



Short communication

Study of Ga₂S₃ crystals grown from melt and PbCl₂ flux

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ABSTRACT

Monoclinic and cubic Ga₂S₃ crystals were obtained by Bridgman and flux methods. For the first time optical properties are measured in the bulk samples including THz range. The transparency range 0.44–25 μm is recorded. Ga₂S₃ crystal demonstrated 20 times higher light induced damage threshold compared to GaSe. No phonon absorption peaks are found in the THz range at wavenumbers below 100 cm⁻¹. IR and THz optical, as well as other physical properties render Ga₂S₃ among the prospective materials for THz applications.

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1. Introduction

High nonlinear and damage threshold, suitably birefringent crystals are of the top interest in the field of efficient phase-matched mid-IR and THz generation. Among known crystals, pure and doped GaSe possesses a range of attractive physical properties including extreme wide transparency window 0.62–20 μm that continues from 50 μm further into the THz. As a result, GaSe occupied for a long time the upper position among intensively studied crystals for THz application. But its layered structure and resulting poor mechanical properties limit the processing and out-of-door application [1]. Recently, a study of Ga₂S₃ powder has shown its perspectives of application in the IR as a nonlinear optical material [2]. The Ga₂S₃ crystals also have a high photo-sensitivity and strong luminescence response. Pure, Fe, transition-metal (Mn) or rear-earth element doped Ga₂S₃ has strong luminescence response all over the visible range [3–6]. 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 [7]. Therefore, Ga₂S₃ crystal seems as quite attractive for multidisciplinary applications.

Ga₂S₃ melts congruently at the temperature ~1120 °C. There are three well-known modifications of Ga₂S₃ from early data [8]. The low-temperature modification is white colored, crystallizes in a cubic defect-type sphalerite lattice F-43m. When heated to 550–600 °C, it transforms into yellowish modification, which crystallizes in the hexagonal disordered defect (ZnS or wurtzite-type) lattice P6₃mc. At 1020 °C, an orange-yellow modification crystallizes in the monoclinic lattice Cc. The lattice 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 positions of almost perfect hexagonal packing and the different ordering in the cation sublattice causes the polymorphism [9].

Nevertheless, there is mismatch in the published data on stability ranges of Ga₂S₃ structures. For example, it was established that the synthesis 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 Å, c = 6.0961 Å [10]. In comparison, these

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parameters are close to those of β -phase (hexagonal) [8]. The melt growth of hexagonal phase by the Bridgman method was reported in [11]. In [12] the Ga_2S_3 phase was obtained from reaction between Ga_2S_3 and S at 350°C and subsequent annealing at 500°C had led to the cubic phase but further heating to 650°C resulted in the γ -phase (P6_1). The growth of Ga_2S_3 from gas phase in the atmosphere of ICl_3 at 850°C [7] and the synthesis at 950°C from Ga_2O_3 and S [2] also had led to preparation of the monoclinic phase. Ga_2S_3 shows anomalous variation in vapor composition with decreasing temperature [13] So, a role of gaseous phase and free-space volume in the ampoule should be concerned. Pardo et al. [14] reported that hexagonal Ga_2S_3 forms in sulfur-deficient conditions in the presence of GaS. Another ambiguity in compiling literature data results from unequal naming of different phases by Greek symbols (α , α' , β and γ).

The absence of inversion symmetry in monoclinic structure of Ga_2S_3 suggests application for phase matched frequency conversion. The cubic phase can also be useful for nonlinear applications with the help of a quasi-phase-matching technique [15]. Nevertheless, a very little work on the optical properties and nonlinear application of Ga_2S_3 has been done. It was found that powder of monoclinic and cubic phases exhibit a good transparency in the wavelength range of $0.44\text{--}25\ \mu\text{m}$. The comparatively large SHG effects of, respectively, about 0.5 and 0.7 times that of KTP was also observed, as well as light induced damage threshold is 100 and 30 times to that of AGS. Besides, SHG phase matching at 1910 nm was demonstrated in monoclinic phase powder [2].

The objective of the present work was to evaluate the possibility of obtaining high-quality Ga_2S_3 material and grow bulk Ga_2S_3 crystals by Bridgman and flux methods. Chemical composition, structure, and optical properties over the entire transparency range, for the first time including THz region, were reported.

