Materials Chemistry and Physics 200 (2017) 250–256

Contents lists available at ScienceDirect

Materials Chemistry and Physics

journal homepage: www.elsevier.com/locate/matchemphys

# Photoconductivity relaxation processes in $AgCd_2GaS_4$ single crystals

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## HIGHLIGHTS

- Optical and photoelectric properties of $AgCd_2GaS_4$ single crystal were explored.
- Temperature dependence of the time kinetics was investigated.
- $AgCd_2GaS_4$ single crystals was grown by Bridgman-Stockbarger method.

## ARTICLE INFO

*Article history:*
Received 8 January 2017
Received in revised form
20 April 2017
Accepted 13 July 2017
Available online 28 July 2017

*Keywords:*
Single crystal growth
Bridgman technique
Carrier relaxation

## ABSTRACT

Optical and photoelectric spectral features of $AgCd_2GaS_4$ single crystal were explored. Optical band gap energy was estimated from the absorption and was varied within 2.18–2.28 eV (at ambient temperature) for the samples cut from different parts of the single-crystalline specimens. The results of the photoconductivity relaxation study within the temperature range 100–280 K were explored within a framework of the adhesion trapping level model. It was established that the $AgCd_2GaS_4$ crystals exhibit long-term relaxation of photoconductivity with adhesion levels at energies about 0.2 eV.

## 1. Introduction

The $A^IC^{III}X_2$ crystalline compounds ($A^I$ = Cu, Ag; $C^{III}$ = Ga, In; X = S, Se, Te) are studied recently quite intensively. During the past decades due to their promising parameters and wide application, e.g. in non-linear optics ($AgGaS_2$, $AgGaSe_2$) [1,2] or photovoltaics ($CuInSe_2$, $CuIn_{1-x}Ga_xSe_2$ etc) [3,4] they are of particular interest. They all (at least their low-temperature modifications) crystallize in the chalcopyrite structure ($CuFeS_2$, SG *I*-42d) which is related to the crystal structure of their isoelectronic analogs $B^{II}X$ ($B^{II}$ = Zn, Cd, Hg). The unit cells of chalcopyrite and sphalerite (ZnX, CdTe, HgX, SG *F*-43 m) are related by the ratios $a_{ch} \sim a_s$ and $c_{ch} \sim 2c_s$ [5], i.e. the chalcopyrite cell results from doubling of the sphalerite cell along *c* axis. A consequence of this similarity is a formation of wide solid state alloy solution ranges for both components in the $A^IC^{III}X_2$–$B^{II}X$ systems, up to continuous solid state alloys series in the cases when $A^IC^{III}X_2$ possess a high-temperature modification with the sphalerite structure [6–10]. A somewhat different situation is observed for the systems possessing CdS and CdSe favoring the crystal structure of wurtzite (SG *P*$6_3$*mc*). Previously we demonstrated that a continuous range of solid solutions (ternary compounds with the sphalerite structure) exists between CdS and the high-temperature modification of $CuInS_2$ [11] and similarly is for in $CuInSe_2$–CdSe system [12]. Additionally the intermediate phases were observed in the systems $AgGaS_2$–CdS (phase diagram is of eutectic type) [13] and $AgGaSe_2$–CdSe [14].

The formation of $AgCd_2GaS_4$ was found from the investigation of the $AgGaS_2$–CdS section [13] for the quasi-ternary system $Ag_2S$–CdS–$Ga_2S_3$ [15]. The compound formed incongruently at

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http://dx.doi.org/10.1016/j.matchemphys.2017.07.053

1284 K and has a homogeneity region for 64–79 mol.% CdS (at 870 K) localized along the $AgGaS_2$–CdS section [13]. It was determined by the X-ray single crystal method, that $AgCd_2GaS_4$ crystallizes in an orthorhombic symmetry (wurtzite-stannite structure type), acentric space group $Pmn2_1$, and the lattice parameters were equal to $a = 8.1395\,(9)$ Å, $b = 6.9394\,(8)$ Å, $c = 6.6014\,(7)$ Å [16]. The unit cell parameters are bound by the ratios $a_{ws}\sim 2a_w$, $b_{ws} \sim a_w\sqrt{3}$, $c_{ws} \sim c_w$. The electron structure of $AgCd_2GaS_4$ was studied in Refs. [17–19]. A*b initio* calculations of linear and non-linear optical susceptibilities by FT-LAPW method show strong negative uniaxial anisotropy [20]. Optical properties of the crystals obtained by Bridgman-Stockbarger method were investigated in Refs. [21,22]. The growth of the crystals with excess $AgGaS_2$ as the solvent results in the change of the composition of the crystal along the boule due to the space homogeneity region. The crystals are photosensitive and exhibit intensive photoluminescence. The energy band gap of $AgCd_2GaS_4$ was determined from the edge of the optical absorption and was equal to 2.15–2.28 eV [21], and the IR transparency region reaches wavelengths up to 13 μm [22]. The $AgCd_2GaS_4$ crystals are *n*-type high-resistance semiconductors; their dark specific conductivity is equal to $10^{-6}\ \Omega^{-1}\text{cm}^{-1}$. All these characteristics indicate that $AgCd_2GaS_4$ may be promising material for non-linear optics and optoelectronics.

