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Structure and optical properties of $Li_2Ga_2GeS_6$ nonlinear crystal

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ABSTRACT

Structure and optical properties of new nonlinear crystal – $Li_2Ga_2GeS_6$ single crystal of optical quality, grown by the Bridgman technique were studied. The data on transmission, Raman scattering, luminescence emission, excitation and thermal quenching as well as thermostimulated luminescence are presented. Fundamental absorption edge is determined by the direct allowed electronic transitions: The values of optical band gap are estimated. Absorption band at 8.0 μm is due to S–S vibrations. Features in photoluminescence spectra are associated with excitons: both free (narrow line at 371 nm) and self-trapped ones (broad bands at 596, 730 and 906 nm). Spontaneous emission in the 80–170 K range, both at crystal heating and cooling, is typical of pyroelectrics: This confirms the absence of symmetry center in $Li_2Ga_2GeS_6$ and an opportunity of laser frequency nonlinear conversion.

1. Introduction

Optical parametric oscillation (OPO) is today one of the most widespread ways to produce tunable coherent radiation. The main part of OPO is a nonlinear crystal. The most widely used nonlinear crystals for the mid-IR are silver thiogallate and selenogallates ($AgGaS_2$ and $AgGaSe_2$) [1,2], zinc germanium phosphide $ZnGeP_2$ [3], etc.: these crystals have been practically used IR NLO materials since the 1970s. However, they possess serious drawbacks of one or another in their properties. For example, $AgGaS_2$ and $AgGaSe_2$ have a low laser-damage threshold, $AgGaSe_2$ is not phase-matchable at 1 μm (Nd:YAG), and $ZnGeP_2$ exhibits strong two-photon absorption of conventional 1 μm (Nd:YAG) or 1.55 μm (Yb:YAG) laser-pumping sources.

Two ways are used to overcome these drawbacks. One way is to synthesize a quaternary compound which is formed by the solid solution between the parent $AgGaS_2$ and GeS_2. The improved laser damage threshold of $AgGaGeS_4$ made it a promising alternative to the widely used $AgGaS_2$ for a frequency down-converter with a Nd:YAG laser pumping as well as for many other applications [4–6]. Another way is to obtain crystals of the $LiBC_2$ family, where B = In, Ga and C = S, Se, Te: these crystals have large band gap up to 4 eV. As a result their optical damage thresholds exceed the parameters of their Ag-containing analogues although nonlinear susceptibility of Li-compounds is somewhat lower [7–9]. During last years one tries to combine these approaches and to create a quaternary compound based both on $LiGaS_2$ and GeS_2. Thus in [10] authors synthesized a fine grained powder of $Li_2Ga_2GeS_6$ and its structure was established as orthorhombic. These authors recorded also the transmission spectra of this powder mixed with KBr and estimated its nonlinear susceptibility as 16 pm/V which is comparable with that for $AgGaS_2$ (19 pm/V) and $AgGaGeS_4$ (15 pm/V) [10]. It is important that 1. nonlinear susceptibility of $Li_2Ga_2GeS_6$ is considerably higher in comparison with $LiGaS_2$ which has d_{31} = 5.8 pm/V [11] and 2. $Li_2Ga_2GeS_6$ is considerably more stable under the pumping from the Nd–YAG laser in comparison with $AgGaS_2$ and $AgGaGeS_2$ [10]. The Ge adding was found to decrease melting temperature from 1050 °C for $LiGaS_2$ to 900 °C for $Li_2Ga_2GeS_6$. This lowers a risk of incongruent evaporation when crystal growing. A consequence of such evaporation may be a deviation from the stoichiometric composition and appearing of inclusions of side phases.

In present work large single crystals of $Li_2Ga_2GeS_6$ were grown and their structure and linear optical properties were studied. The shape of the fundamental absorption edge was analyzed and band gap values were estimated. High quality of $Li_2Ga_2GeS_6$ crystals is confirmed by emission of free and self-trapped excitons. These crystals demonstrate an intense photoluminescence which increases about two orders as crystal is cooled to 80 K.

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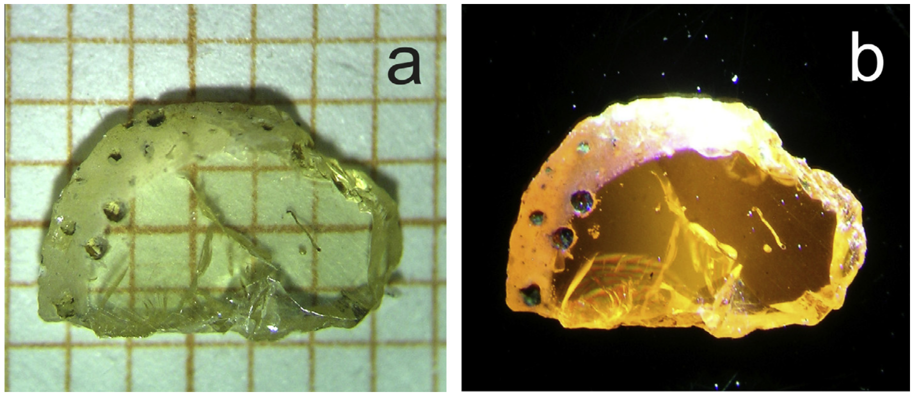

Fig. 1. LGGS plate in reflected light (a) and PL pattern at 365 Hg excitation, at $T = 300$ K (b).

