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Growth and Properties of Defect-Chalcopyrite $CdGa_2Se_4$ Crystals

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$CdGa_2Se_4$ crystal, with the structure of defect-chalcopyrite, is a promising optical and photoelectric material. Single crystal with size of $\Phi 11 \times 60$ mm^3 was grown successfully by vertical Bridgman method. The as-grown crystal was characterized with X-ray diffraction (XRD), energy dispersive X-ray Spectroscopy (EDS), and transmission spectra etc. The results show that the crystalline quality of the crystal is very good, and the atomic ratio is Cd:Ga:Se = 1:2.12:4.05, which is close to the ideal stoichiometry. The crystalline quality and the chemical composition of the cracked section near the end of the crystal were also measured and the cracking reason was analyzed. The transparency range of the crystal was revealed for the first time. The transmittance of a 3.6 mm sample is above 65% in the range of 5 to 12 μm, which demonstrate the high optical quality of the crystal. Based on the transmission spectra, the refractive index and the energy bandgap were calculated to be 2.5 and 1.97 eV respectively.

Introduction

Chalcopyrite compounds are important optical and photoelectric material.[1–3] They are derived from their parent II–VI or III–V compounds with structure of zinc-blende. By replacing the group II with a group-I and group-III element in II–VI compounds or by replacing the group-III element with a group-II and group-IV element in III–V compounds, they become chalcopyrite compounds and their chemical formulas are expressed as I–III-VI_2 or II–IV-V_2, such as $AgGaS_2$, $AgGaSe_2$, and $ZnGeP_2$ etc. They are well known as infrared nonlinear optical crystals. The structure of the defect-chalcopyrite compounds is very similar to the chalcopyrite compounds'. The structure of the defect-chalcopyrite compounds can be seemed as replacing the group-I element of the I–III-VI_2 chalcopyrite compounds with a group-II element and a vacancy orderly. The space group of defect-chalcopyrite becomes *I*-4. Due to the degenerate of the symmetry, defect-chalcopyrite compounds have much richer performance in photosensitivity, high energy ray detection, and nonlinear optical device etc. Additionally, there are so-called stoichiometric vacancies in the structure of defect-chalcopyrite compounds. These stoichiometric vacancies would be used to dope with impurity atoms purposely and to explore for novel functional properties. Many researchers have high interests in them.

$CdGa_2Se_4$ crystal is one of the most promising defect-chalcopyrite compounds. Efforts have been focused on the growth of single crystal and calculations of its optical and electric properties based on density functional theory.[4–10] $CdGa_2Se_4$ crystal with size of $4 \times 1 \times 1$ mm^3 was grown out for the first time by the chemical vapor transport (CVT) method.[11] In 1990, $CdGa_2Se_4$ crystal with size of $7 \times 4 \times 4$ mm^3 were grown from the melt directly.[12] Recent years, O.V Parasyuk et al. have tried to grow $CdGa_2Se_4$ crystal from non-stoichiometric solutions to avoid the crystal decomposition during the polymorphous transformation.[13–15] The grown crystal was up to 25 mm in length and 14 mm in diameter. But solvents incorporation is the major obstacle to acquire high quality crystal. Searching for suitable solvent is a challenging task.

Until now, it is still difficult to grow $CdGa_2Se_4$ single crystal with high optical quality and hard to characterize some properties for the lack of sufficient size of single crystals. $CdGa_2Se_4$ crystals are generally suffered from drawbacks such as optical inhomogeneity, deviation from stoichiometry, and crack etc. The polymorphous transformation during the cooling of crystal growth would be the main reason.[16–17]

In the present work, we focus our efforts on the growth and characterization of $CdGa_2Se_4$ crystal. The polycrystalline synthesis and single crystal growth technology of the $CdGa_2Se_4$ crystal were explored experimentally. Polycrystalline and single crystal with centimeters size were obtained. The crystalline quality, chemical composition, and optical transmission spectra etc. were studied to characterize the as-grown $CdGa_2Se_4$ crystal.

