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Bridgman growth of $CdWO_4$ single crystals

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Abstract

The growth of large size $CdWO_4$ single crystals by vertical Bridgman process is reported in this letter. $CdWO_4$ polycrystalline material with stoichiometric composition was synthesized from CdO and WO_3 as the initial materials by solid-state reaction. In the Bridgman growth, the platinum crucibles charged with material were sealed so as to avoid the harmful volatilization of the melt. By means of the growing parameters such as a crucible lowering rate of 0.5–1.5 mm/h and a temperature gradient around 30–40 °C/cm across the solid–liquid interface under a furnace temperature of 1350–1400 °C, a transparent $CdWO_4$ crystal as large as $\varnothing 40 \times 70$ mm has been grown by the vertical Bridgman process successfully. The crystal was characterized by X-ray diffraction (XRD), optical transmittance, X-ray stimulated luminescence spectrum. The desirable crystalline quality of the grown crystals is verified by XRD rocking curve. The crystal shows a high optical transmittance in the visible wavelength range and a strong emission peaked at 470 nm under X-ray excitation.

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1. Introduction

$CdWO_4$ (CWO) single crystal is a well-known scintillator with excellent properties [1,2]. The crystal has attractive performances such as high light yield, short radiation length, high density and the radiation stability with varied temperature. The unique properties make the crystal to be very valuable for radiation detection application, especially for security checking and medical imaging. Much effort has been made to grow large-size crystals with high quality for radiation detection devices. In the previous works, most investigations were focused on the Czochralski process [3–8]. The main difficulties for Czochralski growth of the crystals are (1) continuous composition change of melts because of volatilization of CdO and WO_3 and (2) cracking in as-grown crystal due to its cleavage nature. In recent years, the vertical Bridgman process was used to grow CWO crystals in our laboratory. In our Bridgman process, the harmful volatilization was avoided effectively by sealing the crucibles and the cracking of the crystals was decreased by the favorable conditions. In this letter, we present what is to our knowledge the first report on the vertical Bridgman growth of CWO crystals.

2. Experimental procedure

2.1. Preparation of feed material

The feed material for CWO crystal growth was synthesized from the high-purity CdO (99.99%) and WO_3 (99.99%) according to the chemical stoichiometry. The starting agents were sintered at 300 °C for 3 h to remove the moisture. The initial agents were weighed accurately and mixed for 3 h in a nylon ball mill. The mixture was sintered at the temperature of 1000–1150 °C for 6 h so that CWO

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phase was synthesized. A white polycrystalline charge with high density was obtained by the solid phase reaction. As a comparison, the feed material was alternatively synthesized from $CdCl_2$ (99.9%) and Na_2WO_4 (99.9%) by the precipitating reaction in aqueous solution. The two agents with the molar ratio 1:1 were dissolved to be saturated solutions and a precipitation occurred as the two solutions mixed together by stirring. The feed material with accurate stoichiometry was obtained after the precipitation was filtered and dried. The feed materials obtained by the above route were identified to be CWO phase by X-ray powder diffraction and DTA analysis.

2.2. Crystal growth

CWO crystals were grown in a resistively heated vertical Bridgman furnace, which was adjusted by a WJK-100A fine temperature controller with an accuracy of $\pm 0.5\,^{\circ}C$. The axial temperature distribution in furnace is shown in Fig. 1. According to the axial temperature distribution, the furnace chamber can be divided into three zones, i.e. the high-temperature zone, the gradient zone and the low-temperature zone. During the crystal growth, the melt was homogenized in the crucibles in the high-temperature zone, while the grown crystal could be annealed in the low-temperature zone. The solid–liquid interface was located in the gradient zone. The high-temperature zone was usually controlled at 1350–1400 °C, which was about 70–120 °C higher than the melting point of the crystal.

The platinum crucible used in the crystal growth was 25–40 mm in diameter and 200–250 mm in length with a seed well of 10–25 mm in diameter at the conical bottom to hold the seed crystal. The crucibles, fabricated from thin platinum sheets, could be used only once for one growth cycle because they must be cut in order to take out the grown crystals. In order to obtain the seed crystals, the initial tries of the growth were performed by spontaneous nucleation process. Later, the crystals were grown along the preferred growth direction [0 0 1] by using the oriented seeds. Transparent single crystals with size of Φ9–24 × 40–50 mm were chosen as the seeds after the crystals were oriented, cut and ground. After the seed was put in the seed well, the feed materials of 400–1200 g were filled in the cylinder of crucibles. To avoid the volatilization of melt during crystal growth, the assembled crucible was sealed firmly. The crucible was installed in a refractory tube filled with Al_2O_3 powder to isolate it from external temperature fluctuations. The refractory tube together with the crucible was put into the furnace chamber.