2. Measurement techniques

The microscopic features and chemical composition of the crystals were determined by a scanning electron microscope MIRA 3 LMU (TESCAN Ltd., Czech) with a dispersion spectrometer INCA Energy 450+ (Oxford Instrument Analytical Ltd., UK) 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 an EM-EDS, the effective time of the spectrum accumulation being 15–20 s. A confocal laser scanning microscope LSM780NLO (Carl Zeiss, Germany) was also used in the study surface morphology of the samples.

Differential thermal analysis was done on the homemade setup based on the S-type thermocouples connected to 2-channel Eurotherm 2604 temperature controller. The charges from synthesized Ga_2S_3 and with addition of PbCl_2 were heated/cooled with the rate 600°C/h several times in order to exclude effects of inhomogeneities. First sample of Ga_2S_3 was analyzed in opened

crucible under N_2 flow. The resulting thermogram had several effects with final melting at $\sim 1000^\circ\text{C}$ meaning a strong evaporation of the sample and the need of closed crucible. Thus other samples were analyzed in sealed quartz ampoules containing $\sim 0.5\text{ g}$ of the charge.

The X-ray diffraction patterns were obtained with a XRD-6000 diffractometer (Shimadzu, Japan) operating with the $\text{Cu K}\alpha$ radiation. Powdered silicon was used as the external standard ($a = 5.4309\ \text{\AA}$). 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.

Vis- and IR absorption spectra of the powdered sample were recorded using the diffuse-reflectance technique. A spectrophotometer Cary 100, Varian (operation range $200\text{--}900\text{ nm}$, spectral resolution of 1 nm) and a FTIR spectrometer Tensor 27, Bruker ($375\text{--}7000\text{ cm}^{-1}$, spectral resolution 4 cm^{-1}) were used, respectively.

Laser damage threshold was estimated by visual appearance of defects on the surface of freshly cleaved samples. 10 ns pulses of a Nd:YAG laser were used for irradiation.

THz spectra were recorded by using finished 10 and $20\ \mu\text{m}$ thick Ga_2S_3 wafers glued to $100\ \mu\text{m}$ Si wafers with extra thin layer of epoxy glue and a FTIR spectrometer Vertex 80 v (Bruker, Germany): operation range $5\text{--}50,000\text{ cm}^{-1}$, spectral resolution $<0.2\text{ cm}^{-1}$, wavenumber accuracy <0.01 @ 2000 cm^{-1} , photometric accuracy 0.1% T. The layer of the epoxy glue did not show any absorption structure. Polishing procedure was identical to that described in [16].

The Raman measurements were carried out using a spectrometer InVia (Renishaw, UK) supplied by microscope with magnification $50\times$ at room temperature. Nonpolarized excitation source operating at 532 nm was employed. Both powder and bulk samples were studied. A wide spectral range $100\text{--}3000\text{ cm}^{-1}$ was analyzed with the resolution 4 cm^{-1} .

3. Material synthesis and crystal growth

All synthesis and growth ampoules were washed up with HNO_3 acid. The starting materials Ga 99.9997 and S 99.99 were additionally purified by remelting under vacuum. To overcome the issue related with high sulfur pressure we used the method proposed for the synthesis of GaSe and GaS compounds [17]. After synthesis the ampoule was broken and polycrystalline white color material was transferred into double wall ampoule.

The unseeded crystal growth was performed by modified vertical Bridgman-Stockbarger methods with heat field rotation [18]. The result of the growth experiment was the crystal 5 cm in length and 8 mm in diameter. A surface of the grown ingot contained many faceted gas cavities. Their reflection of light was simultaneous. Thus, one may suppose that the crystal is a single

