te}_3\text{Mo}_3\text{O}_{16}$, MnTeMoO_6 , ZnTeMoO_6 , MgTeMoO_6 , LiFeP_2O_7 , LiCrP_2O_7 , and $\text{K}_3\text{V}_5\text{O}_{14}$. [49-87]

Equipment

The equipment for TSSG method has been described many times in the 1960's and 70's. [12, 13, 16, 17, 19, 20] A schematic diagram of the furnace used for TSSG in our laboratory is shown in Figure 1.

Figure 1. The schematic diagram of the TSSG furnace.

The furnace chamber is wound by heating coil to form a 45cm-length heating zone. An AI-808P temperature controller is used to program and control the temperature of the furnace. The accuracy is 0.1°C (Fuzhou Keleishi Test Equipment Co., LTD). In order to limit the natural temperature gradient of the furnace, a crucible - usually platinum - is placed in the center of the chamber. A heat-insulating lid with three holes covers the top of the furnace. The center hole is for the crystal seed rod, whereas the other two are used for observation of growth process. A pulling system employs a reversible motor with a pulling speed from 0.0001 - 2.0 mm/min. The rotation system also employs a reversible motor to allow both clockwise and counter-clockwise rotations are speeds between 0.5 - 50.0 rpm. Both the pulling and rotating motors are controlled by the automatic crystal growth system (KLST V1.02, Fuzhou Keleishi Test Equipment Co., LTD).

Top-Seeded Solution Growth (TSSG) process

Prior to TSSG process, a suitable flux system should be available. A phase diagram is ideal to determine a suitable flux system. However, for newly discovered materials a phase-diagram may not be available. There are, fortunately, many ways to determine a suitable flux.[21] The steps for successful TSSG are given below. First, powder samples are synthesized and their purity is confirmed by laboratory X-ray diffraction. The decomposition or melting temperature is determined by thermal analysis, i.e. differential scanning calorimetry (DSC), or thermogravimetric (TG) / differential thermal analysis (DTA) measurements. This will enable the determination of the temperature range for crystal growth. Second, the pure polycrystalline sample is together with the appropriate flux. Here a variety of fluxes may be used to determine the correct one. The mixture is added to a platinum crucible, that is placed in the of the furnace chamber. The furnace is heated to a temperature determined from the thermal analysis measurements to form a homogeneous high temperature solution. It sometimes necessary to stir the solution to accelerate the formation of this solution. Once a homogenous solution is formed - this may be observed through one of the in the lid - a platinum wire is dipped into the solution. The temperature is slowly decrease - typically a cooling rate from 0.25 to 2 °C/d is needed in order for spontaneous crystallization to occur. When sufficient seed crystals have been grown, the platinum wire is removed from the solution and the furnace is cooled rapidly to room temperature. The orientation of the seed crystals can be determined by an X-ray diffractometer before being used to grow larger single crystals. The seed crystals may also be used to determine the saturation point of the high temperature solution through observing the growth or dissolution of the crystal while soaking in the solution. To grow a high quality single crystal, an oriented seed is attached to the platinum wire and introduced to the high temperature solution 2-5 °C higher than the saturation temperature. Figure 2 shows a $\text{Zn}_2\text{TeMo}_2\text{O}_7$ seed crystal attached to a platinum wire. A slightly elevated temperature is used in order to dissolve any impurities on the surface of the seed. Once this is complete, the temperature is decreased to the saturation point over the next 15 minutes. The furnace is then cooled at a rate of 0.25 - 2.0 °C/d to grow the crystal. Meanwhile, the seed rotates at of speed of 5-50 rpm depending on the viscosity of the melt, i.e. the greater the viscosity the more rapid the rotating speed. Typically, a large (centimeter) size crystal may be grown in 1-3 weeks.

Figure 2. $\text{Zn}_2\text{TeMo}_2\text{O}_7$ seed tied with thin platinum wire (~0.2 mm in diameter) and then attached to a twisted thick platinum wire (~ 1 mm in diameter).

