

# Ga<sub>2</sub>S<sub>3</sub>: optical properties and perspectives for THz applications

Zhiming Huang<sup>a</sup>, J.-G. Huang<sup>a</sup>, K.A. Kokh<sup>b,c</sup>, V.A. Svetlichnyi<sup>b</sup>, A.V. Shabalina<sup>b</sup>,  
Yu.M. Andreev<sup>b,d</sup>, and G.V. Lanskii<sup>b,d</sup>.

<sup>a</sup>Shanghai Institute of Technical Physics CAS, Shanghai, 200083, China

<sup>b</sup>Siberian Physical-Technical Institute of Tomsk State University, Tomsk, Russia

<sup>c</sup>Institute of Geology and Mineralogy SB RAS, Novosibirsk, Russia

<sup>d</sup>Institute of Monitoring of Climatic and Ecological Systems SB RAS, Tomsk, Russia

**Abstract**—Optical properties of nonlinear Ga<sub>2</sub>S<sub>3</sub> are studied to reveal possibility for THz applications. The results establish that 3-d (bulky) Ga<sub>2</sub>S<sub>3</sub> is a strong potential competitor to a layered GaSe and its solid solutions those possess outstanding optical properties.

## I. INTRODUCTION

Searching for low optical loss, high nonlinear and optical damage threshold, suitably anisotropic materials is the top issue in the field of efficient phase matched THz generation. Among most attractive materials, GaSe shows extreme low mechanical properties due to the layered structure that hold back the out-of-door and commerce applications. Last decade, attention turned to modify its physical properties by doping with isovalent elements. Heavy S-doped or solid solution crystals GaSe<sub>1-x</sub>S<sub>x</sub>,  $x < 0.44$ , had been demonstrated to be of impressive results in usability and mid-IR & THz generation efficiency [1-3]. However, these crystals are still layered structure that limits sample fabrication with high optical quality facets.

Recently, a 3-d (bulky) gallium sesquisulfide (Ga<sub>2</sub>S<sub>3</sub>) semiconducting material was characterised as promising anisotropic nonlinear material with a direct band gap around 2.8 eV. It possesses very high laser induced damage threshold (30 times larger than that of AGS), wide transparency range (0.44-25 μm) and nonlinearity similar to that for GaSe [4]. Its birefringence of 0.025 is something larger than that of CdSe that allows SHG phase matching for wavelength longer than 1910 μm. However, transparency spectrum presented in Ref. [4] does not show transparency edges and specific features in the mid-IR but THz optical properties and applications is not considered at all.

In this study, single crystals Ga<sub>2</sub>Se<sub>3</sub> were grown by vertical Bridgman and flux methods. Optical properties related to the efficiency of frequency conversion were carefully verified and compared with that for pure GaSe and GaSe<sub>1-x</sub>S<sub>x</sub> crystals. The chemical composition were determined by a scanning electron microscope. The X-ray diffraction patterns were obtained with a Shimadzu XRD-6000 diffractometer operating with the Cu Kα radiation. The Raman measurements were carried out using an InWia (Renishaw, England) spectrometer in a backscattering or surface normal reflection configuration at the room temperature under microscope with ×50 magnification. First measurement in THz region are carried out with a FTIR spectrometer Vertex 80v (Bruker): 5-680 cm<sup>-1</sup>, spectral resolution <0.2 cm<sup>-1</sup>, with using LHe cooled Si bolometer.

## II. RESULTS

The Ga<sub>2</sub>S<sub>3</sub> boule grown by Bridgman method is easy fractioned (Fig. 1A) on subcentimeter sections due to rich quantity of cracks of a few tens of microns in length (Fig. 1B), which are probably the cause of the samples opacity.

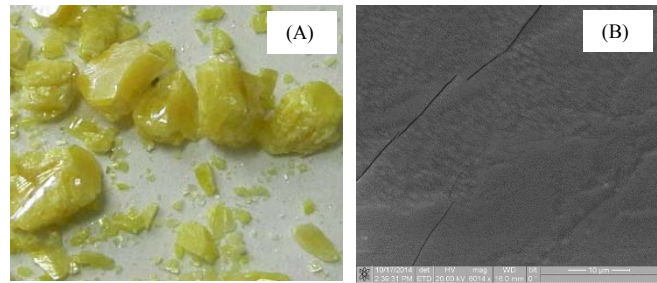


Fig. 1. (A) Photograph of Ga<sub>2</sub>S<sub>3</sub> grown by Bridgman method and (B) cracks pictured with 50 μm space resolution.

