

Phase diagram of the CdGa₂Se₄-Sb₂Se₃ system and single crystal growth of CdGa₂Se₄

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The phase diagram of the CdGa₂Se₄-Sb₂Se₃ system was investigated by differential-thermal analysis, powder X-ray diffraction, and metallography. The system is of the eutectic type with coordinates of the eutectic point ~88 mol.% Sb₂Se₃ and 835 K. From the constructed phase diagram, an optimum concentration of the Sb₂Se₃ solvent was selected, and single crystals of CdGa₂Se₄ were grown by the solution-melt method. Absorption spectra of the grown crystals were studied. The estimated optical band gap is 1.95±0.05 eV. A weak absorption band at 1.5-1.7 eV is attributed to the antimony impurity.

Inorganic Materials / Crystal Growth / X-ray diffraction / Phase diagram / Thermal analysis

Introduction

Among complex semiconductors with a diamond-like structure, defect ternary compounds A^{II}B^{III}C^{VI}₄ are of a high interest because of the presence of so-called stoichiometric vacancies. Moreover, these compounds exhibit a very low sensitivity to unwanted impurities and a high resistance against ionization radiation. The CdGa₂Se₄ compound belongs to the wide-gap semiconductors, and is known as a luminescent and photosensitive material [1,2]. Its optical properties were studied in [1,3-8], both on thin films and bulk crystals. The energy gap was reported to be 2.41 eV [3], 2.51 eV [4], or 2.33 eV [5]. The low-temperature (LT) modification of CdGa₂Se₄ crystallizes in the tetragonal structure of cadmium thiogallate or defect chalcopyrite (space group $I\bar{4}$, $a = 0.5743$, $c = 1.0756$ nm [9]). However, its practical application is hindered by technological difficulties in producing high-quality bulk crystals. Although CdGa₂Se₄ is formed congruently, it possesses a polymorphous transformation [10,11], which complicates the growth of single crystals from the stoichiometric melt.

Previously, CdGa₂Se₄ single crystals were grown by the chemical vapor transport (CVT) method, directional crystallization of the stoichiometric melt, or crystallization from non-stoichiometric solutions. The CVT method was reported in [12,13]. In both cases, iodine was used as transport agent with a concentration of 5 mg/ml. The ratio between the temperature in the evaporation/condensation zone was 1173/1023 K in [12] (crystals up to 4×1×1 mm³), or 1093/853 K in [13] (crystal length 10±15 mm). A two-

zone furnace, keeping 1200–1170 K in the crystallization zone and 870–920 K in the annealing zone, was employed for the directional crystallization of the stoichiometric melt [14]. The temperature gradient at the crystallization front was 10 K/cm, whereas the rate at which the growth container was moved down was 0.5 mm/h. Under these conditions, single crystal blocks of 10×5×5 mm³ were obtained. Single crystal growth of CdGa₂Se₄ was also performed using non-stoichiometric melts of the ternary compound with GeSe₂, SnSe₂, or SnSe [15-17]. The composition of the initial charges was selected from the field of primary crystallization of the LT-modification of CdGa₂Se₄. The grown crystals were up to 25 mm in length and 14 mm in diameter. However, a drawback of the used solvents is their incorporation in the lattice of the growing crystal (according to the constructed phase diagrams, the solid solution range of CdGa₂Se₄ extends to 3÷4 mol.%). Therefore, the search for a suitable solvent for the CdGa₂Se₄ crystal growth is a challenging task.

In this study, we investigate the phase diagram of the CdGa₂Se₄-Sb₂Se₃ system and demonstrate the potential of CdGa₂Se₄ single crystal growth employing Sb₂Se₃ as solvent.

Experimental

The alloys for the investigation of the CdGa₂Se₄-Sb₂Se₃ phase equilibria were prepared from high-purity elements: Cd – 99.9999 wt.%, Ga –

99.9997 wt.%, Sb – 99.99 wt.%, and Se – 99.997 wt.%. The synthesis was performed by alloying calculated amounts of elements in evacuated quartz ampoules. The ampoules were heated to 1273 K at a rate of 40–50 K·h⁻¹, held at the maximum temperature for 6 hours, and then cooled down to room temperature at a rate of 10 K·h⁻¹.

The obtained alloys were investigated by differential-thermal analysis (DTA), X-ray diffraction (XRD) and metallography. DTA curves were recorded on a Paulik–Paulik–Erdey derivatograph with a Pt/Pt-Rh thermocouple. The XRD patterns were obtained on powders using a DRON 4–13 diffractometer with CuK_α-radiation. The microstructure of the alloys was observed on a Leica VMHT Auto microhardness tester.

