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IR operated novel $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$ single crystals

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ABSTRACT

In this work, we report on the structural and optical properties of novel $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$ single crystals that were synthesized by the Bridgman–Stockbarger technique. We have performed illumination by 10.6 μm CO_2 pulsed laser working in the microsecond time duration regime. Such illumination allows causing substantial changes for both pure electronic nonlinear optical effects like optical second harmonic generation as well as piezooptical effects described by the fourth rank tensors. The measurements of the piezo-optical effects were carried out at different temperatures. The effects are observed only during the IR CO_2 laser illumination and are disappeared after switching off the illumination. Simultaneously the IR induced optical second harmonic generation at Er:glass laser fundamental wavelength 1540 nm was performed during illumination by nanosecond Nd:YAG and Er^{3+}:glass laser. The observed effects allow to use the studied materials as promising for IR-optoelectronic devices.

1. Introduction

Relatively high resistance to IR laser damage is one of the crucial requirements for parametric crystals for their applications in mid-IR spectral range. It is well known that the most promising crystals with respect to the laser light resistance are $HgGa_2S_4$ crystals (threshold power density 370 MW/cm^2) and their solid state alloys $Hg_{1-x}Cd_xGa_2S_4$ (271 MW/cm^2) [1]. Also the quaternary phase $AgGaGeS_4$ and $AgGaGe_5Se_{12}$ (230 and 225 MW/cm^2, respectively) crystals are considered as promising for the above applications. Taking into account the complicated technology of the growth of mercury-containing crystals, caused by high vapor pressure of HgS, these crystals require specialized growth techniques. Besides, the crystals of the quaternary compounds are more suitable, currently, for the practical applications according to the price/efficiency ratio. The $AgGaGeS_4$ and $Ag_xGa_xGe_{1-x}Se_2$ single crystals are similar to $AgGaS_2$ (146 MW/cm^2) and $AgGaSe_2$ (139 MW/cm^2), respectively. They were discovered in an attempt to improve the features of the ternary phases by addition of germanium dichalcogenides [2–4]. Both quaternary phases have significant homogeneity ranges and possess improved properties compared with the ternary compounds. In addition to the nearly two-fold higher laser radiation resistance, their birefringence relatively increases, the spectral transparency region is wide, and the melting points are relatively lower, the latter simplifying the crystal growth technology.

The $Ag_xGa_xGe_{1-x}Se_2$ phase formed in the $AgGaSe_2$–$GeSe_2$ system has a homogeneity range extending from 65 to 88 mol% $GeSe_2$ at 720 K, with the melting point maximum equal to 995 K corresponding to the composition of $AgGaGe_3Se_8$ (SG *Fdd2*; $a=1.2431$, $b=2.3806$, $c=0.7135$ nm) [2–4]. The $Ag_xGa_xGe_{1-x}Se_2$ single crystals with various x values were reported by several authors and their properties are well documented [2–11]. The laser resistance depends significantly on the quality of the fabricated crystals. The lattice defects lead to "static disorder", which is responsible for the appearance of electron states in the band gap that diminishes the transparency of the crystals. It was shown [12] that doping with copper leads to color change of the single crystals in the transparency region, which occupies the visible and near-IR range in the electromagnetic spectrum.

In the present work we report on the influence of microsecond CO_2 laser illumination with pulse power density up to 250 MW/cm^2 on the birefringence for 1064 nm wavelength. Simultaneously we investigate the influence of other nanosecond lasers on the optical second harmonic generation.

2. Experimental

The $AgGaGe_3Se_8$:Cu single crystals were grown by the Bridgman–Stockbarger method in a vertical two-zone furnace.

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Here the silver ions have been replaced by the equivalent copper ions. The starting batch composition corresponds to the chemical formula $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$. The synthesis and growth processes were performed in the same ampoule. Considering the nature of the liquidus and the near-flat melting maximum of the quaternary phase, we have expected its partial dissociation upon melting. To suppress the dissociation, a silica plug seal was used to decrease the free container volume as far as possible. The single crystals were obtained under the following conditions:

- crystallization zone temperature 1250 K;
- annealing zone temperature 720 K;
- temperature gradient at the solid–melt interface 5 K/mm;
- growth rate 2 mm/24 h;
- annealing duration 150 h and
- rate of cooling to room temperature 5 K/h.

Using the above conditions, we have obtained a single-crystalline boule of $AgGaGe_3Se_8$:Cu with 18 mm diameter and 30 mm length, respectively.