In turn, the millimeter-sized crystals grown by flux method are faceted and transparent (Fig.2).



Fig.2. Photograph of polycrystalline Ga<sub>2</sub>S<sub>3</sub> grown by flux method.

Chemical composition shows the crystals are small Ga excess. XRD-diffraction patterns of the powders verify Cc monoclinic structure for all grown crystals. X-ray diffraction patterns of the crystal powders correspond well to the monoclinic phase Ga<sub>2</sub>S<sub>3</sub> (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 Ga<sub>2</sub>S<sub>3</sub> polymorphs in the probe.

The Ga<sub>2</sub>S<sub>3</sub> fine powder was pressed in a tablet with fine KBr powder as a buffer. Restored absorption spectrum for Ga<sub>2</sub>S<sub>3</sub> powder is presented in Fig.3. It shows that the transparency window is 0.48-25 μm with the only specific feature as a

multiphonon absorption peak at 24  $\mu\text{m}$ . So, it has demonstrated that  $\text{Ga}_2\text{S}_3$  really possesses the widest transparency range and shortest absorption edge among anisotropic mid-IR crystals.

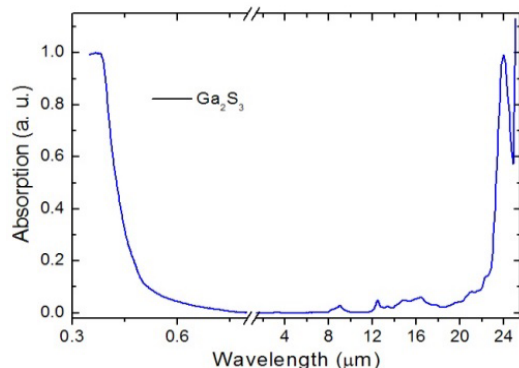


Fig.3. Absorption spectrum for  $\text{Ga}_2\text{S}_3$  powder.

To record THz transparency spectra,  $\text{Ga}_2\text{S}_3$  was first glued to 0.45-mm Si wafer with extra thin epoxy glue layer (reference transparency was recorded). Then it was abraded down to about 20 and further to about 10  $\mu\text{m}$  for transparency spectra testing. Estimated THz spectra for  $\text{Ga}_2\text{S}_3$  are shown in Fig.4.

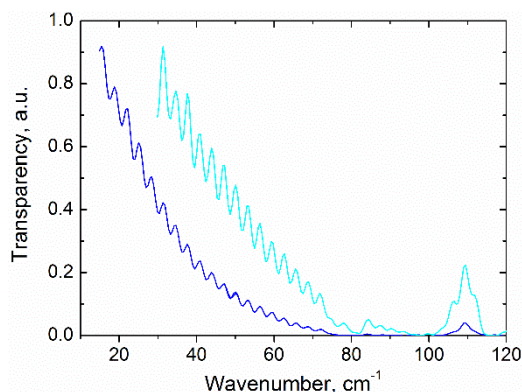


Fig.4. Transparency spectra for the thickness of about 20  $\mu\text{m}$  (blue) and 10  $\mu\text{m}$  (Cyan)  $\text{Ga}_2\text{S}_3$  crystals.