Results

Phase diagram of the CdGa₂Se₄–Sb₂Se₃ system

The CdGa₂Se₄–Sb₂Se₃ system is quasi-binary, of the eutectic type (Fig. 1). Its liquidus consists of three fields of primary crystallization: high- (HT) and LT-modifications of CdGa₂Se₄, and Sb₂Se₃. The coordinates of the eutectic point, estimated by constructing a Tamman triangle, are ~88 mol.% Sb₂Se₃ and 835 K. A non-variant horizontal at 1087 K corresponds to the phase transformation of CdGa₂Se₄. A small temperature decrease indicates the peritectic process L+α↔α', which corresponds to the horizontal. Investigation of the sub-solidus region showed that the solid solution ranges of the system components do not exceed 2 mol.%.

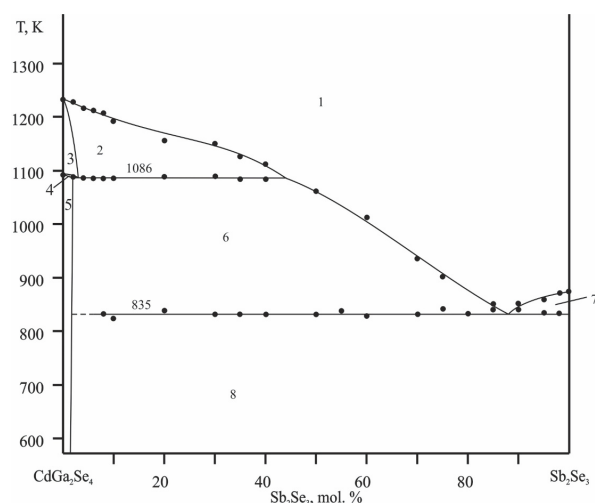


Fig. 1 Phase diagram of the CdGa₂Se₄–Sb₂Se₃ system: (1) L; (2) L+α; (3) α; (4) α+α'; (5) α'; (6) L+α'; (7) L+Sb₂Se₃; (8) α'+Sb₂Se₃.

For instance, an alloy containing 2 mol.% of Sb₂Se₃ is already a two-phase one (Fig. 2a). Dark grains, which occupy the major part of the metallographic section, belong to CdGa₂Se₄. Small eutectic inclusions are visible at grain borders. With increasing Sb₂Se₃ content, the size of the primary grains of the ternary compound gradually decreases, whereas the eutectic fields enlarge (e.g. the alloy with 50 mol.% Sb₂Se₃ in Fig. 2b). The alloy with 90 mol.% Sb₂Se₃ is closest to the eutectic point (Fig. 2c). Further increase of the Sb₂Se₃ content leads to inversion of the primary crystallization. A typical microsection of the alloy containing 95 mol.% Sb₂Se₃ is shown in Fig. 2d. The light grains represent the binary compound, which is surrounded by eutectic fields.

Some typical XRD patterns of the alloys are shown in Fig. 3. All of them exhibit sharp diffraction peaks. The alloy corresponding to the CdGa₂Se₄ compound was indexed in the structure of defect chalcopyrite, space group $I\bar{4}$ with lattice parameters $a = 0.57430(6)$ and $c = 1.0752(2)$ nm, which is in good agreement with reported data [18]. A diffraction pattern of the Sb₂Se₃ alloy was indexed in an orthorhombic structure (space group $Pbnm$) with lattice parameters $a = 1.1619(2)$, $b = 1.1767(2)$, $c = 0.39718(6)$ nm, which are close to those in [19]. Diffraction patterns of the intermediate alloys exhibit a mixture of two sets of diffraction reflections, which belong to the system components. The lattice parameters of the components, calculated for the intermediate alloys, do not differ from those obtained for pure CdGa₂Se₄ or Sb₂Se₃.