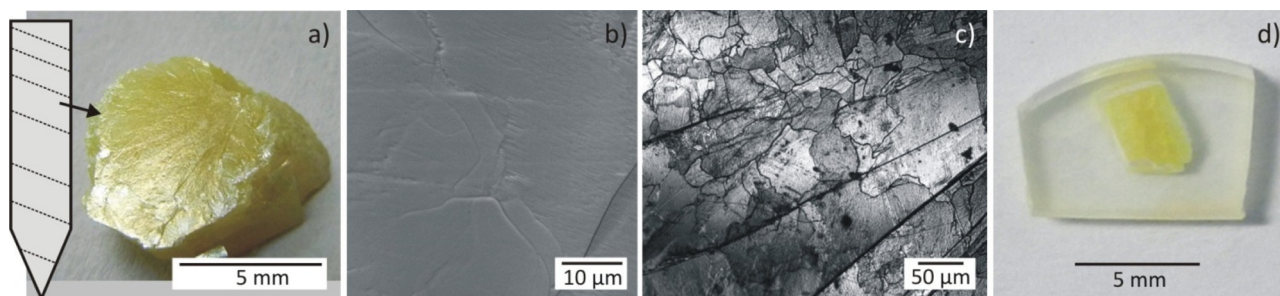


Fig. 1. Melt grown Ga_2S_3 : (a) cleaved section from the boule, photos from (b) electron and (c) laser confocal microscopy (scattered light from 405 nm laser), (d) polished plate embedded in polymethylacrylate.

crystalline material. However, the ingot was easily disintegrated due to a large number of parallel cracks suggesting a presence of poor cleavage in the crystal. It seems that milky appearance of the crystals is due to phase transition in Ga_2S_3 during cooling. As a result, the sample consists from small, down to 200 μm , disoriented grains whose boundaries are severe cracked (Fig. 1b, c). Finally, even thin samples look opaque by naked eye (Fig. 1d). EDX analysis showed that composition of Ga_2S_3 has slight excess of Ga relative to stoichiometry: Ga and S contents are 40.49 and 59.51 mol%, respectively.

In order to decrease the temperature of crystallization below phase transition we have used flux crystallization. PbCl_2 was chosen as a solvent since it is widely used for the growth of chalcogenides [19,20].

A trial experiment on heating the composition $\text{Ga}_2\text{S}_3/\text{PbCl}_2$ in 1:1 ratio to 1000 °C resulted in full remelting of the sample. XRD analysis showed the presence of initial components only meaning no chemical reaction between the components. After that, a series of samples with various flux concentration were analyzed by DTA. As a result, a phase diagram for the system $\text{Ga}_2\text{S}_3\text{--PbCl}_2$ was constructed (Fig. 2). The liquidus of PbCl_2 was assumed according to the known data of the melting point. All samples with addition of PbCl_2 have eutectic effect at $\sim 430^\circ\text{C}$. By extrapolation of liquidus the composition of eutectic may be estimated as ~ 32 mol% of PbCl_2 . Further interpretation of DTA data was done using results of XRD analysis of the samples after thermal analysis. Before grinding the samples were soaked in dimethyl sulfoxide to remove PbCl_2 .

XRD pattern of pure Ga_2S_3 after DTA (Fig. 3d) matches monoclinic modification (Fig. 3b, ICSD card #000160500) and thermal effect at 1000 °C corresponds to polymorphic transition to hexagonal phase. This temperature agrees well with in-situ measurement [10]. The crystal grown from melt by Bridgman method has the same diffraction pattern (Fig. 3c) which confirms the cause of its milky appearance due to phase transition. Same effect at 1000 °C was found for the sample with 10% of PbCl_2 . Also this and next composition (25% PbCl_2) have another thermal effect at $\sim 830^\circ\text{C}$. A composition with 40% of PbCl_2 does not have this effect since the sample melting is reached at lower temperature $\sim 790^\circ\text{C}$.

XRD data gives reliable reason to treat the effect at 830°C as phase transition between monoclinic and cubic modifications. Diffraction profiles of the samples with 10 and 25% of PbCl_2 have

both monoclinic and cubic peaks (Fig. 3e,f), while the samples with PbCl_2 concentration of 40% and more have only cubic pattern (Fig. 3g). It may be assumed that direct transition from monoclinic to cubic structure is not realized in Ga_2S_3 . The samples crystallized from pure melt do not contain cubic phase. This may be confirmed by Raman data (Fig. 5). While the appearance of cubic Ga_2S_3 in the samples with solvent may be explained by solute segregation. A melt gradually shifts to PbCl_2 -rich composition during crystallization. So, after growth of monoclinic Ga_2S_3 the melt falls into the region of primary crystallization of cubic phase. According to DTA the transition in cubic phase takes place at much higher temperature than $550\text{--}600^\circ\text{C}$ referred in previous studies [8]. Besides, the XRD patterns of cubic samples are presented as broadened peaks with maxima shifted from those of etalon ICSD card #76753 (Fig. 3h). All these may be caused by localization of Pb and/or Cl in Ga_2S_3 crystal structure.

