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Czochralski crystal growth of $Zn_2Te_3O_8$

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ABSTRACT

Crystal growth in the ZnO–TeO_2 system was investigated using Czochralski technique in a 2.5 kHz induction heating system. Several runs and experiments helped optimize the $Zn_2Te_3O_8$ growth process, which was limited by quite a few difficulties. These difficulties include the evaporation of TeO_2 material above 700 °C, the formation of more than one phase during the growth, and the lack of a $Zn_2Te_3O_8$ single crystal to initiate the growth. The main and most persisting problem is that there is no stable phase in the system that forms a line compound at which the crystal growth should be attempted. The resulting material was formed of many single crystals and a mixture of other phases. Single $Zn_2Te_3O_8$ crystals of sizes ranging between 50 and 200 mm^3 resulted when the pulling rate was 1.1 mm/h and the rotation speed was 12 rpm. These single crystals were extracted and their optical and electrical properties were studied for the first time. Using other pulling rates and rotation speeds returned smaller crystals with sizes ranging between 15 and 35 mm^3.

1. Introduction

Although the development of crystal growth started early in the 20th century [1], Czochralski (CZ) crystal growth was only well established by the mid-1950s. It had shown a great potential to pull oxide crystals [2–4], as well as semiconductor crystals such as silicon [5] and germanium [6]. Many other types of crystals were also grown by the CZ technique [7–9]. In CZ growths, the material is placed inside a suitable crucible and heated either by a radio frequency (RF) coil [10] or a regular ceramic heater. The mixture of the materials is preferred to be at the congruent melting point of the constituents to avoid complications of forming undesired phases while growing. Some researchers were able to pull single crystals at incongruent points [11]. Other workers reported the growth of single crystals from non-stoichiometric melts [12,13], while others grew multi-phase semiconductor crystals at the peritectic phase transformation [14].

The II–VI oxide crystals have high refractive indices and are optically active [15]. They present non-linear optical properties [11,16], second harmonic generation effect, and birefringence. This makes the crystals to be good materials in manufacturing fiber optics, polarizers, wave plates, depolarizers, and optical filters. The zinc oxide (ZnO) crystals have a wide band gap width of 3.3 eV at room temperature [17]. This makes the crystal a good candidate for applications in optoelectronic devices such as short-wavelength lasers and light-emitting diodes [18]. The average refractive index and the average static dielectric constant of ZnO crystals are 2.0 and 10.0, respectively [19]. Paratellurite (TeO_2) crystals have useful applications in acousto-optic devices [20,21], many of which are used in data display devices [22]. TeO_2 crystal has a band gap of 3.5 eV [23] and a refractive index of about 2.2 [19].

There are several phases that could form as ZnO–TeO_2 melt is cooled down [24]. A quick investigation of the phase diagram and phase formation was done by several authors [25–28]. Most of their studies focused on the glass form of the material as it is quenched from melt. In this research paper, the procedure to grow $Zn_2Te_3O_8$ single crystals was established and optimized for the first time. The sizes of these crystals permitted the performance of important electrical and optical measurements.

2. Experimental procedure

ZnO and TeO_2 powders (Alpha Aesar 99.999%) were mixed using a jar mill. The average mixing time was 15 h. Grinding zirconia beads were used to enhance mixing and milling. The mixture was melted in a platinum crucible heated by a RF coil in

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Table 1
A summary of 35.5:64.5 runs used to grow $Zn_2Te_3O_8$ single crystals

Run #	Crucible	Seed used	Pulling speed (mm/h) ± 0.1 mm/h	Rotation speed (rpm) ± 1 rpm	General color	Single crystal size (mm^3)	Microprobe analysis of single crystals
1	60 ml Pt dish	$Zn_2Te_3O_8$ with minor TeO_2 inclusions	0.9	10	Yellow	~5–15	$Zn_2Te_3O_8$ only
2	60 ml Pt dish	$Zn_2Te_3O_8$ from $ZTO_8)_1$	0.9	15	Light yellow. Single crystals are greenish	10–35	$Zn_2Te_3O_8$ with minor TeO_2 inclusions
3	15 ml Pt dish	Platinum wire	0.8	20	Yellow and green	~5–20	N/A
4	125 ml 95%Pt/5%Au straight wall	Multicrystals from a previous 35.5 run	1.1	12	Clear white and green	50–200	$Zn_2Te_3O_8$ only done by X-ray