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Results and discussion

Crystalline Quality

The upper curve in the **Figure 1** is the diffraction pattern of the synthesized $CdGa_2Se_4$ polycrystalline, which is consistent with

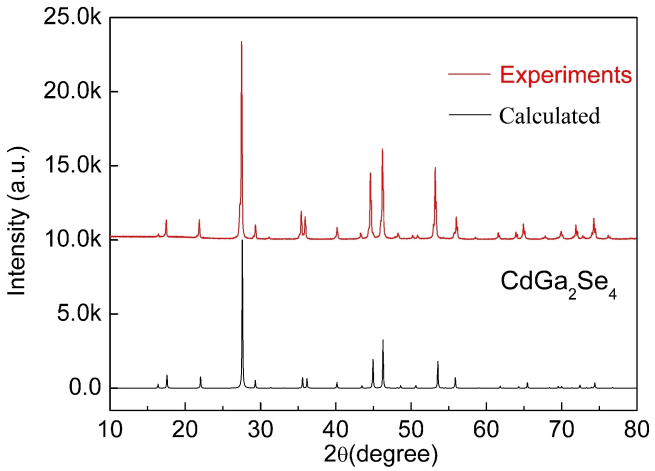

Figure 1. The X-ray powder diffraction patterns of the $CdGa_2Se_4$. The upper curve is the experimental pattern and it is quite agree with the lower one that simulated.

the simulated pattern, both the peak position and the relative intensity. No impurity phase was observed in the X-ray powder diffraction pattern, which indicates the synthesized polycrystalline is pure. The lattice constant parameters were calculated: $a = b = 0.574141$ nm, $c = 1.076199$ nm.

Figure 2a is the as-grown $CdGa_2Se_4$ crystal boule. The size of crystal is about 11×60 mm^3. The as-grown crystal was cracked at the 15 centimeter of the ruler and the crystal was divided into two parts. Cleavage planes could be seen with naked eyes on the cracked section. **Figure 2b** is the (001) plane sample that fabricated from the left part. The sample size is $4 \times 8 \times 1.6$ mm^3. To determine the phase composition of the as-grown crystal, the XRD pattern of powders ground from the left part, the right part and the cracked section were measured. They are the same as the diffraction pattern of the synthesized polycrystalline. This shows that the phase composition is mainly the defect-chalcopyrite $CdGa_2Se_4$ except the end part of the boule.

Forth-order XRD diffraction peaks of the {002} planes of the sample in **Figure 2b** are observed. They are (002), (004), (006) and (008) diffraction peaks, which are shown in **Figure 3a**. The rocking curve of the (002) diffraction peak is shown in **Figure 3b**. From the rocking curve, it can be seen that the intensity of diffraction peak is high and the symmetry of the peak shape is good. The full width at half maximum (FWHM) of the rocking curve is about 0.09°. This illuminates that the crystallinity of the sample is high.

Other part, include the right part of the crystal were also examined by the rocking curves, they are just like the crystalline quality of the **Figure 2b** sample. The crystalline quality of the