Single crystal growth of CdGa₂Se₄

Since the system liquidus includes a field of primary crystallization of LT-CdGa₂Se₄, this concentration range can be used for the growth of LT-CdGa₂Se₄ crystals. In this work we employed an initial charge containing 50 mol.% Sb₂Se₃. The charge of 15 g was synthesized according the procedure described above. Afterwards, it was ground into fine powder and transferred into a conical quartz ampoule, which was then evacuated and soldered. The single crystal growth was performed in a two-zone furnace with a constant temperature profile. The temperature of the upper zone was 1273 K, and the temperature of the lower zone varied from 870 to 1220 K. After charge melting, the ampoule was moved down at a rate of 5 mm/day to crystallize 4–5 mm of the melt. The re-crystallization annealing lasted for 100 hours. Later, first 2–3 mm of the seed was melted back, and the crystal was growing by slow (2–3 mm/day) moving of the growth container down to the colder zone. When using higher rates, we observed incorporation of residual eutectic between single crystal blocks, which, apparently, was due to the high viscosity of the solution and slow equalization of component concentrations in the melt. The temperature gradient at

Table 1 The stoichiometric and experimental composition of CdGa₂Se₄ single crystals measured by EDX.

Element	stoichiometric (at.%)	experimental (at.%)
Cd	14.29	14.23
Ga	28.57	27.67
Se	57.14	58.10

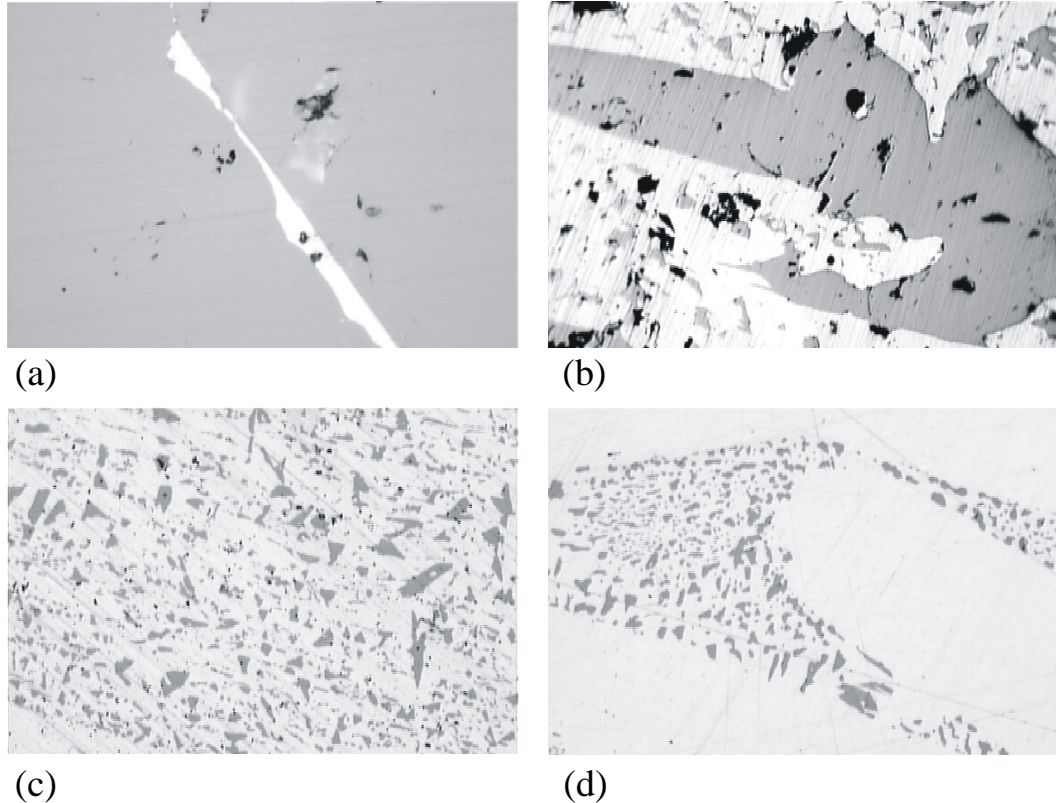


Fig. 2 Optical photographs of some microsections of the CdGa₂Se₄–Sb₂Se₃ system (composition in mol.% Sb₂Se₃): (a) 2, (b) 50, (c) 90, (d) 95 (320×240 μm²).

