

Synthesis and Bridgman Growth of Ga₂S₃ Crystals

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Abstract. In this work, Ga₂S₃ crystals were obtained by vertical Bridgman method. The presence of cracks in the grown crystals was interpreted as a result of phase transition into monoclinic structure during cooling. This suggests the use of another approach for the growth of high quality samples, e.g. chemical transport method or melt-solution method. Maximal transparency range of 0.48-22.5 μm and at least 10 times higher damage threshold to that for GaSe render anisotropic Ga₂S₃ crystal among the most prospective crystals for nonlinear applications.

Introduction

Gallium sesquisulfide (Ga₂S₃) is a semiconducting material with a direct band gap around 3 eV. The crystals have a high photosensitivity and strong luminescence response. Doped (by Cr or Fe) and undoped Ga₂S₃ can be a luminescent material for generation of long wavelength part of the visible spectrum [1]. Doping with the rare earth elements leads to luminescence in all visible range [1-3]. It is worthy to note that Ga₂S₃ does not show a luminescence quenching for up to 7 mol.% of some light generating impurities. In addition, the ability to convert the UV radiation in solar cells was claimed [4]. Another possible application for monoclinic Ga₂S₃ is nonlinear optics [5].

There are three known modifications of Ga₂S₃ from early data [6]. The low-temperature α-modification is white colored, crystallizes in a cubic defect type sphalerite lattice F-43m. When heated to 550-600°C, it becomes light yellow β-modification, which crystallizes in the hexagonal disordered defect (wurtzite-type) lattice P6₃mc. At 1020°C, an orange-yellow α'-modification crystallizes in the monoclinic lattice Cc. Also, there is an evidence of the existence of another high temperature γ-modification with the space group P6₁. Ga₂S₃ melts congruently at the temperature ~ 1230°C.

The structures of all phases are similar. Their prototype is the ZnS structure with the vacant places of gallium in every third position. Sulfur occupies the nodes of almost perfect hexagonal packing, and the polymorphism is caused by the different ordering in the cation sublattice. Due to superposition of the diffraction lines, it is difficult to see the difference between these phases by X-ray methods. Perhaps, this is the reason for the differences in the data on structures of the crystals grown at different temperatures. For example, in paper [7] the synthesis of Ga₂S₃ at 1000°C from elementary Ga and S and small addition of iodine gave a material with the monoclinic structure at room temperature, while during the heating of this material the structure transition at 987°C was fixed in situ with the cell parameters $a = 3.73053 \text{ \AA}$, $c = 6.0961 \text{ \AA}$. These parameters are close to those for β-phase. The melt growth of hexagonal phase by the Bridgman method was reported in [8]. In [9] the Ga₂S₃ was obtained at 350°C and subsequent annealing at 500°C had led to the cubic

phase, and to the γ -modification ($P6_1$) after heating at 650°C. The growth of Ga_2S_3 from gas phase in the atmosphere of ICl_3 at 850°C [4], and the synthesis at 950°C from Ga_2O_3 and S [5], had led to preparation of the monoclinic phase.

In this paper we evaluated the possibility of obtaining high-quality Ga_2S_3 crystals directly from the melt. The synthesis and crystal growth Ga_2S_3 by Bridgman method are described. Chemical composition, structure, and the transparency range of the grown crystals were revealed; the manufactured samples were also characterized by Raman and electron microscopy.