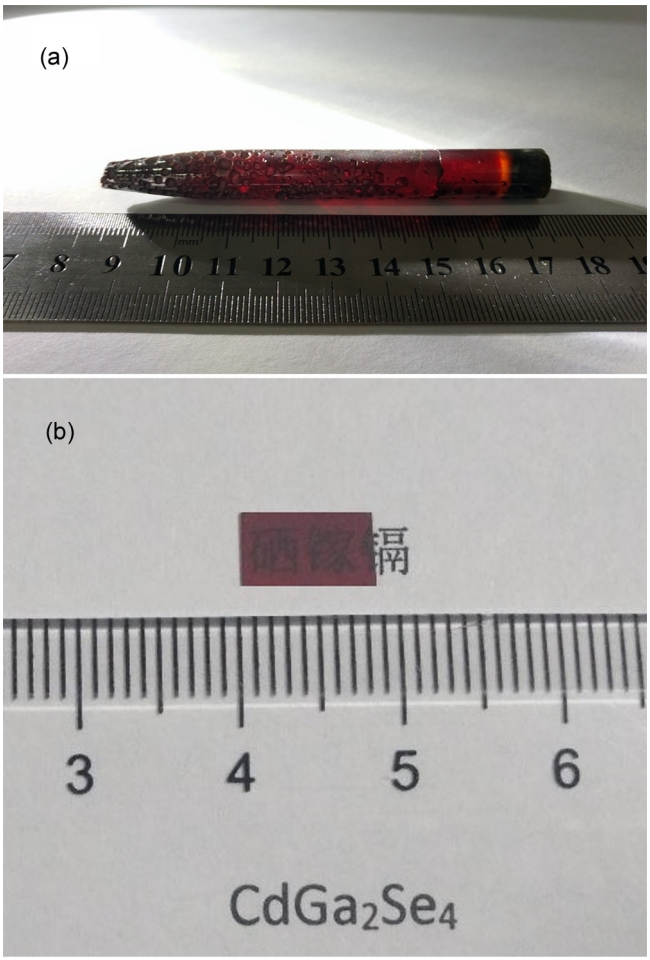

Figure 2. (a) The as-grown $CdGa_2Se_4$ crystal boule, (b) The (001) plane $CdGa_2Se_4$ sample fabricated from the left part of the crystal.

cleavage plane on the cracked section was also examined. **Figure 4a** is its diffraction pattern. By indexing of the diffraction pattern, the two diffraction peaks are correspond to the (112) and (224) planes. Small impurity peaks around the (112) diffraction peaks can be seen in the XRD pattern. The rocking curve of the (112) diffraction peak is shown in **Figure 4b**. It can be seen that the intensity of diffraction peak is not very high and the peak shape is splitting severely. So the quality of the crystalline near the cracked section is not so good. This could be the reason that the crystal cracked there. In general, the crystalline quality of the as-grown crystal is very good, except the position of the cracked section of the crystal.

Chemical Composition

The EDS of three random areas of the sample in **Figure 2b** are measured. **Figure 5** is a typical EDS of the sample in **Figure 2b**. There is no impurity element detected except the three principal elements. The atomic ratios of the three areas are generally the same and the atomic ratio of Cd, Ga, and Se is 1: 2.12: 4.05, which are very close to the ideal stoichiometry of $CdGa_2Se_4$ crystal. Few amount of Cd and Se deviation are still

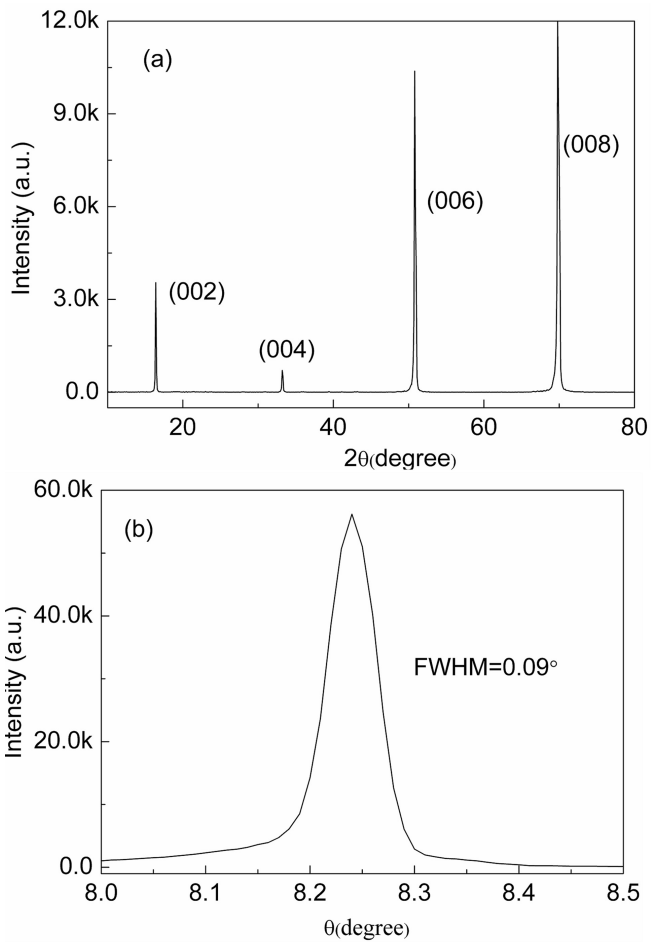

Figure 3. (a). XRD pattern of the {002} planes, (b) The rocking curve of the (002) diffraction peak.

