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$AgGaGeS_4$ CRYSTAL AS PROMISING OPTOELECTRONIC MATERIAL

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We have discovered a possibility to use the $AgGaGeS_4$ crystal as a promising optoelectronic material. The photoconductivity relaxation of the $AgGaGeS_4$ crystal in the temperature range 220–300 K was analyzed within the concept of the sticking levels. The presence of long-term photoconductivity relaxation is controlled by *s*- and *r*-recombination centers. Determined energy depth of the sticking levels was ~0.13 eV.

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1. Introduction

One of the most promising non-linear optical materials for mid-IR region that is studied quite actively in the recent years is $AgGaGeS_4$ (AGGS) [1–10]. Due to high double refraction, huge laser damage threshold, absence of absorption peaks at the solid-state laser wavelengths, the possibility of synchronicity matching, AGGS crystals may be used for the development of parametric frequency converters (parametric light generators pumped by solid state lasers, up-convertors of CO_2 lasers radiation to the visible range, frequency doubling) [1]. One of the factors that hinder the widespread use of AGGS is the low manufacturability of crystals. They are mainly obtained by Bridgman-Stockbarger method [2–10].

. The majority of the researchers note the importance of the preparation of the quality initial batch for the growth that affects the crystal quality and the reproducibility of its properties. This is due to the difficulty in achieving its homogeneous state, which in turn is caused by the existence of broad areas of glass formation in the Ag_2S–Ga_2S_3–GeS_2 system [8] and consequently high viscosity of the melts. Most of the researchers synthesize $AgGaGeS_4$ in a two-zone furnace, with lengthy annealing and then crushing obtained alloy into powder after cooling, though other approaches were also attempted. For instance, Ni et al. [7] composed the growth batches from previously prepared $AgGaS_2$ and GeS_2. We have used in Ref. [9] the synthesis of small portions of substances (2-3 g) at 1270 K and 48-hr. rotation of the ampoule with the batch in a rotating

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furnace. The recent work by Rame et al. [10] on the technological aspects of AGGS growth showed that substantial improvement of the optical characteristics of the crystals may be achieved by additional annealing at 870 K during 250 hrs.

Other than non-linear optical applications, AGGS crystals are of interest in acousto-optics [11, 12] and optoelectronics as they have significant luminescence and quite high photoconductivity values. Spectral distribution of photoconductivity investigated in Ref. [13] established the existence of two maxima λ_{max1}=420 nm and λ_{max2}=600 nm. It was determined that λ_{max1} lies in the region of the fundamental absorption band and corresponds to intrinsic conductivity, while λ_{max2} is in the admixture band. It was suggested that the same defect centers are responsible for the thermal activation of dark conductivity and for the admixture conductivity, namely deep donor centers Ge_{Ga}. Here, we present the results of the investigation of photoconductivity relaxation. The interest in long-term photoconductivity relaxation is caused by the possible use of this phenomenon in various memory systems and the necessity of explore the causes of the instability of photoelectronic devices. The experimental results are mainly explained by the existence of collective recombination barriers for majority carriers, which are formed on the boundaries of electrically active macro-irregularities of the structure. Other suggested mechanisms are related to inter-impurity recombination and the reformatting the structural defects that are implemented at low-temperatures [14–16]. The long-term photoconductivity relaxation at high temperatures may be caused by the processes of radiation-induced formation and transformation of centers [17, 18], induced desorption [19], migration of defects in semiconductors [20]. We investigated the relaxation processes in the $AgGaGeS_4$ crystals to study the photoconductivity kinetics of the impurity excitation and to determine the parameters that characterize long-term relaxation processes.

2. Experimental

The AGGS crystals used in the photoconductivity relaxation measurements were obtained by Bridgman-Stockbarger method. The growth procedure is described in detail in our previous papers [3,9,11–13]. Experimental measurements were performed using a Keithley 6430 Sub-Femtoamp SourceMeter electrometer. The excitation of the samples was performed by the diode laser illumination (λ=600 nm, P=400 mW).

3. Results and discussion

AGGS crystallizes in a non-centrosymmetric space group *Fdd2* with the lattice periods a = 12.028 Å, b = 22.918 Å, c = 6.874 Å (Z = 12) [21, 22]. Three sorts of sulfur atoms in this structure occupy 16*b* sites, germanium and gallium atoms statistically share sites 8*a* and 16*b*. The crystal structure of $AgGaGeS_4$ may be presented (Fig. 1) as the packing of the tetrahedra of sulfur atoms around Ga/Ge atoms in sites 8*a* (red figures) and 16*b* (yellow figures). Silver atoms are located in the crystallographic site 16*b*, with the occupation coefficient 3/4, which lies in the canals between the tetrahedra. Such canals may be seen as the crystallographic directions 00z (Fig. 1a), 0y0 (Fig. 1b) or x0z (Fig. 1c). Long-term photoconductivity relaxation may be caused by the migration of defects in the positions of silver atoms in these directions.