Experimental Section

Single crystal growth

Single crystals of $\text{Zn}_2\text{TeMoO}_7$ were grown by the top seeded solution growth (TSSG) method. Polycrystalline $\text{Zn}_2\text{TeMoO}_7$ retrieved from solid state reaction was mixed thoroughly with TeO_2 and MoO_3 in the molar ratio $\text{Zn}_2\text{TeMoO}_7$: TeO_2 : MoO_3 = 1 : 0.2 : 0.2, and placed in a platinum crucible. The mixture was heated to 800 °C in a vertical furnace equipped with a Pt-Rh/Pt thermocouple and an AI-808P controller. The temperature was held for 48 h in order to form a homogenous melt. Once a homogeneous melt had formed, the temperature of the melt was rapidly cooled down to 750 °C in 30 minutes. A piece of platinum wire held on an alumina rod was then dipped into melt. The melt was subsequently cooled slowly at a rate 5 °C/h. At 722 °C, it was observed that several small crystals had spontaneously nucleated on the platinum wire. These small crystals were carefully extracted and confirmed to be $\text{Zn}_2\text{TeMoO}_7$ by powder x-ray diffraction (see Figure 3). The exact saturation temperature, 735 °C, was determined by observing the growth or dissolution of a seed crystal while soaking in the melt. After several growth runs with a seed crystal, a crystal of sufficient size was obtained and cut as an oriented crystal seed. In order to obtain a large and high quality single crystal, a *b*-oriented seed was introduced into the homogenous melt at a rotation rate of 10 rpm at 2 °C higher than the saturation temperature. This was followed by decreasing the temperature to the saturation point over 15 minutes. From the saturation temperature, the melt was cooled at a rate of 0.25 °C/d to about 1 °C below the saturation point. After 4 days growth, an as-grown single crystal was then hung above the melt surface and cooled slowly to room temperature. Additional single crystals were obtained using the same procedure but different rotation speeds (see Figures 4a and 4b).

Figure 3. Powder X-ray diffraction of spontaneous crystalized $\text{Zn}_2\text{TeMoO}_7$ crystal.

Figure 4. As grown $\text{Zn}_2\text{TeMoO}_7$ crystals at rotation speed of 10 rpm (a), and 30 rpm (b), ideal morphology (c), and crystal wafer (d).

Powder X-ray Diffraction

Powder X-ray diffraction data were collected using a PANalytical X'Pert PRO diffractometer equipped with Cu K α radiation ($\lambda = 1.54056 \text{ \AA}$) in the 2θ range from 10° to 70° . The experimental and calculated patterns are in good agreement (Figure 3).

Optical Spectra Measurement

UV-Vis transmission spectra were collected with a Varian Cary 5000 scan UV-Vis-NIR spectrophotometer over the spectral range of 250-2500 nm at room temperature. Infrared (IR) transmission spectra were recorded on a Matteson FTIR 5000 spectrometer in the $400 - 4000 \text{ cm}^{-1}$ range perpendicular to the (010) wafer (see Figure 4d).

Refractive Indices Measurements

A (020) wafer was polished using the Unipol-300 grinding/polishing machine (MTI Co.). One of the optical axes, y -axis, is coincident to the crystallographic b -axis. The other two optical axes x , and z in crystallographic ac -plane were determined by a polarized microscope (Olympus BX41, Leeds Instruments, Inc.). Following, the refractive indices along x , y , and z axes were measured using the Metricon Model 2010/M prism coupler (Metricon Co.) at different wavelengths - 532, 633, 980, 1310, and 1550 nm.

Piezoelectric Measurements

Direct piezoelectric coefficients were collected on YE2730A d_{33} meter (APC international, Ltd.). According to the IEEE standard,[88] a Y -cut sample (faces perpendicular to b -axis) was cut from $\text{Zn}_2\text{TeMoO}_7$ single crystal with the size of 6 (width) $\times$ 7 mm (length) $\times$ 1 mm (thickness) to perform the measurements.

Results and Discussion

Growth and Morphologies of $\text{Zn}_2\text{TeMoO}_7$ Crystal

Although thermal analysis indicated that $\text{Zn}_2\text{TeMoO}_7$ melts congruently,[10] crystal growth from a stoichiometric melt was not successful. As such, the TSSG method was used with a $\text{TeO}_2\text{-MoO}_3$ flux. Well-shaped transparent colorless single crystals of $\text{Zn}_2\text{TeMoO}_7$ were grown by the TSSG method using b -oriented seeds. Figures 4a, b, and c show the as-grown crystals at different rotation speeds and simulated with indexed (hkl) planes by Bravais, Friedel, Donnay and Harker (BFDH) theory.[89, 90] As shown in Figure 4a, hereafter called crystal a, the crystal grown with a rotation speed of 10 rpm has a size of $16 \times 8 \times 2 \text{ mm}^3$ and reveals a morphology enclosed by (001), (110), $(-1-11)$, (011), and (01-1) faces. The other crystal, hereafter called crystal b, grown with a rotation speed of 30 rpm (Figure 4b) has a size of $18 \times 13 \times 1 \text{ mm}^3$ and shows morphology enclosed by (020), (001), $(-1-11)$, (110), (-101) , and (100) faces.