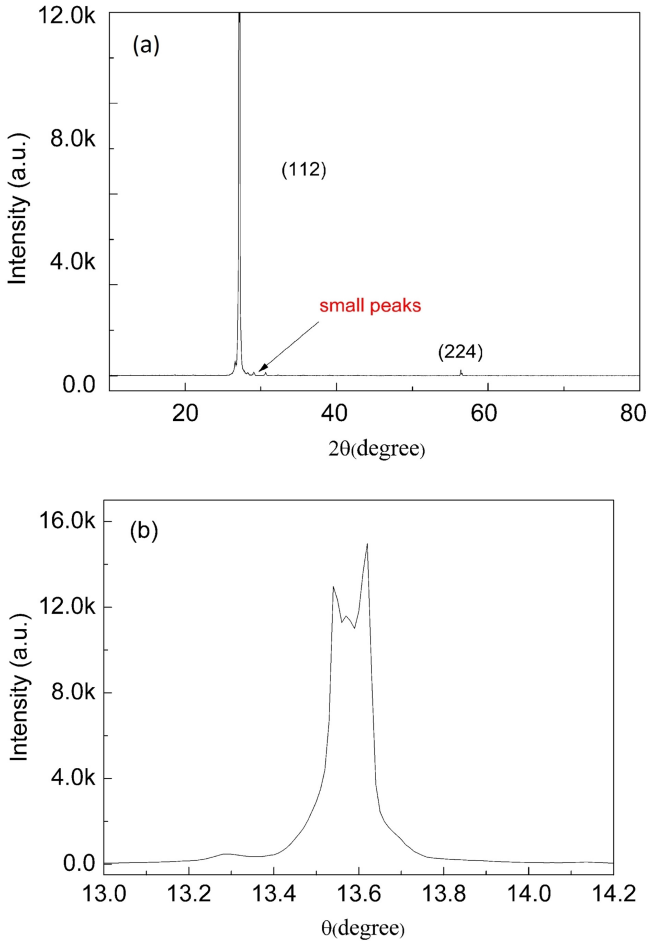

Figure 4. (a) XRD pattern of the {112} planes, there are small peaks in the {112} planes diffraction pattern. (b) The rocking curve of the (112) diffraction peak. The rocking curve shows that the intensity of diffraction peak is not very high and the peak shape is splitting severely.

unavoidable, although certain pressure of Ar were refilled to prevent the component from volatilizing. The EDS of three random areas of the cracked section are also measured. There is also no impurity element detected except the three principal elements. The atomic ratios of them are generally the same, but they are different from the ideal stoichiometry of $CdGa_2Se_4$ crystal and the atomic ratio of Cd, Ga, and Se is 1: 2.40: 4.17. The chemical compositions of the **Figure 2b** sample and the cracked section were listed in **Table 1**. The components deviation from the ideal stoichiometry were detected on the cracked section, although there was no impurity phase in the XRD measurement. The components deviation would result in the decrease of the crystalline quality, and eventually lead to

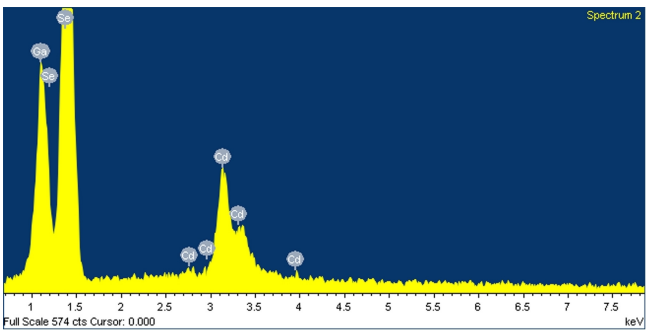

Figure 5. A EDS of the $CdGa_2Se_4$ crystal. Only three principal elements were detected and there is no impurity element.