In order to perform detailed studies, we have realized the experiment on slow, 1°C/h , cooling of the charge 50 mol% Ga_2S_3 + 50 mol% PbCl_2 . After removing PbCl_2 , the sample consisted of yellow octahedra-like crystals (Fig. 4a). They also have cleavage (Fig. 4b), but polished sections are transparent in visible light (Fig. 4c). Chemical analysis revealed a presence of Pb and Cl in the crystal composition, 4 and 2.5 mol%, correspondingly. These impurities explain the shift of XRD peaks for flux-grown cubic Ga_2S_3 (Fig. 3).

4. Optical properties

Raman spectra of the samples obtained both after DTA and crystal growth experiments are shown in Fig. 5. The spectra for bulk and powder samples of monoclinic phase were found to be the same due to disoriented grains in both cases (Fig. 1c). For monoclinic samples. From spectra (a) and (b) it may be concluded that difference in melt cooling rate does not lead to principal changes in the Raman peaks. So, a broadening of major peak at 250 cm^{-1} and appearance of intensive peak at $\sim 290\text{ cm}^{-1}$ may indicate the presence of cubic phase in the sample. However, in one of the previous studies of Ga_2S_3 [21] it was affirmed that Raman spectra of different modifications are indistinguishable due to the likeness of crystal structure.

Increment of PbCl_2 concentration in the DTA sample results in the gradual shift of Raman lines. The same effect could be seen for XRD peaks. It may be caused by variation of Pb and Cl

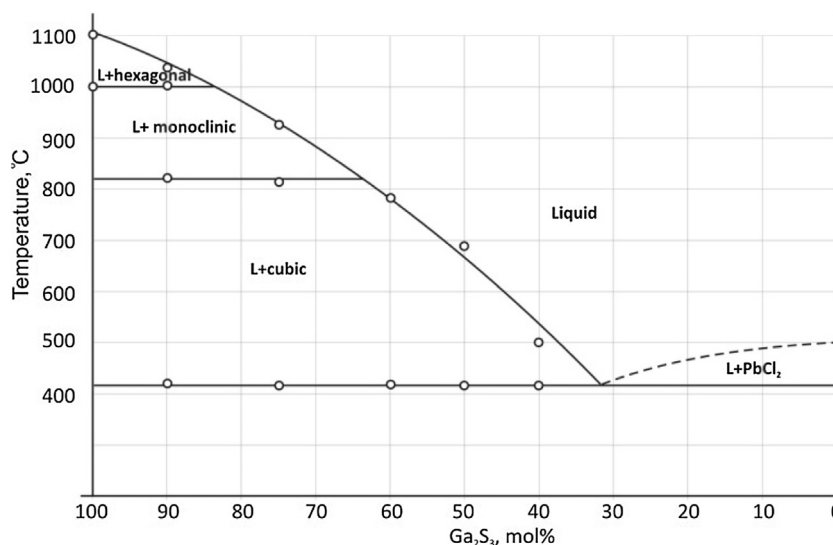


Fig. 2. $\text{Ga}_2\text{S}_3\text{--PbCl}_2$ phase diagram according to the thermal analysis.