Materials and methods

All synthesis and growth ampoules were washed with concentrated HNO_3 acid. After following washing in distilled water and drying in air box, the ampoule for synthesis was filled with the starting materials: Ga 99.9997 and S 99.99, which were additionally purified by remelting under vacuum. Weighing was performed with accuracy ± 0.1 mg. The molar ratio was $Ga/S=2/3$. Both growth and synthesis ampoules were evacuated to residual pressure $\sim 10^{-4}$ torr. High vapor pressure of volatile components is the main problem for synthesis of chalcogenide compounds. In this work, we used the method proposed for the synthesis of GaSe and GaS compounds [10]. The method uses single-zone horizontal furnace. The ampoule with the charge was partially inserted inside the furnace and the temperature was raised up to 1100°C. The sulfur accumulates in the ampoule part outside the furnace. After finding the ampoule position, when the sulfur melt becomes red, the ampoule is gradually pushed inside the furnace. When no liquid S was observed in the cold part, the ampoule is entirely moved inside the furnace for several hours for melt homogenization. After that, the furnace is switched off. For the growth process, the synthesis ampoule was broken and polycrystalline white material was loaded into double wall ampoule. The internal conical container was covered with pyrolytic carbon which protects the melt from reaction with quartz.

The unseeded crystal growth was performed by modified vertical Bridgman-Stockbarger methods with heat field rotation. Details of application of that approach are described in Ref. [11]. The sealed growth ampoule was loaded into the furnace with temperature gradient ~ 15 K/cm at the estimated level of crystallization front. After homogenization of the melt at the temperature 30K above the melting point, the ampoule was mechanically lowered with the speed 10 mm/day. When the growth was completed, the furnace was switched off. The grown crystal was analyzed by different methods.

The microscopic features and chemical composition were determined by a MIRA 3 LMU (TESCAN Ltd) scanning electron microscope with an INCA Energy 450+ dispersion spectrometer based on a highly sensitive XMax-80 silicon-drift detector at the accelerating voltage of 20 kV and the probe current of 1.5 nA. The most analyses were carried out by using EM-EDS, the effective time of the spectrum accumulation being 15–20 sec.

The X-ray diffraction patterns were obtained with a Shimadzu XRD-6000 diffractometer operating with the $Cu\ K\alpha$ radiation. Powdered silicon was used as the external standard ($a = 5.4309$ Å). The diffraction data were collected from 10 to 80° of the 2θ angular range with a step of 0.03° and accumulation time of 1 s per step. The phase composition was identified using PDF4 database.

The Raman measurements were carried out using InVia (Renishaw, England) spectrometer at the room temperature under microscope with $\times 50$ magnification. Two excitation sources (operating at 532 and 785 nm) were used. A wide spectral range 100–3000 cm^{-1} was analyzed with the resolution ~ 4 cm^{-1} .

Vis- and IR absorption spectra of the powdered sample were investigated using the diffuse-reflectance technique. Spectrophotometer Cary 100, Varian (spectral range of 200–900 nm with a resolution of 1 nm) in visible region and FTIR spectrometer Tensor 27, Bruker (spectral range of 375 to 7000 cm^{-1} (~ 26 –1.4 μm) with a resolution of 4 cm^{-1}) were used.

Results and discussions

The result of the growth experiment was the crystal of 5 cm in length and 8 mm in diameter. There were many cavities on the crystal surface due to the gas bubbles contacting the growth container. On the base of a simultaneous light reflection from micro-faces in these cavities, one may suppose that the crystal is a single crystalline material. Nevertheless, the crystal was broken into fragments due to a large number of cracks (Fig. 1a).