Table 1. The chemical composition of the ideal stoichiometry and the different parts of the $CdGa_2Se_4$ crystal.

Elements	Cd		Ga		Se	
Samples	Weight%	Atomic%	Weight%	Atomic%	Weight%	Atomic%
Ideal stoichiometry	19.80	14.29	24.57	28.57	55.63	57.14
Figure 2b sample	19.38	13.95	25.49	29.57	55.13	56.49
Cracked section	18.79	13.47	27.17	31.39	54.05	55.14

the cracking of the grown crystal. So the component deviation should be suppressed to the maximum for growing crack free crystal. Generally, the following two aspects should be taken into account. One aspect, high pure polycrystalline should be synthesized for the single crystal growth. The other aspect, appropriate temperature control program of the crystal growth should be designed to avoid the component deviation, especially when the temperature passes through phase transition region during the cooling process.

Thermal analysis

The TGA and DTA curves of $CdGa_2Se_4$ are shown in **Figure 6**. From the TGA curve, we can see that the weight begin loss

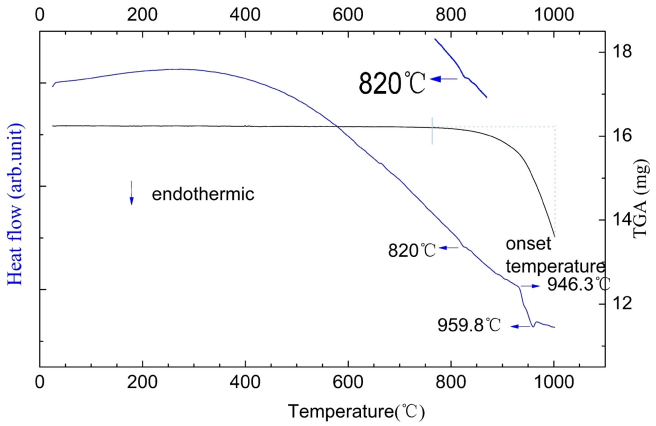

Figure 6. The TGA/DTA curves of the $CdGa_2Se_4$ crystal. $CdGa_2Se_4$ begin to evaporate from 760°C. The melting of $CdGa_2Se_4$ crystal is 959.8°C.

from 760°C, which indicate that $CdGa_2Se_4$ begin to evaporate from the temperature. As the temperature goes up, the weight loses speed up. From the DTA curve, it can be seen that there is a small endothermic peak around 820°C, which may correspond to polymorphous transformation according to [16]. A big endothermic peak observed at 959.8°C, which correspond to the melting of $CdGa_2Se_4$ crystal.[17] The thermal analysis results are useful for designing the temperature control program of the polycrystalline synthesis and crystal growth.

Optical properties

Figure 7 is the transmission spectra of the $CdGa_2Se_4$ crystal and the thickness of the wafer is 3.6 mm. The near-IR cutoff wavelength is 0.61 μm, and long-wave IR cutoff wavelength is about 20.9 μm. The transmittance is above 65% in the range of 5 to 12 μm, which demonstrate the optical quality of the as-grown crystal is high. To our knowledge, this is the first time to obtain the transparency range of the $CdGa_2Se_4$ crystal. The broad transparency range means that the crystal would have many applications in infrared band.