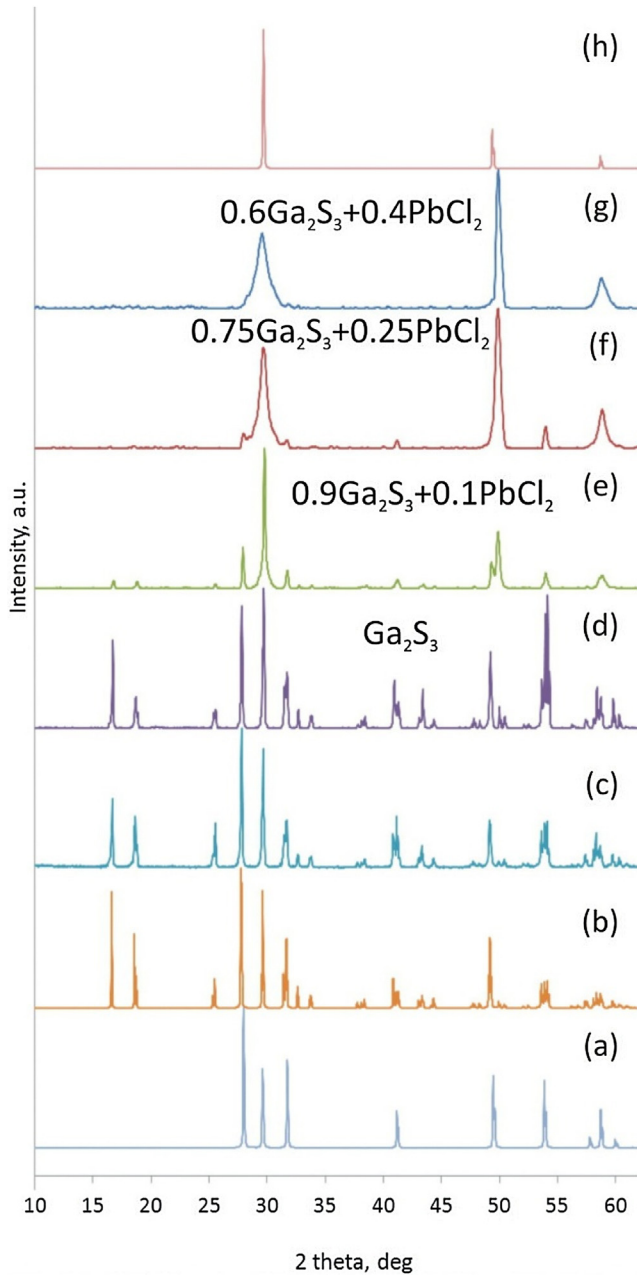


Fig. 3. X-ray diffraction data for Ga_2S_3 : etalon patterns for (a) hexagonal and (b) monoclinic phases; (c) after melt growth; (d–g) after thermal analysis of specified composition; (h) etalon pattern for cubic modification.

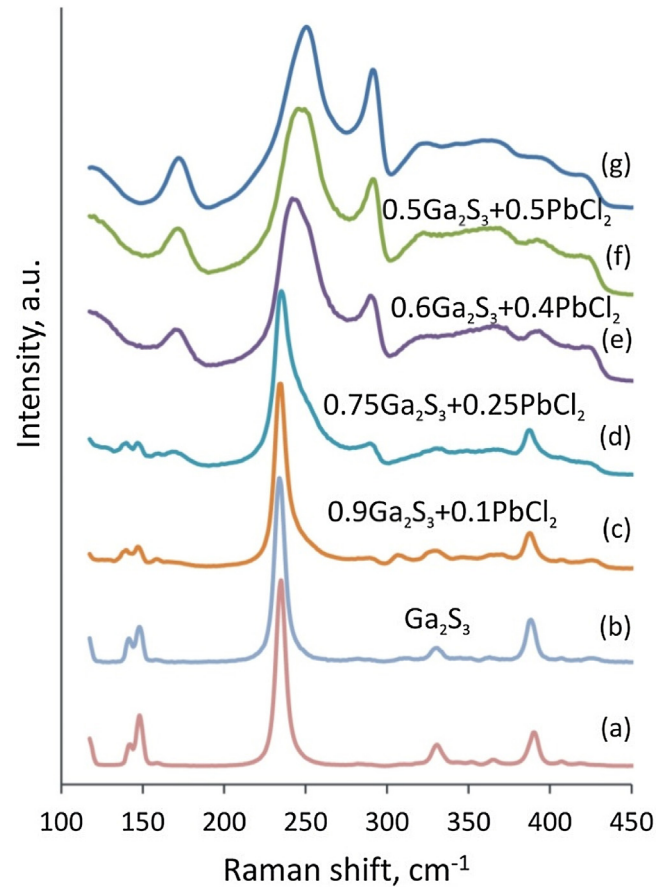


Fig. 5. Raman scattering spectra of Ga_2S_3 after: (a) melt growth; (b–f) thermal analysis of specified composition; (g) slow cooling the composition $0.5\text{Ga}_2\text{S}_3 + 0.5\text{PbCl}_2$.

concentration in the Ga_2S_3 , which should be gradually decreased with lowering of crystallization temperature. Also, an effective distribution coefficient is quite sensitive to crystallization speed. The latter may be responsible for the difference in Raman lines for composition solidified under 1 and $600^\circ/\text{h}$ (Fig. 5f,g).

The main transparency window of monoclinic Ga_2S_3 at “0” level seems to cover $0.44\text{--}25\text{ }\mu\text{m}$ range (Fig. 6a). Transmission curves recorded for pure monoclinic Ga_2S_3 powder and diluted with KBr powder, demonstrated the same short-wave 415 nm edge that confirms adequacy of the measurement. This absorption edge was found to be different to that of cubic phase (Fig. 7). For monoclinic phase the value well agrees with recent data of Ho and Chen [7].