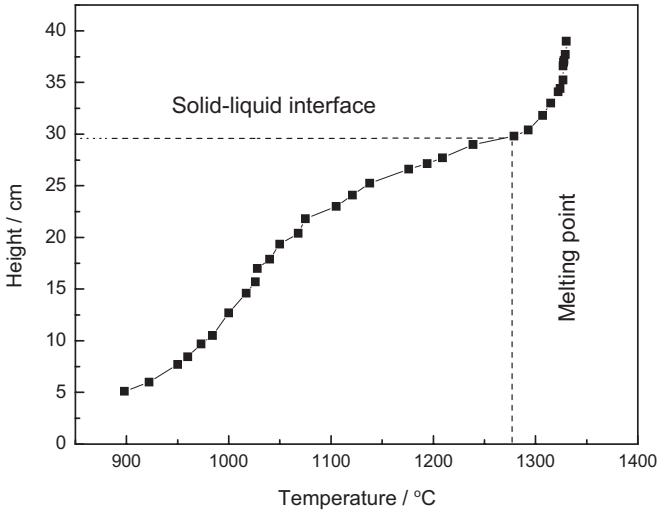

Fig. 1. Axial temperature distribution in furnace.

After the furnace had been heated to the controlled temperature, the seeding process was performed by adjusting the crucible to such a position that only the top of the seed was melted. The feed material and the seed were kept at the melting state for 4–6 h and a stable solid–liquid interface with a temperature gradient around 30–40 °C/cm was established on the top region of the seed. Growth process was driven by lowering the crucible at a rate of 0.5–1.5 mm/h. The furnace was cooled to room temperature at a rate of 20–60 °C/h after the growth had finished. After the crucible was taken out from the refractory tube, as-grown crystal was obtained by cutting and stripping the crucible. In order to eliminate the residual stress inside the crystal, it was annealed at 950–1050 °C for 24 h in a resistant furnace.

2.3. Characterization

X-ray powder diffraction analysis of grown crystals was performed with a Bruker D8 Focus diffractometer, using monochromatic CuKα radiation with a working voltage of 40 kV and current of 100 mA. The crystallinity of the crystal is investigated by X-ray diffraction (XRD) rocking curve analysis of the (0 1 0) reflection. The XRD rocking curve was measured by a Philips materials research diffractometer equipped with a four-crystal (2 2 0) Ge Bartels-tape monochromator. The transmission spectrum of the sample with 2 mm in thickness was measured with an UV-2501PC spectrometer in the range of 200–850 nm at room temperature. X-ray stimulated luminescence (XSL) spectrum was measured by X-ray stimulated fluorescence spectrophotometer, which was equipped with a Cu target running at 80 kV and 2 mA. The instrument was controlled by a computer and the XSL spectrum was recorded at room temperature.

3. Results and discussions

3.1. Composition of melt

Theoretically, the feed material with accurate stoichiometric composition is favorable for growing high quality crystals with congruent melting behavior. However, it is difficult to control the stoichiometry of melt in the Czochralski growth of CWO crystals. The serious volatilization of CdO results in the continuous composition shift

of the melt during growth. Trying to compensate the volatilization of CdO, the feed material containing excess of CdO is usually used in the Czochralski growth. But it is not easy to compensate the weight loss precisely to avoid the composition deviation of the melt. The optical quality of crystals deteriorates with the increasing composition deviation during growth. In this work, the Bridgman growing process was performed in the sealed platinum crucibles. Compare to the Czochralski method, no evident weight losses occurred during in the Bridgman process because the vapor could be enclosed in the sealed crucibles. The harmful CdO volatilization could be avoided effectively and the composition of the melt was kept stable in the growth. This is helpful to grow high-quality crystals with the stoichiometric composition.