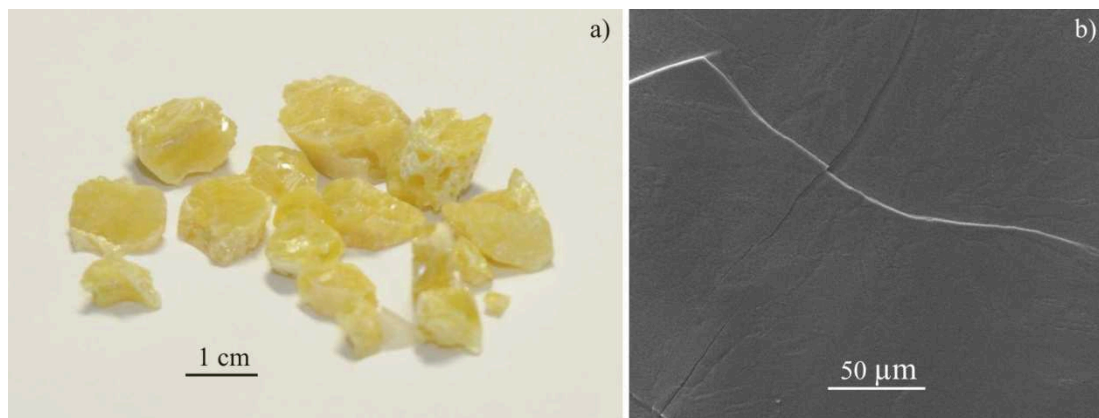


Fig.1. Fragments of the Ga₂S₃ crystal (a) and SEM photo of the surface (b).

A numerous micro cracks of a few tens of microns in length are seen in a scanning electron microscope (Fig. 1b), which are probably the cause of opacity of the samples in visible light (Fig. 2a). According to the X-ray fluorescence analysis (Fig. 2b), the obtained crystals have a composition Ga₂S₃ with slight excess of Ga relative to the Ga₂S₃ stoichiometry: Ga and S contents are 40.49 and 59.51 mol. %, respectively.

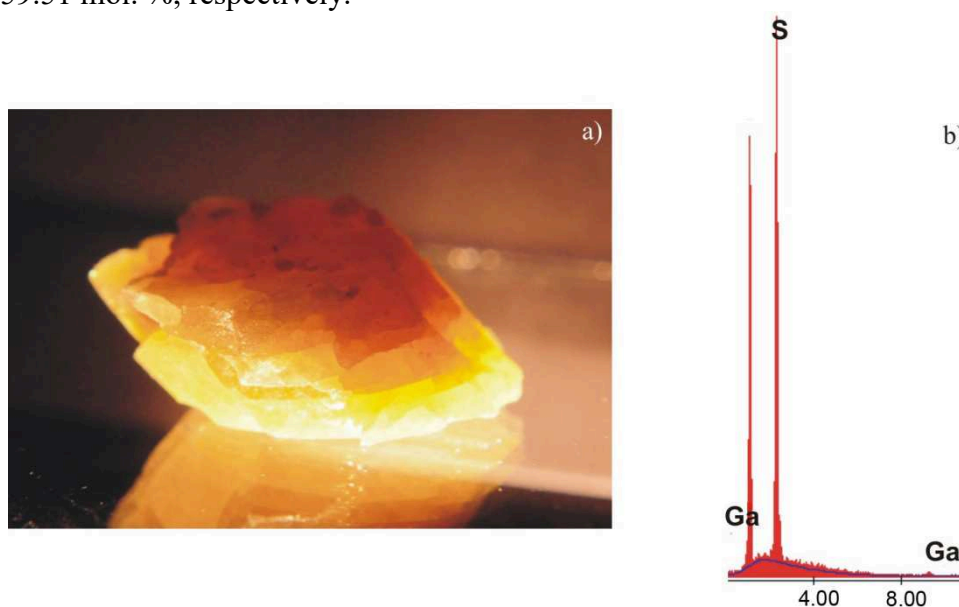


Fig.2. Ga₂S₃ fragment under spot light (a) and X-ray fluorescence spectrum of Ga₂S₃ sample (b).

X-ray diffraction pattern of the crystal powder (Fig. 3) corresponds well to the monoclinic phase Ga₂S₃ (PDF Card # 00-016-0500), but intensities of the peaks do not fully coincide with the reference. The latter may be caused by the presence of other Ga₂S₃ polymorphs in the probe.