Both crystals are similar to the simulated morphology (Figure 4c). However, there are still distinct differences between these two crystals. Along [020] (2mm in thickness) and [001] (13 mm in width) directions, the size of crystal b is much larger than that of crystal a which are 1 mm and 8 mm respectively. Although the growth mechanism is not well understood, diffusion-controlled crystal growth can aid in our understanding.[91] The diffusion layer between the crystal and melt controls the transport speed of the ‘growth unit’ between the crystal and the melt. The ‘growth’ is defined as the ‘unit’ from the flux that adheres to the crystal surface and promotes crystal growth. A thicker diffusion layer results in a slower transport speed of the ‘growth unit’. The thickness of this diffusion layer is related to the rotation speed. Lower rotation speed results in a thicker diffusion layer. Thus at lower rotation speed, the growth rate of the crystal is determined by the thickness of the diffusion layer regardless of the growth rate along specific crystallographic directions. Conversely, at higher rotation speeds the growth around crystal faces is faster attributable to the thinner diffusion layer. In this situation, a faster growth rate along certain directions is dominant. Based on the diffusion-controlled theory, we can explain the size deviation along different directions of crystal b is larger than crystal a. At low rotation speeds (rpm), the growth rate is determined by the diffusion layer. Therefore, the size is small along different directions for crystal a, as the flux is a homogenous system. At high rotation speed (30 rpm), the growth rate is determined by the anisotropic growth rate along specific crystallographic directions. From crystal b, it is clear that the rate along [001] increases and the growth rate along [020] decreases. This also gives a hint that we can control the crystal size and morphology by controlling the rotation rate.

Optical Spectra Analyses of $\text{Zn}_2\text{TeMoO}_7$ Crystal

The UV-Vis transmission spectra and infrared (IR) transmission spectra along *b*-axis are shown in Figures 5 and 6 respectively. From the UV-Vis transmission spectra, we can clearly see that the UV absorption edge is around 300 nm which confirmed its gap (4.1 eV) reported earlier based on powder measurement.[10] From the IR transmission spectra, the $\text{Zn}_2\text{TeMoO}_7$ crystal shows a well transmission ratio up to μm with an IR absorption edge at 5.75 μm . Table 1 lists the transmission spectra of all the telluromolybdates and tellurotungstates crystals grown recently. In Table 1, $\text{Zn}_2\text{TeMoO}_7$ crystal has the broadest transmission range. Considering its noncentrosymmetric and polar nature, the $\text{Zn}_2\text{TeMoO}_7$ crystal may find potential applications in frequency conversion in the mid-IR nonlinear optical field.

Figure 5. UV-Vis-NIR transmission spectra of $\text{Zn}_2\text{TeMoO}_7$ crystal.

Figure 6. Infrared (IR) transmission spectra of $\text{Zn}_2\text{TeMoO}_7$ crystal.

Table 1. Transmission range of $\text{Zn}_2\text{TeMoO}_7$ crystal comparing with other telluromolybdates and tellurotungstates crystals.[72, 75, 79-82, 87, 92]

Crystal	Transmission range (μm)
$\text{Zn}_2\text{TeMoO}_7$	0.3-5.75
$\text{BaTeMo}_2\text{O}_9$	0.5-5.0
$\text{Na}_2\text{Te}_3\text{Mo}_3\text{O}_{16}$	0.42-5.4
ZnTeMoO_6	0.35-5.4
MgTeMoO_6	0.36-5.2
MnTeMoO_6	0.41-5.4
CdTeMoO_6	0.345-5.4
$\text{Cs}_2\text{TeMo}_3\text{O}_{12}$	0.43-5.38
$\text{Na}_2\text{TeW}_2\text{O}_9$	0.36-5.0