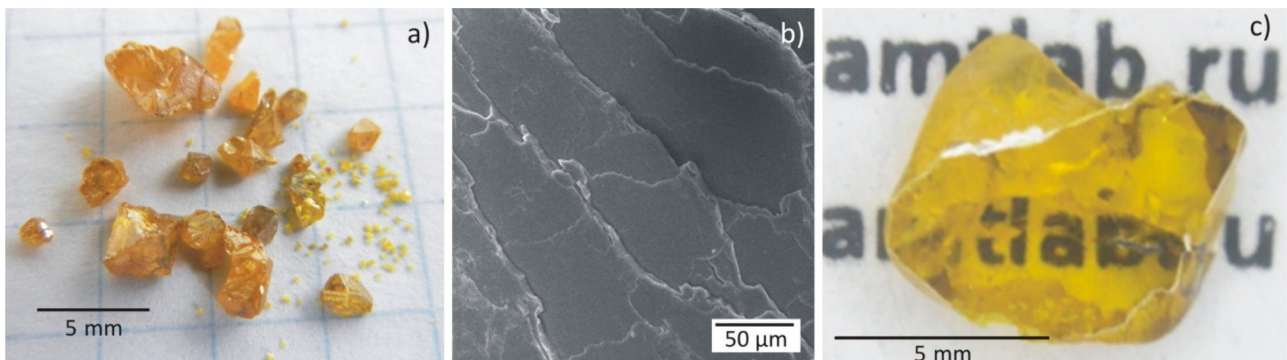


Fig. 4. Ga_2S_3 crystals grown from 50 mol% PbCl_2 flux: (a) external view after removing PbCl_2 ; (b) SEM photo of the cleavage; (c) transparent plate for optical measurements.

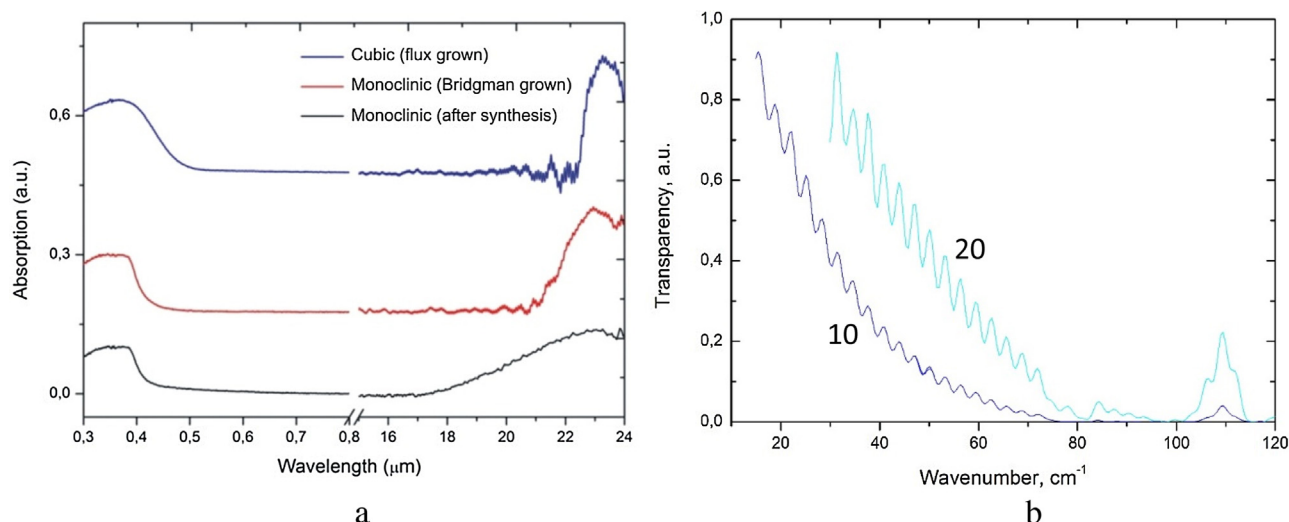


Fig. 6. (a) absorption spectra of Ga₂S₃ samples grown by different methods within main transparency window; (b) transparency spectra of 10 and 20 μm wafers of monoclinic Ga₂S₃ in the THz region.

While the presence of cubic phase may partially explain the existing discrepancy of bandgap values for Ga₂S₃ [22,23].