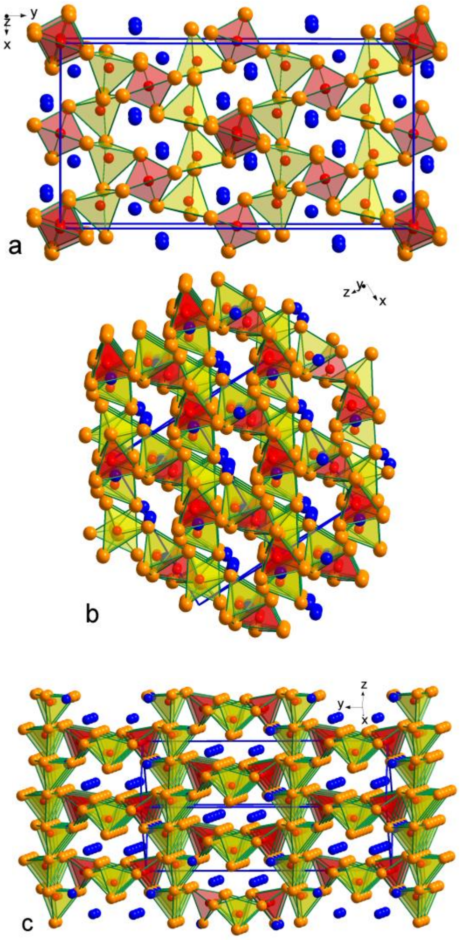

Fig. 1. Packing of the tetrahedra of sulfur atoms around Ga/Ge atoms in the $AgGaGeS_4$ structure

Typical photoconductivity relaxation curves upon the excitation by monochromatic light of various intensities are presented in Fig. 2 (a).

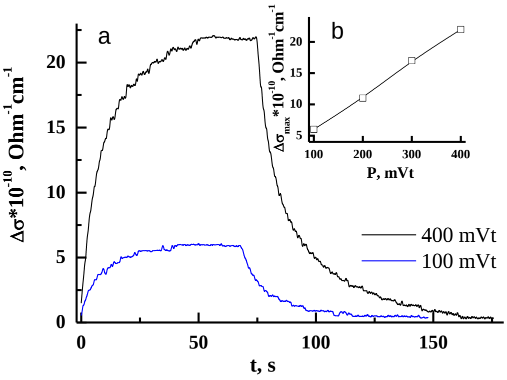

Fig. 2. Photoconductivity relaxation curves for various intensity of monochromatic light excitation (λ = 800 nm, T=300 K)

The photoactivation effect of the increase of photosensitivity with time is observed for all excitation intensities. The saturated photoconductivity is proportional to the intensity ($\sigma_{st} \sim I/h\nu$), therefore we will use linear recombination law (Fig. 2 (b)).

As we investigated the relaxation of photoconductivity caused by impurities, the model of long-term relaxation caused by trapping free charge carriers on point centers of localization (traps) is more appropriate in the analysis of experimental results.

AGGS has a rich spectrum of localized centers within the band gap [3, 9, 10]. The presence of trapping centers in a semiconductor affects the photoconductivity kinetics. Free electrons not only recombine with holes but are also trapped by sticking centers, which decreases the rate of the saturation of the carrier concentration. The devastation of traps lengthens the decrease of the carrier concentration upon removing the excitation. This results in slowing the processes of the rise and decrease of the photoconductivity (Fig. 3). In that case the photoconductivity relaxation time will not equal the lifetime of photoexcited carriers but will significantly exceed it since some electrons will be stored at *t*-levels. The higher relaxation time compared to inter-band recombination is also caused by the fact that the principal channel of the recombination processes is the transitions of electrons to defect centers [23, 24].

The kinetics of the rise and decrease of the photoconductivity has complex long-term character shown in Fig. 3. The initial stage of the rise of photoconductivity exhibits a deviation from the exponential dependence (Fig. 3). A more detailed analysis shows that photoconductivity after the start of the photoexcitation linearly increases with time. Such behavior of the increasing photoconductivity relaxation, according to the literature data [23, 25], is observed in the case of weak occupation of the sticking levels with electrons, i.e. in strongly compensated semiconductors of which AGGS is one [13]. The reason of the appearance of the linear sections is that the equilibrium of *c*-band and *t*-levels is established after some time after the start of the photoexcitation.