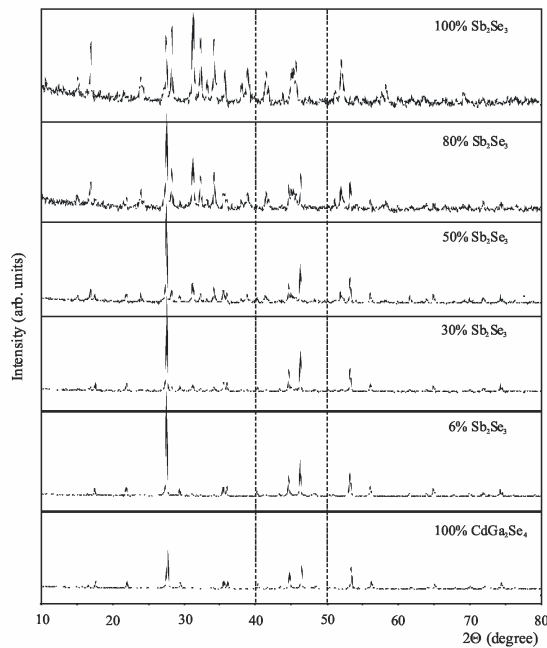


Fig. 3 Typical XRD patterns of the alloys of the CdGa₂Se₄–Sb₂Se₃ system.

the crystallization front varied from 12 to 35 K/cm. After complete crystallization, the furnace was cooled to room temperature at a rate of 5 K·h⁻¹.

The grown boule consisted of two parts. The lower (cone) part was the single crystal of the ternary phase (in most cases several single crystal blocks), and the top part was the solidified eutectic (LT–CdGa₂Se₄ + Sb₂Se₃). The length of the single crystal part was about 15–20 mm, depending on the diameter of the growth container and the sharpness of its cone.

The composition of the grown crystal was examined on a Philips XL 30 FEG scanning electron microscope with excitation energy of 20 keV. The Oxford Instruments INCA software package was used for energy-dispersive X-ray analysis (EDX) quantification. The obtained results are shown in **Table 1** together with the expected stoichiometric concentrations for the CdGa₂Se₄ composition. Only three principal elements and no antimony impurities could be detected by EDX. However, the red color of the grown crystals, which is different from the expected orange color of CdGa₂Se₄, indicated a small (less than 2 mol.%) solubility of Sb₂Se₃ in the

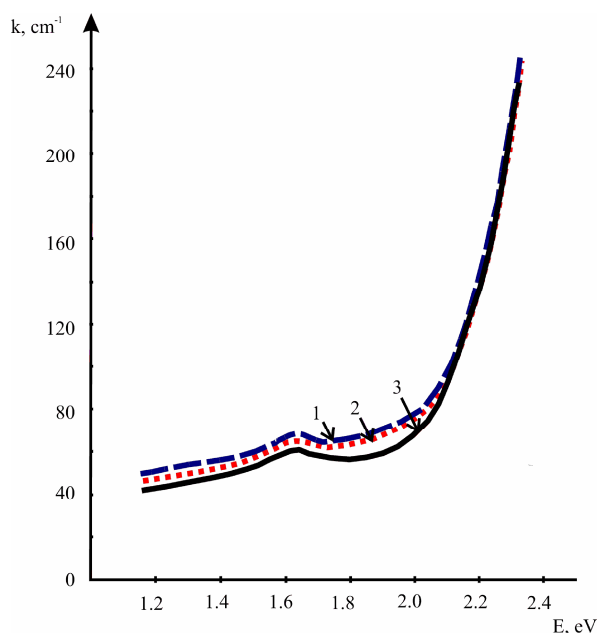


Fig. 4 Room-temperature optical absorption spectra of CdGa₂Se₄ single crystal plates cut from different parts of the crystal boule: (1) lower, (2) middle, and (3) upper part.

CdGa₂Se₄ crystals. This fact was also taken into account when constructing the phase diagram.

Absorption spectra of the CdGa₂Se₄ single crystal

We investigated absorption spectra of the grown CdGa₂Se₄ crystals. For that, the boule was cut perpendicular to the growth direction into several plates. The absorption was measured with a spectrofluorimeter CM-2203. Fig. 4 presents the spectral distribution of absorption coefficients for plates cut from the lower (sample 1), middle (2), and upper (3) parts of the boule. A diffused absorption band in the range 1.5–1.7 eV, centered at 1.63 eV, is observed for all samples. Its intensity does not depend on the nature of the sample. Likely, this band can be attributed to the impurity levels formed by antimony atoms. The absorption coefficient slightly decreases from the lower to the upper part of the boule, but remains in the range 40–63 cm⁻¹. The optical band gap at 298 K, directly measured from the absorption spectra, is 1.95±0.05 eV. This value is significantly different from the energy gap of undoped CdGa₂Se₄ [3–5], which also indicates a certain solid solution range of the ternary compound.

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