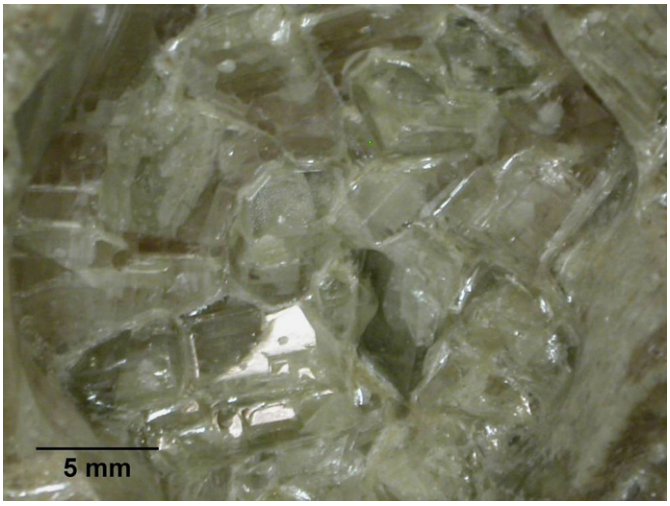

Fig. 1. A bottom view of the 35.5:64.5 as grown crystals.

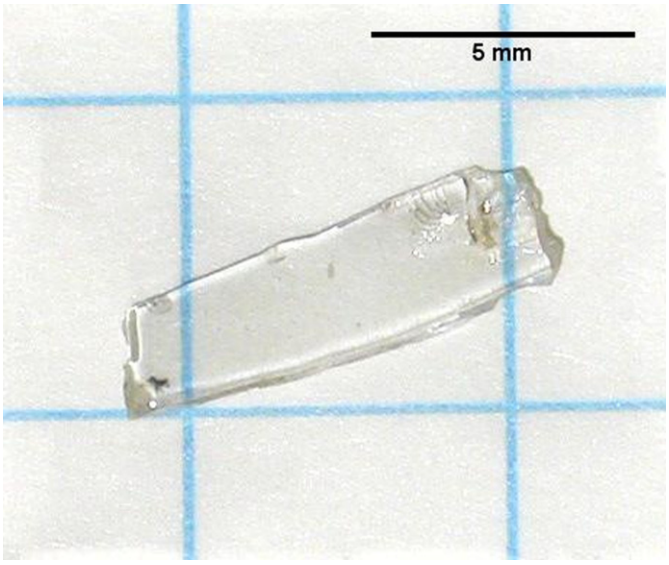

Fig. 2. $Zn_2Te_3O_8$ single crystal.

air. The crucible was placed inside a cylindrical build up constructed from insulating materials. A set of thermocouples were used to measure the temperature of the crucible. After the material melted, the temperature was raised between 20 and 40 °C and kept at that temperature to stabilize for 1 h. A seed attached to the seed holder was dipped onto the melt surface. The seed was made to rotate at a speed between 10 and 15 rpm while being pulled at a speed ranging from 0.8 to 3.0 mm/h.

The most frequent mole percentages that were tested for growths are (in ZnO:TeO_2 order): 33.3:66.7, 36.5:63.5, and 35.5:64.5. The choices were limited by several factors, such as the melting temperature and phase formation. Surplus phases always formed during each growth. Microprobe analysis of the grown single crystals of 33.3:66.7 showed an excess of TeO_2. The second mole percentage (36.5:63.5) formed 5–15 mm^3 crystals. Other growths showed that the 35.5:64.5 mol% formed single crystals of sizes that are bigger than 35 mm^3 and less surplus phases. This mole percentage falls at the peritectic phase transformation and has a melting point of 650 °C.

To optimize the growth of 35.5:64.5, several runs were conducted. A brief description of the procedures and results of these runs are discussed in the following table.

For run number 4 in Table 1, a conglomeration of 40–50 single crystals of numerous sizes were grown; each one is separated from the other by the surplus phases. A further increase in the pulling rate resulted in the detachment of the crystal from the melt. Fig. 1 shows the bottom view of the grown material. It is also noticed that bigger single crystals were grown in a bigger crucible. Single crystals were isolated, cut, polished, and then sputtered with gold contacts for analysis. Fig. 2 shows a polished sample crystal.

The crystal structure, the lattice constants, and the direction of the samples were obtained using a single-crystal diffractometer equipped with a software package that includes a PDF and CIF libraries.

3. Results and discussion

Crystals were tested for glow discharge mass spectroscopy; it shows that these single crystals included some impurities, such as (in ppm): 350 Al, 30 Zr, 72 Pt, and 8 Au. The unexpected large presence of aluminum in the crystal, perhaps, came from the aluminum foil where the powder was separated from the grinding media after mixing the two powders. Zirconium impurities came from the grinding zirconia beads, while platinum and gold came from the crucible.

3.1. Electrical and optical properties

3.1.1. Dielectric constant measurement

The dielectric constant and the loss factor are measured using the Tenny Environmental Test Chamber, where the temperature was increased in 5 °C steps starting from −75 to 185 °C. The chamber is connected to the QuadTech 7600 Precision LCR meter, and interfaced with a computer. The (0 0 1) dielectric constant as a function of temperature is shown in Fig. 3. The dielectric constant