3.2. Cleavability

A difficulty to grow large-size CWO crystals is the cracking occurring in the crystal growth process due to its strong cleavability nature. The crystals often cleave along the cleavage plane (0 1 0) during the growth due to the stress and thermal shock. It was confirmed that the crystals should be grown along the preferred growth direction [0 0 1] to decrease the cracking in the crystal growth. In our Bridgman growth, the temperature gradient across the solid–liquid interface was usually smaller than that of Czochralski growth and the crystal was annealed in the low-temperature zone simultaneously, which were helpful to decrease the cracking of the crystals. After the crystal growth had been finished, the crystals were annealed further in order to avoid the cracking in the fabrication process.

3.3. Characterization

By means of the process described above, CWO single crystals have been grown successfully by the vertical Bridgman process. Fig. 2 shows the as-grown crystals, which are pale yellow and transparent. The bigger one is as large as 40 mm in diameter by 70 mm in length. The crystals have polished sections on the two sides, through which the words on the background can be seen clearly. Compare to the Czochralski grown CWO crystals in previous literatures, the crystals grown in this work shows to be more pale-color owing to the simultaneous annealing with the growing process. The crystal was examined to be free of scattering centers inside by a He–Ne laser beam. The sample was characterized by X-ray powder diffraction. Fig. 3 presents the X-ray powder diffraction pattern, which accords with the data of JCPDF-14-0676 [9]. The grown crystal was verified to be CWO without other phases.

To evaluate the crystalline quality, the crystal was characterized by the XRD rocking curve. Fig. 4 shows the XRD rocking curve, which exhibits a FWHM value of ~41 s. The result shows that the crystallinity of the grown crystal is desirable. Fig. 5 presents the transmission spectrum of crystal, in which the absorption edge is located around 325 nm and the transmittance above 380 nm is about 70%. It is notable that there appears a small

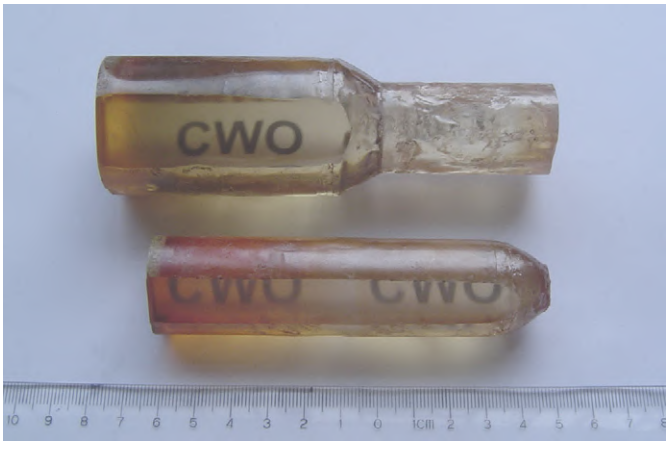

Fig. 2. CWO single crystal grown by vertical Bridgman process.

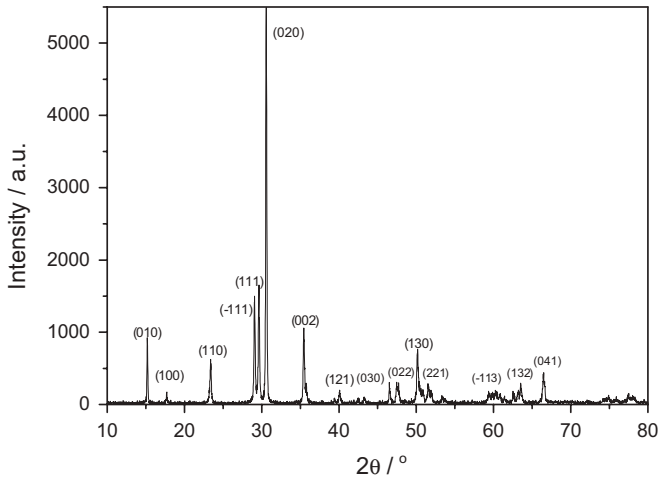

Fig. 3. X-ray diffraction pattern of CWO crystal.