It is seen that long wave ( $> 100 \mu\text{m}$ ) THz range is free of strong phonon absorption peaks. This data are in full accordance with recorded Raman scattering lines (Fig.5). Inte-

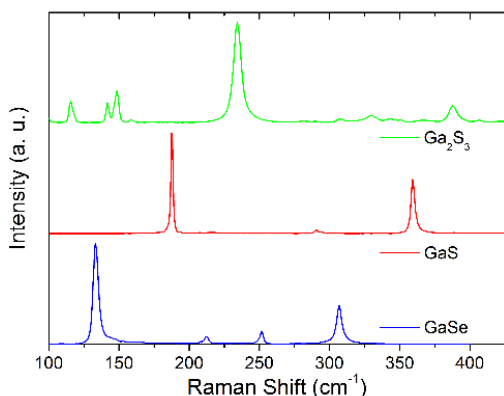


Fig.5. Intensive Raman scattering spectra for GaSe and GaS (as parent crystals) for solid solution  $\text{GaSe}_{1-x}\text{S}_x$  and  $\text{Ga}_2\text{S}_3$  crystal.

nensive Raman lines shifted for less than  $100 \text{ cm}^{-1}$  are not found. It should be noted that 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 state, that none of the lines originates from luminescence and all they are scattered Raman lines.

Besides, it has demonstrated that higher damage threshold of a fresh cleaved facets of  $\text{Ga}_2\text{S}_3$  single crystal from 20 up to 30 times than facets of a fresh cleaved GaSe crystal under expose to 10 ns pulses of a Nd:YAG laser ( $\lambda = 1.064 \mu\text{m}$ ).

Based on the recorded and available data it can be assumed that  $\text{Ga}_2\text{S}_3$  monoclinic phase is not the high temperature one as described in Ref. [4]. 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  $\text{Ga}_2\text{S}_3$  it is necessary to conduct crystallization at lower temperature, which would be below the transition point to the monoclinic structure.

Verified and developed properties render  $\text{Ga}_2\text{S}_3$  as a serious competitor to pure and doped GaSe in mid-IR and THz applications. It is because shorter wave transparency edge (Fig.3) that decreases multiphoton absorption for near IR pump; from 20 to 30 times higher optical damage threshold and good mechanical properties that allow processing; suitable anisotropy for PM down-conversion of 1- $\mu\text{m}$  two-frequency OPO emission into THz range. In difference to data in [4], multiphonon absorption peak is recorded at 24  $\mu\text{m}$ . Raman spectra (Fig.5) shows shorter wave THz edge in relation to GaSe and  $\text{GaSe}_{1-x}\text{S}_x$ . Unfortunately,  $\text{Ga}_2\text{S}_3$  hydrolyses in water and should be well water protected.

The research was supported in parts by China foundation (Grants No. MYHT-201402, 61274138), the Tomsk State University (8.1.51.2015, crystal syntheses) and RNF (15-19-10021, physical properties study), Russian Ministry of Education and Science No.14.594.21.0001 (RFMEFI59414X0001).

#### REFERENCES

- [1] J.-G. Huang, Z.-M. Huang, J.-C. Tong, C. Ouyang, J.-H. Chu, Yu. Andreev, K. Kokh, G. Lanskii, and A. Shaiduko, "Intensive terahertz emission from  $\text{GaSe}_{0.91}\text{S}_{0.09}$  under collinear difference frequency generation," *Appl. Phys. Lett.* vol. 103, pp. 81104, 2013.
- [2] J. Guo, D.-J. Li, J.-J. Xie, L.-M. Zhang, Z.-S. Feng, Yu. M. Andreev, K. A. Kokh, G. V. Lanskii, A. I. Potekaev, A. V. Shaiduko and V. A. Svetlichnyi "Limit pump intensity for sulfur-doped gallium selenide crystals," *Laser Physics Let.* vol. 11, pp. 055401, 2014.
- [3] K.A. Kokh, J.F. Molloy, M. Naftaly, Yu.M. Andreev, G.V. Lanskii, and V.A. Svetlichnyi, "Growth and optical properties of solid solution crystals  $\text{GaSe}_{1-x}\text{S}_x$ ," *Mater. Chem. & Phys.*, vol. 154, pp. 152-157, 2015.
- [4] M.J. Zhang, X.M. Jiang, L.J. Zhou, and G.C. Guo, "Two phases of  $\text{Ga}_2\text{S}_3$ : promising infrared second-order nonlinear optical materials with very high laser induced damage thresholds," *J. Mater. Chem. C.* vol. 1, pp. 4754-4760, 2013.
- [5] Z.S. Medvedeva, Chalcogenides of IIIB subgroup of Mendeleev periodic table, Nauka, Moscow, 1968. (in Russian)