3. Results and discussion

3.1. X-ray diffraction analysis

X-ray diffraction using DRON 4-13 diffractometer with CuK_α radiation source has shown that the structure of the doped single crystal is identical to that of the pure compound (Fig. 1). The lattice parameters are $a=1.24497(8)$ nm, $b=2.3836(2)$ nm, $c=0.71437(4)$ nm, and $V=2119.9(4)$ nm^3, respectively. Ag atoms occupy 16-fold site, with 37.5% occupancy ratio. The statistical mix of Ga/Ge atoms with 1:3 ratio occupy 8-fold and 16-fold sites, and Se atoms occupy three 16-fold sites, all with full occupation. The $AgGaGe_3Se_8$ structure can be presented as the packing of the tetrahedra of sulfur atoms around the atoms of metal components (Fig. 2). The tetrahedra around Ga and Ge atoms are woven into a 3D framework as shown in Fig. 2: the tetrahedra around silver atoms are paired and packed along crystallographic (000z) direction. In the case of $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$ single crystal, it is assumed that copper atoms would most likely substitute isovalently silver atoms, which agrees well with the ionic radii of the metal components compared with the surrounding in the original compound $AgGaGe_3Se_8$. However, the partial occupation by silver atoms of its crystallographic sites lead to the abnormally high value of temperature displacement parameters ($B_{is/eq}=9.5$), which in turn makes impossible the test of this assumption by the XRD method.

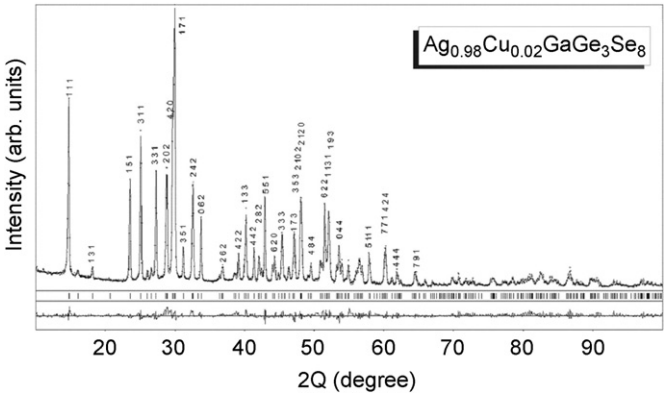

Fig. 1. Experimental and theoretical diffraction patterns of $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$.

3.2. IR-induced optical effects

The basic principle of the IR-induced experiments consists in a possible photoexcitation of the electron and phonon subsystems in the titled compounds under influence of the light intensity. Following the performed features of the energy gap carriers and their mobility one can expect that principle role may here be played by different effective mass of electrons and holes in the conduction and valence bands, respectively, for such kinds of crystals [13,14]. This means, both effects described by electronic contribution to the corresponding susceptibilities as well as the effects determined by the IR phonon contributions might be comparable. For this reason we have performed illumination by 10.6 μm CO_2 laser working in the microsecond pulse regime. Such illumination allows us causing substantial changes to both pure electronic nonlinear optical effects like optical second harmonic generation as well as piezooptical effects described by the fourth rank tensors.

Fig. 3 shows the dependence of the piezooptical effect versus the IR-inducing laser power density. From Fig. 3, it is observed that for the power density up to 100 MW/cm^2 there is a substantial increment in the birefringence caused prevailingly by the optical Kerr effect, which is substantially dependent on the temperature. We found that at LHeT the changes of the birefringence for the cw 1064 nm laser beams measured by the Senarmont method are maximal and these values achieve absolute

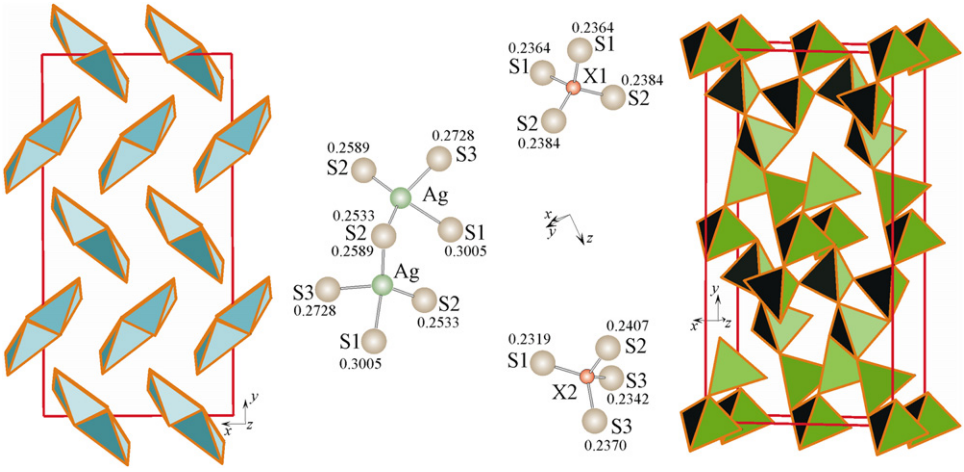

Fig. 2. Packing of the tetrahedra of anion atoms around the cation atoms in the $Ag_{0.98}Cu_{0.02}GaGe_3Se_8$ structure.