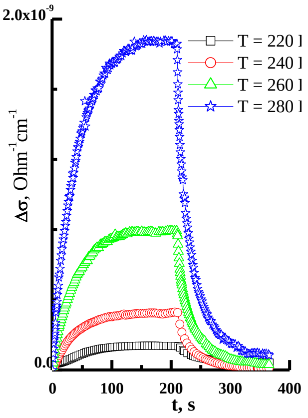

Fig. 3. Kinetics of the rise and decrease of the photoconductivity in the AGGS crystal at various temperatures

At the following stages, with the established equilibrium, the photoexcitation of electrons competes simultaneously with the recombination via *r*- and *s*-centers; therefore the increasing photoconductivity relaxation is described by the formula (1).

$$\Delta\sigma = \Delta\sigma_{st} \cdot \left(1 - \exp\left(-\frac{t}{\tau_1}\right)\right) \tag{1}$$

where τ_1 is the photoconductivity relaxation time after the start of illumination, $\Delta\sigma_{st}$ is the stationary non-equilibrium conductivity.

Within the scale of Fig. 3, the photoconductivity rise curves are described in a large time range by straight lines the slope of which determines the photoconductivity relaxation time (τ_1) after the start of the photoexcitation. Thus calculated τ_1 data are presented in Table 1. High τ_1 values indicate the participation of shallow sticking levels in the photoconductivity relaxation.

Table 1. Time parameters of the relaxation processes in $AgGaGeS_4$

T, K	τ_1, s	τ_2, s	τ_3, s
220	49.3	47.0	120.3
230	40.1	29.0	90.9
240	37	27.2	68.9
250	36.4	15.9	65.1
260	29.9	15.8	51.3
270	30.1	13.4	43.4
280	27.5	11.1	33.9
290	21.7	10.5	28.5
300	20.1	5.9	19.5

After stopping the photoexcitation, the photoconductivity relaxation in the AGGS single crystals is characterized by at least two channels of the recombination of non-equilibrium carriers. The photoconductivity relaxation process in this case is described well by the sum of two exponents:

$$\Delta\sigma = A\cdot\exp\left(-\frac{t}{\tau_2}\right)+B\cdot\exp\left(-\frac{t}{\tau_3}\right), \tag{2}$$

where $A\approx B\approx\Delta\sigma_{st}$. The photoconductivity relaxation times τ_2 and τ_3 were determined from the slope of the linear sections in the semi-logarithmic scale (Fig. 3) of the dependence of the conductivity on time. According to the calculations, the photoconductivity relaxation has a "fast" and”slow” components with characteristic relaxation times presented in Table 1. According to the theoretical representation [23] the relaxation time decreases exponentially with increasing temperature, which agrees well with our results. This in turn makes possible the estimate of the trap energy E_t from the slope of the temperature dependence of the relaxation time $ln\ \tau$ vs $1/T$ (Fig. 4).

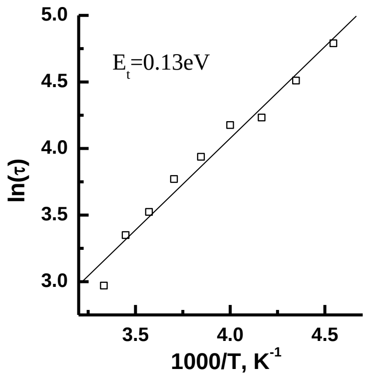

Fig. 4. Dependence of the relaxation time of the slow component of photoconductivity relaxation on temperature in the $AgGaGeS_4$ *crystals*

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Thus obtained values of the energy depth of *t*-centers is close to the value of thermal activation energy of these centers that was determined from thermoinduced conductivity spectra of AGGS crystals [26].

4. Conclusions

Photoconductivity relaxation was investigated to study the effect of the point defects of the crystal lattice on the photovoltaic properties of AGGS. The relaxation kinetics in AGGS is characterized by the presence of at least two types of relaxation processes, slow and fast. The estimates show that the fast and slow components of the photoconductivity kinetics decrease with increasing temperature and have characteristic times τ_2=5.9 s and τ_3=19.5 s at 300 K. The activation energy of the sticking levels was estimated from the temperature dependence of the photoconductivity relaxation time as 0.13 eV.

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