The maximal transparency window of any studied phase of Ga₂S₃ was found wider than 0.62–20 μm window of GaSe [24]. Besides, the short-wave edge of Ga₂S₃ vanishes completely nonlinear (two photon) absorption of Ti:Sapphire and Nd:YAG lasers. No phonon absorption peaks are seen in the THz region below 100 cm⁻¹ but etalon patterns (Fig. 6b).

The as-cleaved monoclinic Ga₂S₃ had shown at least 20 times higher damage threshold than a facet of a cleaved GaSe crystal. Both modifications exhibit comparatively large second harmonic (SH) generation effects of about 0.7 and 0.5 times to that of commercial KTiOPO₄ (KTP), for the monoclinic and cubic Ga₂S₃ respectively. Calculated birefringence $B = 0.0025$ [2] is satisfactory high at least for THz generation by down-conversion.

5. Conclusions

Two phases of Ga₂S₃ crystals with different space groups Cc and F-43m were obtained by vertical Bridgman and flux methods. PbCl₂ flux was found to be suitable for growth of transparent cubic

phase. However, contamination of flux material induces the search of new solvent for pure Ga₂S₃ growth. The transparency windows 0.44–25 μm of all phases are almost identical and wider than 0.62–20 μm transparency window of GaSe. The short-wave edge of Ga₂S₃ excludes two photon absorption for Ti:Sapphire and Nd:YAG lasers widely used as pump sources for parametric frequency converters. No phonon absorption peaks are available in the THz range at wavenumbers below 100 cm⁻¹. As-cleaved Ga₂S₃ samples demonstrate 20 times higher light induced damage threshold to that for GaSe. Good mechanical properties allow high quality processing and out-of-lab application. Physical properties presented render monoclinic Ga₂S₃ among the most prospective nonlinear materials in IR-THz. However cubic phase may also be applicable in optical rectification devices.

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References

- [1] J. Guo, J.J. Xie, D.J. Li, G.L. Yang, F. Chen, C.R. Wang, L.M. Zhang, Yu.M. Andreev, K. A. Kokh, G.V. Lanskiy, V.A. Svetlichnyi, Doped GaSe crystals for laser frequency conversion, *Light Sci. Appl.* 4 (2015) e362.
- [2] M.J. Zhang, X.M. Jiang, L.J. Zhou, G.C. Guo, Two phases of Ga₂S₃: promising infrared second-order nonlinear optical materials with very high laser induced damage thresholds, *J. Mater. Chem. C* 1 (2013) 4754.
- [3] T. Aono, K. Kase, Green photoemission of α-Ga₂S₃ crystals, *Solid State Commun.* 81 (1992) 303.
- [4] C.S. Yoon, F.D. Medina, L. Martinez, T.Y. Park, M.S. Jin, W.T. Kim, Blue photoluminescence of α-Ga₂S₃ and α-Ga₂S₃: Fe²⁺ single crystals, *Appl. Phys. Lett.* 83 (2003) 1947.
- [5] J.S. Lee, Y.H. Won, H.N. Kim, C.D. Kim, W.T. Kim, Photoluminescence of Ga₂S₃ and Ga₂S₃:Mn single crystals, *Solid State Commun.* 97 (1996) 1101.
- [6] M.S. Jin, Y.G. Kim, H.L. Park, W.T. Kim, Photoluminescence of Ga₂S₃:Ho single crystal, *J. Korean Phys. Soc.* 39 (2001) S97.
- [7] C.H. Ho, H.H. Chen, Optically decomposed near-band-edge structure and excitonic transitions in Ga₂S₃, *Sci. Rep.* 4 (2014) 6143.
- [8] Z.S. Medvedeva, Chalcogenides of Subgroup IIIB of the Periodic System, Nauka, Moscow, 1968, pp. 216 (in Russian).
- [9] G. Collin, J. Flahaut, M. Guittard, A.M. Loireau-Lozach, Preparation et structure de Ga₂S₃ α type wurtzite lacunaire, *Mat. Res. Bull.* 11 (1976) 285–292.
- [10] C.Y. Jones, J.G. Edwards, Observation of a phase transformation of Ga₂S₃ in a quartz effusion cell above 1230 K by means of neutron scattering, *J. Phys. Chem. B* 105 (2001) 2718.