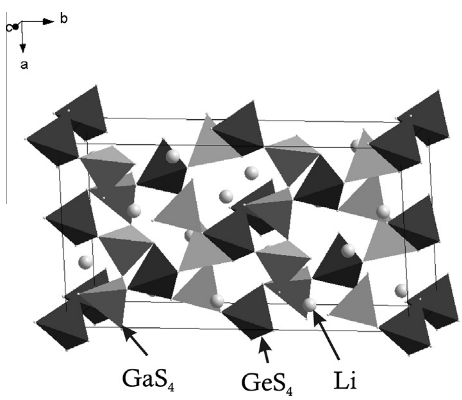

Fig. 2. Crystal structure of $Li_2Ga_2GeS_6$.

2. Experimental

2.1. Crystal growth

Two different furnaces were used for charge synthesis and crystal growth. Crystals of $Li_2Ga_2GeS_6$ were grown in a vertical two-zone furnace by the Bridgman technique. Provisionally synthesized charge was filled into a glass–carbon crucible with a conic bottom, which, in turn, was placed inside a sealed silica ampoule. Ampoule with a crucible was shifted at a rate of 1 mm/day from the upper hot zone (900 °C) to a cold zone (700 °C). Temperature gradient in the crystallization area was about 10 °C/cm.

2.2. X-ray structural analysis

The powder diffraction data of $Li_2Ga_2GeS_6$ for Rietveld analysis were collected at room temperature with a Bruker D8 ADVANCE powder diffractometer (Cu Kα radiation) and linear VANTEC detector. The step size of 2θ was 0.016°, and the counting time was 1.2 s per step. Rietveld refinement was performed by using TOPAS 4.2 [12].

Table 1
Main parameters of processing and refinement of the $Li_2Ga_2GeS_6$ sample.

Compound	$Li_2Ga_2GeS_6$
Space group	*Fdd*2
a (Å)	12.0796 (2)
b (Å)	22.7300 (4)
c (Å)	6.84048 (11)
V (Å^3)	1878.19 (5)
Z	8
2θ-interval (°)	5–110
No. of reflections	329
No. of refined parameters	62
R_{wp} (%)	13.04
R_p (%)	9.49
R_{exp} (%)	8.22
χ^2	1.59
R_B (%)	3.68

2.3. Optical spectroscopy

Transmission spectra were recorded using a UV-2501 PC Shimadzu spectrometer in the UV to near IR, whereas in the mid-IR we used a Fourier transform spectrometer Infralum 801. The photoluminescence (PL) spectra were measured using a SDL1 luminescence spectrometer with excitation from the 1 kW Xe lamp through the MDR2 monochromator. To record the PL emission we used a cooled FEU83 photomultiplier which is sensitive in the 350–1200 nm range. The photoluminescence excitation (PLE) spectra were corrected to a constant number of incident photons using Na salicylate and Rhodamine 640. Raman spectra were measured using a Horiba Jobin Yvon LabRAM HR800 spectrometer with 1024 pixel LN/CCD detector using the 532-nm Nd:YAG laser. The curves of thermostimulated luminescence (TSL) were recorded when heating crystals at the rate $\beta = dT/dt \sim 20$ °C min^{-1} after UV excitation during 5 min. at 80 K.

3. Results and discussion

3.1. Crystal growth

Compound $Li_2Ga_2GeS_6$ was obtained by pyrosynthesis from elementary 3N lithium, 7N gallium and germanium as well as 5N

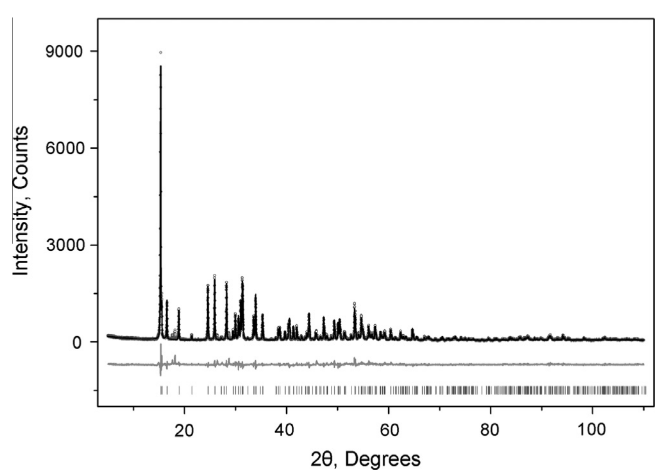

Fig. 3. Difference Rietveld plot of Li2Ga2GeS6. Gray circles represent experimental diffraction pattern, black line shows the simulated X-ray pattern, gray line at the bottom shows the difference between experimental and simulated data, sticks at the bottom represent Bragg reflections.