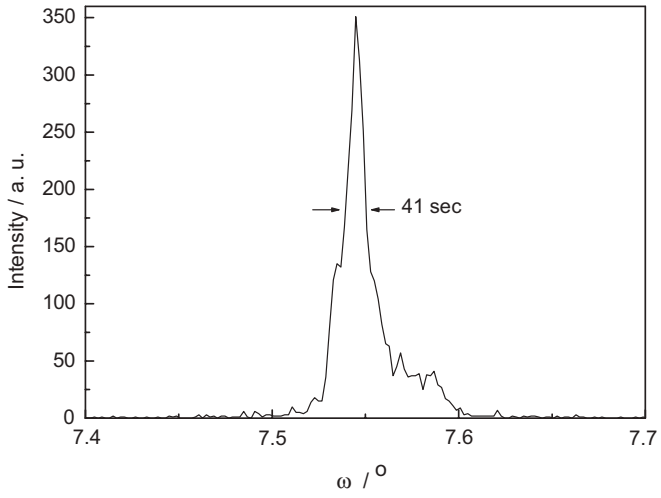

Fig. 4. X-ray diffraction rocking curve of CWO crystal.

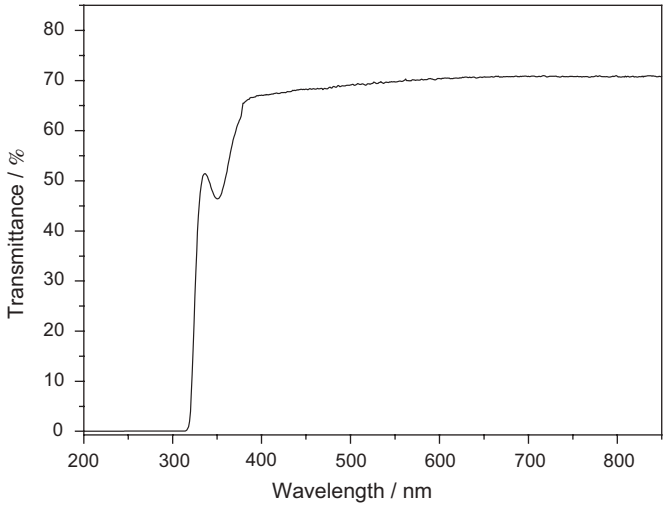

Fig. 5. Transmission spectrum of CWO crystal.

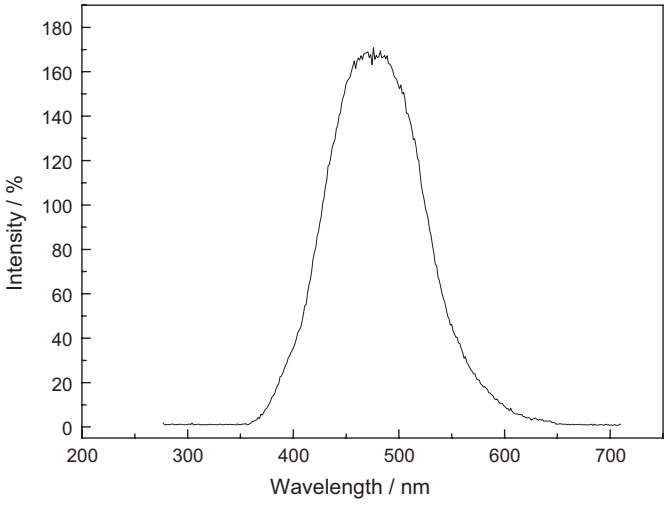

Fig. 6. X-ray stimulated luminescence spectrum of CWO crystal.

absorption peak in 350 nm. According to Refs. [10–11], the additional absorption peak may be attributed to the small quantity of Bi^{3+} ions remained in the initial material. XSL spectrum shown in Fig. 6 indicates a strong emission with central wavelength at 470 nm under X-ray excitation. The optical transmittance around this emission wavelength is as high as 70%, which is favorable to acquire a high light yield. The scintillation properties of the crystal are further under investigation.

4. Conclusion

Large size CWO crystals have been grown successfully by the vertical Bridgman process. The feed material with strict stoichiometric composition was used in the Bridgman growth. To avoid the continuous composition change of the melt, the crystals were grown in a stable ambience with the sealed platinum crucibles. The growth parameters is controlled as the crucible lowering rate of 0.5–1.5 mm/h coordinated with the temperature gradient of 30–40 °C/cm across the solid–liquid interface under the furnace temperature of 1350–1400 °C. The characterizations indicate that the grown crystals have desirable crystallinity and high optical transmittance. This work demonstrates that the vertical Bridgman process is promising for growing large-size CWO single crystals with high quality.

Acknowledgments

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