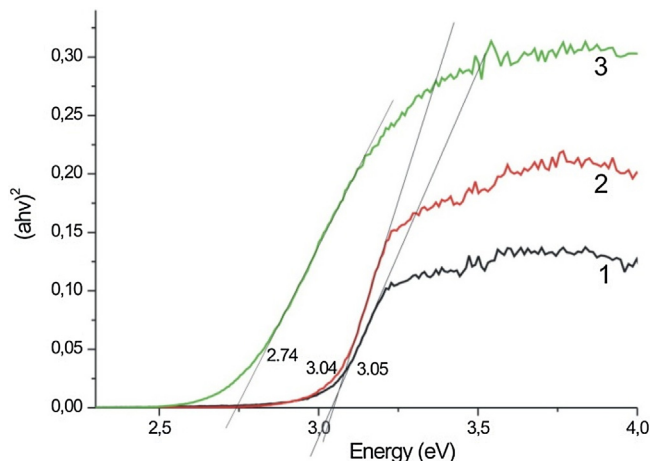


Fig. 7. Optical bandgaps of synthesized (1) and melt grown (2) monoclinic phase, and cubic Ga₂S₃ (3) grown from flux with composition Ga₂S₃:PbCl₂ = 1:1.

- [11] A.T. Nagat, F.S. Baharbi, R.H. Orainy, M. Abou Zied, S.E. Al-Garni, W.S. Al-Ghamadi, Growth and transport properties of some gallium chalcogenides from the group $M_2^{III}X_3^{VI}$ semiconductor compounds, *JKAU Sci.* 23 (2011) 31.
- [12] V. Vel'muzhov, M.V. Sukhanov, A.M. Potapov, A.I. Suchkov, M.F. Churbanov, Preparation of extrapure Ga_2S_3 by reacting Ga_3 with sulfur, *Inorg. Mater.* 50 (2014) 656–660.
- [13] R. Uram, J.G. Edwards, Vaporization chemistry in the gallium-sulfur system, *Thermochim. Acta* 204 (1992) 221.
- [14] M.P. Pardo, A. Tomas, M. Guittard, Polymorphisme de Ga_2S_3 et diagramme de phase Ga-S, *Mater. Res. Bull.* 22 (1987) 1677.
- [15] H. Ito, T. Hatanaka, S. Haidar, K. Nakamura, K. Kaewase, T. Taniuchi, Periodically poled $LiNbO_3$ OPO for generating mid IR to terahertz waves, *Ferroelectrics* 253 (2001) 95.
- [16] J.F. Molloy, M. Naftaly, Yu Andreev, K. Kokh, G. Lanskii, V. Svetlichnyi, Absorption anisotropy in sulfur doped gallium selenide crystals studied by THz-TDS, *Opt. Mater. Express* 4 (2014) 2451.
- [17] K.A. Kokh, Yu.M. Andreev, V.A. Svetlichnyi, G.V. Lanskii, A.E. Kokh, Growth of GaSe and GaS single crystals, *Cryst. Res. Technol.* 46 (2011) 327.
- [18] K.A. Kokh, B.G. Nenashev, A.E. Kokh, G.Yu. Shvedenkov, Application of a rotating heat field in Bridgman-Stockbarger crystal growth, *J. Crystal Growth* 275 (2005) E2129.
- [19] E. Post, V. Kramer, Crystal growth of $AgGaS_2$ by the Bridgman-Stockbarger and travelling heater methods, *J. Crystal Growth* 129 (1993) 485.
- [20] A.-D. Weber, M. Muller, D. Hofmann, A. Winnacker, Growth stability of zinc selenide bulk crystals from solutions, *J. Crystal Growth* 184 (1998) 1048.
- [21] G. Lucazeau, J. Lorey, Etude vibrationnelle de α - Ga_2S_3 , *Spectrochim. Acta Part A* 1 (1978) 29.
- [22] V.P. Mushjinskii, L.I. Palaki, V.V. Chebotaru, Optical absorption in α - Ga_2S_3 single crystals, *Phys. Status Solidi B* 83 (1977) K149.
- [23] H.A. Shaikh, M. Abdal-Rahman, A.E. Belal, I.M. Ashraf, Photoconductivity studies of gallium sesquisulphide single crystals, *J. Phys. D: Appl. Phys.* 29 (1996) 466–469.
- [24] D.N. Nikogosyan, *Nonlinear Optical Crystals: a Complete Survey*, Springer, Media, 2005 427 p.