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Photoconductivity and nonlinear optical features of novel $Ag_xGa_xGe_{1-x}Se_2$ crystals

A.S. Krymus[a,e], G.L. Myronchuk[a], O.V. Parasyuk[b], G. Lakshminarayana[c], A.O. Fedorchuk[d], A. El-Naggar[f,g], A. Albassam[g], I.V. Kityk[h,*]

[a] Physics Department, Eastern European National University, 13 Voli Avenue, 43025 Lutsk, Ukraine
[b] Department of Chemistry, Eastern European National University, 13 Voli Avenue, 43025 Lutsk, Ukraine
[c] Wireless and Photonic Networks Research Centre, Faculty of Engineering, Universiti Putra Malaysia, 43400 Serdang, Selangor, Malaysia
[d] Department of Inorganic and Organic Chemistry, Lviv National University of Veterinary Medicine and Biotechnologies, Pekarska St. 50, 79010 Lviv, Ukraine
[e] Institute of Physics, AJD Czestochowqa, 42-201, Poland
[f] Physics Department, Faculty of Science, Ain Shams University, Abassia, Cairo 11566, Egypt
[g] Research Chair of Exploitation of Renewable Energy Applications in Saudi Arabia, Physics & Astronomy Dept., College of Science, King Saud University, P.O. Box 2455, Riyadh 11451, Saudi Arabia
[h] Faculty of Electrical Engineering, Czestochowa University of Technology, Armii Krajowej 17, PL-42-201, Czestochowa, Poland

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ABSTRACT

Complex studies of photoconductivity, two-photon absorption (TPA) and third harmonic generation (THG) were performed for three principal representatives of chalcogenide crystals. Comparison of carrier transport kinetics and third order nonlinear optical properties was performed and the principal role of the anionic co-ordination is discussed. Specific features of photoconductivity in synthesized crystals show that the relaxation kinetics of photoconductivity can be determined by the existence of at least two types of relaxation processes: slow and quick. The control of the relaxation processes for s- and r-centres was carried out by temperature dependences of t-levels relaxation photoconductivity. The maximum THG is observed for the sample $AgGaGe_5Se_{12}$. The less THG exists for the sample $AgGaGe_3Se_8$ and the lowest for the $AgGaGe_4Se_{10}$.

1. Introduction

Novel compounds $A^IB^{III}C_2^{VI}$ are similar with respect to binary compounds $A^{II}B^{VI}$ and show promising applications in nonlinear optics and solid state electronics. These applications arise due to their extreme light sensitivity threshold, high transparency, birefringence, nonlinear optical susceptibility, optical activity, and piezoelectricity with respect to traditional materials [1]. Particularly, $AgGaSe_2$ crystals with localized levels possess different perspecitve electronic parameters [2,3]. The compounds $Ag_xGa_xGe_{1-x}Se_2$ are similar to the ternary phase compounds $AgGaSe_2$ and were grown during technological search by the addition of Ge dichalcogenides [4]. The obtained crystals have a higher range of homogeneity, surface stability to laser irradiation, more spectral transparency range, higher birefringence, and lower melting temperature, which makes the synthesis process cheaper and leads to lower prices [4–9]. Continuous variation of energy gap and other parameters of $Ag_xGa_xGe_{1-x}Se_2$ ($x = 0.333$, 0.250, 0.200, 0.167) allows to extend their applications in optoelectronics [10]. Moreover, by appropriate doping one can operate by free carrier lifetimes in the studied semiconductors and polarization of the titled materials. In the present work, for deeper clarifications of recombination processes closely related to nonlinear optics for the $Ag_xGa_xGe_{1-x}Se_2$ ($x = 0.250$, 0.200, 0.167) content, additionally we explored photoconductivity kinetics.

2. Experimental

Details of the synthesis of the titled crystals were described in our earlier publications [8,10]. The crystals of three different compositions of the quaternary phase $Ag_xGa_xGe_{1-x}Se_2$ with $x = 0.250$, 0.200, 0.167 were grown using modified Bridgman-Stockbarger method. The synthesis and growth processes were combined without modifications in the same container of quartz glass for each crystal with different “x” content. Elementary compounds of high-purity (Ag, 99.999 wt.%, Ga, 99.9997 wt.%, Ge,

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[*] Corresponding author.
E-mail address: iwank74@gmail.com (I.V. Kityk).

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99.9999 wt.%, and Se, 99.9999 wt.%) were used. Evacuated ampoules were soldered, and the synthesis of the respective alloys was performed in a shaft-type furnace under the conditions stated in [8]. Then, the ampoules with the synthesized starting alloys were placed in pre-heated growth furnaces. Separate procedures were applied for the formation of a seed crystal in the pear-shaped bottom part of each container. Then, the growth onto the single-crystalline seed at a constant rate was performed. The rate for the crystals with $x = 0.250$, 0.200 was 3 mm/day, and 5 mm/day for $x = 0.167$ was used. The temperature gradient created by the selection of the temperature of the two zones of the furnace (1250–1273 K and 700–730 K for top and bottom zones, respectively) was similar in all experiments, and varied in the range of 3–4 K/mm. After the completion of the oriented crystallization of the melts, annealing was carried out for 5 days. Then both zones of the furnaces were synchronously cooled to room temperature over 7 days. Obtained single crystals were dark red and were up to 18 mm in diameter and up to 40 mm in length.