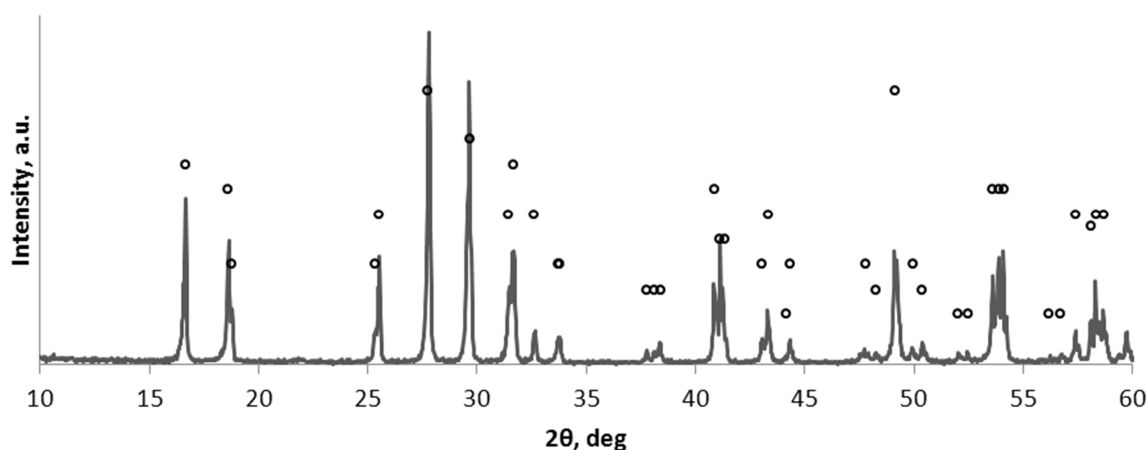


Fig. 3. X-ray diffraction profile of the grown crystal powder. Circles correspond to positions of diffraction peaks for monoclinic Ga_2S_3 phase from PDF Card # 00-016-0500.

The Raman spectra of powdered samples are shown in Fig. 4. It should be noted that, on the other hand, the Raman patterns from different blocks and powdered samples are identical, which confirms the homogeneity of composition and the absence of other phases from Ga-S system. The spectra from different excitation wavelength agree very well, so it may be stated, that none of the lines originates from luminescence and all they are scattered Raman lines.

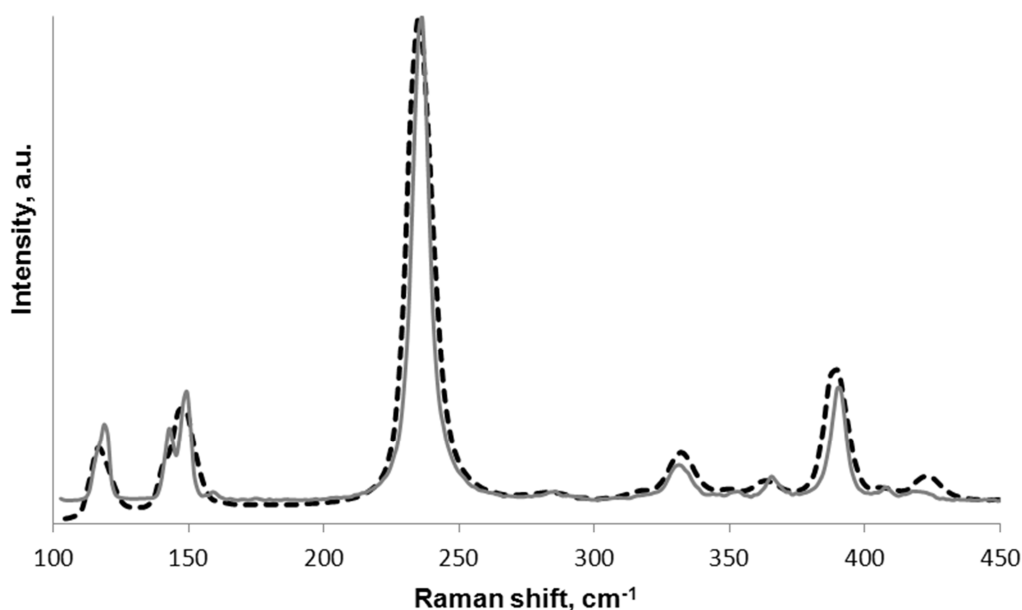


Fig. 4. Raman spectra from powdered Ga_2S_3 with different excitation wavelengths: dot line, 532 nm; solid line, 785 nm.