Corresponding to the relationship between the absorption coefficient (α) and the transmittance (T):[18]

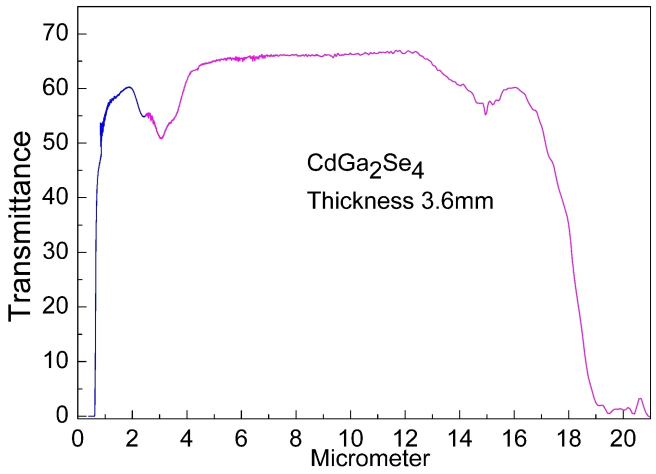

Figure 7. The transmission spectra of the $CdGa_2Se_4$ crystal. The thickness of the sample is 3.6 mm.

$$\alpha = -\left(\ln\left(\left\{\left[(1-R)^2/2TR^2\right]^2 + 1/R^2\right\}^{1/2} - (1-R)^2/2TR^2\right)\right)/L \quad (1)$$

where L is the thickness of the sample, $R=(1\text{-}n)^2/(1+n)^2$ is the Fresnel power reflection coefficient and n is the refractive index. We can deduce the crystal's refractive index is about 2.5. Meanwhile, the $CdGa_2Se_4$ is a direct band semiconductor. The absorption coefficient and the bandgap (E_g) obey the following relation for high photon energies (hν):[19]

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \quad (2)$$

in which A is a constant. A plot of Variation of $(\alpha h\nu)^2$ versus $h\nu$ is shown in **Figure 8**. The energy band gap E_g was estimated to

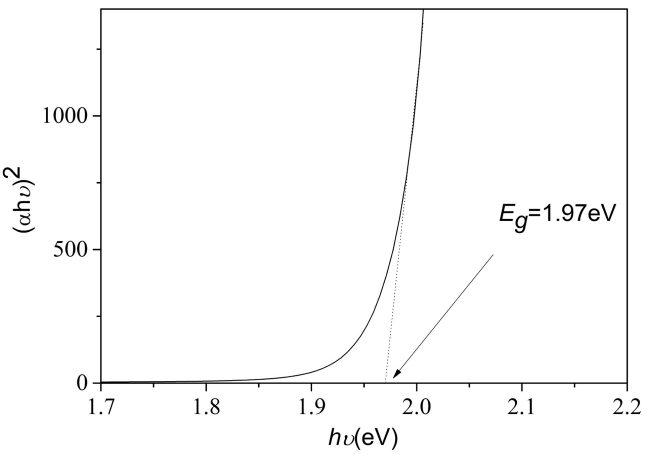

Figure 8. Plot of $(\alpha h\nu)^2$ versus photon energy $h\nu$ of the $CdGa_2Se_4$ crystal.

be 1.97 eV, which is very consistent with the short-wave absorption edge.

Conclusions

The $CdGa_2Se_4$ polycrystals were synthesized by single temperature zone method and the $CdGa_2Se_4$ single crystal with size of $\Phi 11 \times 60\ mm^3$ was grown by vertical Bridgman method. The synthesized polycrystalline and grown single crystal were examined by XRD. The polycrystalline is high pure. The intensity of the single crystal's diffraction peak is high and the symmetry of the peak shape is good. The chemical composition of the grown crystal was measured by EDS, which are close to the ideal stoichiometry of $CdGa_2Se_4$. Meanwhile, the crystalline quality and the chemical composition of the cracked section near the end of the crystal were also measured. Proposals are given to avoid the crystal cracking. The TG/DTA analysis shows the $CdGa_2Se_4$ begin to evaporate from 760°C and the melt point is about 959.8°C. The transmission range of the $CdGa_2Se_4$ crystal was revealed for the first time, which is 0.61–20.9 μm. The refractive index and the energy bandgap were calculated to be 2.5 and 1.97 eV, respectively.

Supporting Information Summary

All experimental details are found in the Supporting Information.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: $CdGa_2Se_4$ crystals · chemical composition · transmission spectra · synthesis design · crystal growth

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