Photoconductivity spectra were measured by MDR-206 monochromator with 0.5 nm spectral resolution. The current sensitivity of the experimental set-up (Keithley 6514) was higher than 1 pA + 5%. This set-up allows performing at least 500 measurements/s. The current contacts were made by sticking of metallic In and were Ohmic for all the considered conditions. The temperature was stabilized by using Utrex K 41-3 thermoregulator with accuracy equal to about 0.1 K. A 100 W halogen lamp was used as a light source. The excitation of non-equilibrium conductivity was carried out by 808 nm cw laser with power about 300 mW.

3. Results and discussion

According to the previous publications [8–11], the crystalline structure of $Ag_xGa_xGe_{1-x}Se_2$ (x = 0.250, 0.200, 0.167) could be presented as repeating isovalent substitution of Ge^{4+} atoms simultaneously by Ag^+ and Ga^{3+} for compound $GeSe_2$. The package of (Ga, Ge)Se_4 tetrahedra and inter-atomic distances Ag-Se for $Ag_xGa_xGe_{1-x}Se_2$ (x = 0.250, 0.200, 0.167) are presented in Fig. 1. It is crucial that Ga^{3+} occupy positions of Ge^{4+} atoms and Ag^+ are situated in the voids as shown in Fig. 1. Thus different compounds can be formed for different "x" values; when x = 0.250 – $AgGaGe_3Se_8$, x = 0.200 – $AgGaGe_4Se_{10}$, and x = 0.167 – $AgGaGe_5Se_{12}$. These crystals are isostructural and are distinguished due to varying Ga/Ge ratio and content of Ag atoms. At the same time the occupation by the silver atoms is only partial. It is crucial that Ag-Se bond distances (see Fig. 1.) here are maximal. Following the presented structural data, we performed quantum chemical simulations of the ground state dipole moments for principal structural clusters within a framework of traditional DFT B3LYP model. It is established that their values are maximal for the (Ga, Ge)Se_4 tetrahedra and were as follows: $AgGaGe_4Se_{10}$ – 3.6 D; $AgGaGe_3Se_8$ – 5.8 D and $Ag_5GaGe_5SeGe_{12}$ – 7.1 D. It is well known that for the optical linear and nonlinear properties these magnitudes are crucial. At the same time, for the Ag-S bonds they are almost fixed – about 2.9 D. So, one can expect that the dipole moments of the (Ga, Ge)Se_4 tetrahedra will play a crucial role in the optical and non-linear optical dependences.

In Fig. 2 are given spectral features for the $Ag_xGa_xGe_{1-x}Se_2$ (x = 0.250, 0.167). One can see existence of two spectral maxima. The first maximum is situated near the fundamental absorption edge and is caused by fundamental inter-band photoconductivity of the titled compounds which is in agreement with an earlier report [12]. With increasing "x" one can see blue spectral shift caused by enhanced E_g (see Table 1). The second maximum is likely due to hole photoexcitation from acceptor level of near the valence band. Its fixed energy position versus compound concentration confirms close connection of the defect centers responsible for

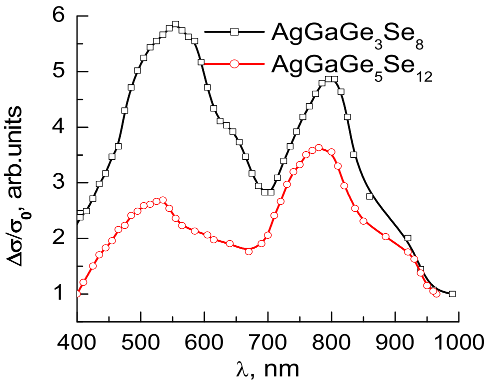

Fig. 2. Photoconductivity spectra for $Ag_xGa_xGe_{1-x}Se$ at T = 240 K.

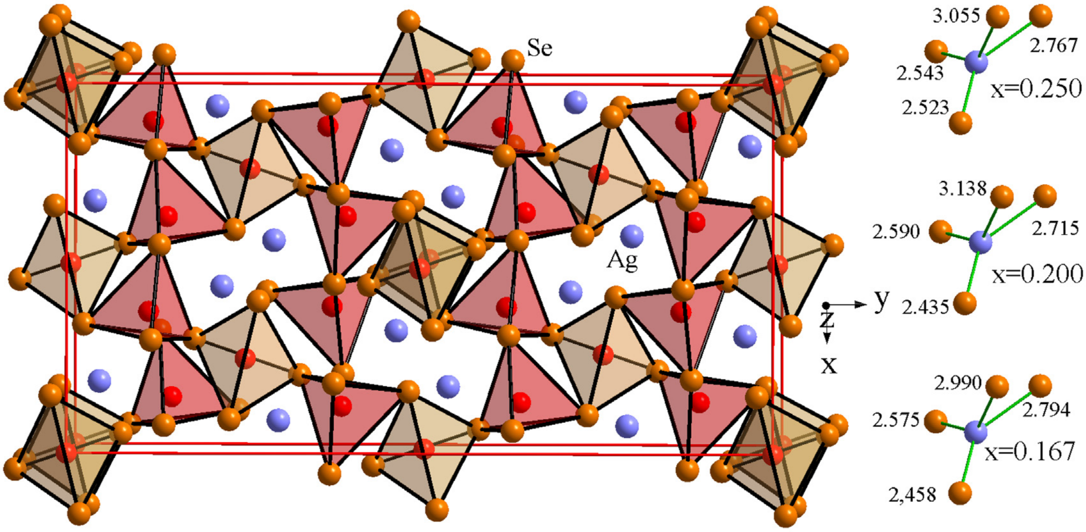

Fig. 1. Package of principal atomic clusters (Ga, Ge)Se_4 and inter-atomic distances Ag-Se for $Ag_xGa_xGe_{1-x}Se$ (x = 0.250, 0.200, 0.167).