Refractive Index Measurement

The refractive indices $n(\lambda)$ of $\text{Zn}_2\text{TeMoO}_7$, as a function of wavelength λ , were measured by using Metricon Model 2010/M prism coupler. The accuracy of the measurements is estimated to be 2×10^{-4} . When monochromatic sources are incident the (010) plane with polarization parallel to the x-, and z-axes respectively (TE mode), two orthorhombic refractive indices n_x and n_z are obtained. While monochromatic

sources are vertically incident to the (010) plane (TM mode), another refractive index n_y is obtained. The refractive index n_y polarization direction is parallel to crystallographic b -axis. The measured refractive index along x, y, and z axes at different wavelengths are listed in Table 2. The dispersion parameters of the refractive index n_i were fitted by the least-squares method according to the Sellmeier equation:[93]

$$n_i^2 = A + \frac{B}{\lambda^2 - C} - D\lambda^2,$$

where λ is the wavelength in micrometers and A, B, C, and D are the Sellmeier parameters. For each refractive index, the four coefficients are listed in Table 3. To verify the obtained results, we estimated the differences between the measured data and the calculated values. The curves obtained from the fit according to this equation and the experimental data are in good agreement, as can be seen in Figure 7. The larger difference between the values of n_z and n_y than that between the values of n_y and n_x indicate that the $\text{Zn}_2\text{TeMoO}_7$ crystal is an optically positive biaxial crystal.

Table 2. Measured refractive index along x, y, and z axes at different wavelengths.

Wavelength (μm)	n_x	n_y	n_z	$\Delta n (n_z - n_x)$
0.532	1.9625	1.9737	2.0466	0.0841
0.6328	1.9435	1.9539	2.0209	0.0774
0.986	1.9180	1.9268	1.9877	0.0697
1.3024	1.9092	1.9180	1.9837	0.0745
1.5533	1.9047	1.9133	1.9717	0.067

Table 3. Sellmeier coefficients derived from the measured refractive indices

Sellmeier coefficients	n_x	n_y	n_z
A	3.63032	3.65808	3.90338
B	0.05457	0.05993	0.06509
C	0.03947	0.03352	0.05558
D	0.01059	0.00933	0.01464

Figure 7. Dispersion of the refractive indices along x, y, and z optical axes and calculated fit curves from the Sellmeier coefficients for $\text{Zn}_2\text{TeMoO}_7$ crystal.

Piezoelectricity of $\text{Zn}_2\text{TeMoO}_7$ Crystal

Piezoelectric measurements were performed on a Z-cut $\text{Zn}_2\text{TeMoO}_7$ crystal by direct methods. The estimated d_{22} , 6.7 pC/N, is listed in Table 4 along with comparisons to other telluromolybdates and tellurotungstates crystals. From Table 4, crystal shows a comparable piezoelectric coefficient with some of the telluromolybdates and tellurotungstates crystals. All these telluromolybdates and tellurotungstates crystals have much larger piezoelectric coefficient than commercial piezoelectric α -silica crystal ($d_{11} = -2.31$ pC/N).[71]

Table 4. Piezoelectric Coefficients of $\text{Zn}_2\text{TeMoO}_7$ crystal comparing with other telluromolybdates and tellurotungstates crystals.[71, 75, 78]

Piezoelectric Coefficients (pC/N)	Crystals			
	$\text{Zn}_2\text{TeMoO}_7$	$\text{BaTeMo}_2\text{O}_9$	$\text{Cs}_2\text{TeMo}_3\text{O}_{12}$	$\text{Na}_2\text{TeW}_2\text{O}_9$
d_{11}	0	0	0	4.0
d_{22}	6.7	-10.8	0	0
d_{33}	0	0	20.3	13.9

Conclusion

Top-seeded solution growth (tssg) techniques may be used to grow large crystals - centimeter size - of a variety of functional materials. Critical to the tssg method are the determination of the flux, and the subsequent growth of a high quality seed crystal. Once a high quality seed crystal is grown, the growth of a large single crystal may be accomplished in 1-3 weeks. We used the tssg method to grow large crystals of non-centrosymmetric and polar $\text{Zn}_2\text{TeMoO}_7$. The material has a large transparency range, 0.3 - 5.75 μm , and a birefringence of ~ 0.07 at 1302nm. As such the material may find uses as a mid-IR NLO material.

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[Graphical abstract]

Top-seeded solution crystal growth of Noncentrosymmetric and Polar $\text{Zn}_2\text{TeMoO}_7$ (ZTM)

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[Graphical abstract]

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Large, centimeter size crystals of noncentrosymmetric and polar $\text{Zn}_2\text{TeMoO}_7$ (ZTM) were successfully grown by a top-seeded solution growth (TSSG) method. A TeO_2 - MoO_3 mixture was used as a flux with the parent compound. The morphologies of as-grown single crystals with *b*-oriented seeds can be controlled at different rotation speeds. The optical spectra indicate that ZTM can transmit up to $5.25\mu\text{m}$ with a UV absorption edge of 300 nm. The refractive index along optical *x*, *y*, and *z* axes was measured as well at different wavelengths.