The structure of Ga_2S_3 is composed of GaS_4 tetrahedra. By Lucazeau and Lorey [12] the Raman lines may be interpreted as stretching modes of the tetrahedra at frequencies above 270 cm^{-1} , while frequencies below 200 cm^{-1} can be assigned to its bending modes. Some lines may correspond to external vibrations: rotational and translational modes in the molecular substructure of GaS_4 . The strongest line, located at $\sim 250\text{ cm}^{-1}$ is likely to be the A_1 mode of the GaS_4 groups: vibrations of the sulfur anions around vacancies in the anion–vacancy direction.

It should be noted that because of the small distortion in lattice structures of Ga_2S_3 polymorphs, it is very difficult to identify the polymorph type with Raman spectroscopy.

To the best of our knowledge the transparency spectrum (Fig. 5) was recorded for the first time.

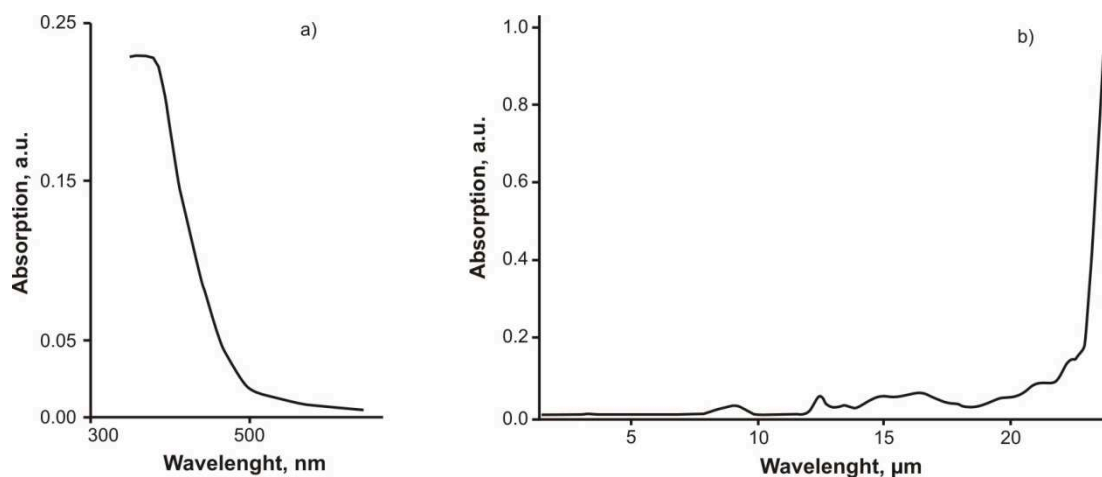


Fig. 5. (a) Short and (b) long wave edges of the Ga_2S_3 transparency spectra.

In Fig. 5 it is seen that the spectral positions of short and long wave edges of Ga_2S_3 lie outside the transparency range of GaSe widely used for nonlinear applications: 0.62–20 μm . Maximal transparency range of Ga_2S_3 seems to cover 0.48–22.5 μm range. Moreover, a powder of Ga_2S_3 has shown at least 20 time higher damage threshold than a facet of a cleaved GaSe crystal under expose to 10 ns pulses of a Nd:YAG laser. These two facts make Ga_2S_3 crystal among the most prospective crystals for nonlinear applications.

Conclusions

Based on the data of [4,5,7] we can assume that Ga_2S_3 monoclinic phase is not the high temperature one as described in [6]. The crystal grown from the melt is likely to undergo a phase transition to monoclinic structure during cooling. This in turn may cause the occurrence of macro and micro cracks in the sample. Thus, to obtain high quality samples Ga_2S_3 it is necessary to conduct crystallization at lower temperature, which would be below the transition point to the monoclinic structure. This can be done by other growth techniques, for example through the gas phase or using a solvent. Maximal transparency range of 0.48–22.5 μm and at least for 10 times higher damage threshold to that for wide used GaSe make Ga_2S_3 crystal among the most prospective crystals for nonlinear applications.

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