One of the principal difference of the titled chalcogenide crystals with respect to the just known is a fact that they possess very large electron-phonon anharmonicities [23–25]. The trapping levels which are originated due to this process may substantially change the relaxation processes in the case of such interactions.

The development of the technological processes of the growth of quality crystals of compounds and solid solutions required a complex electrical and optical studies to assess the influence of deviations from the stoichiometry on the principal optical parameters of the material. As a result of the research, one can determine and subsequently monitor these parameters during the process. In this work we have studied band gap energy and the relaxation of photoconductivity of the samples cut from different parts of the $AgCd_2GaS_4$ specimens.

In Section 2 is presented technology of crystal growth. The crystallochemistry is given in Section 3. The principal results are given in Section 3.

## 2. Experimental

Bridgman-Stockbarger method was used for the growth of $AgCd_2GaS_4$ single crystals. The detailed crystal growth process was earlier described by us in detail in Refs. [21,22]. Taking into account the incongruent type of the formation of the quaternary compound, the starting batch composition was selected from the field of its primary crystallization for 60 mol.% CdS. The alloy was synthesized from high-purity elements [13], then crushed into powder and poured into a quartz container with a conical bottom. To prevent the interaction of the melt with quartz, the container was previously graphitized by acetone pyrolysis in the flame of oxygen-gas burner. The upper zone temperature (growth zone) was equal to 1350 K, that of bottom (annealing) zone was 1020 K, temperature gradient at the solid-melt interface was 35 K/cm. The rate of temperature cooling of the ampoule was 5 mm/day. After the finishing of the crystallization the ampoule was transferred to the annealing zone and kept for 100 h. Then both furnaces were synchronously cooled to ambient temperature also during 100 h. The obtained boule consisted of two parts. The bottom conical part was the single crystal of the quaternary compound while the top portion contained the eutectic $AgGaS_2+AgCd_2GaS_4$.

The quantitative and qualitative EDAX analysis of the single crystals was performed using Philips 515-PV9800 SEM. Three different parts of the single-crystalline boule were analyzed – the beginning of the cone (sample 1), exactly the middle (sample 2), and the portion that immediately bordered the eutectic (sample 3). The change of the composition of the $AgCd_2GaS_4$ crystal is caused by a wide homogeneity region of the compound itself [13] and solution-melt method of its production.

Optical studies were performed on 0.08 mm thick parallel-plane plates with polished optical-quality surfaces. The measurement of the absorption spectra were carried out MDR-206 monochromator with spectral resolution 1 nm.

The absorption coefficient was determined from Lambert-Bouger law. Taking into account the reflection of light from internal surfaces of the sample and from the incident surface:

$$I = I_0\frac{(1-R)^2 e^{-\alpha d}}{1-R^2 e^{-2\alpha d}} \quad (1)$$

If *d* is large, and neglecting the second member of the denominator, we obtain:

$$I \approx I_0(1-R)^2 e^{-\alpha d} \quad (2)$$

where $I$ is the intensity of the transmitted light; $I_o$ is the intensity of the incident light; $R$ is the reflection coefficient for the normal incidence; $\alpha$ is the absorption coefficient; $d$ is the thickness of the sample.

The investigation of photoelectric properties was performed of the samples shaped as regular parallelepipeds. The average dimensions of the samples were $6 \times 2 \times 1\ \text{mm}^3$. The surfaces were polished by diamond abrasives. Relaxation and photoconductivity spectra were studied in the temperature range 100–300 K. Kinetics of the rise and decay of the photoconductivity was recorded after the illumination of the samples by a KLM-H980-200-5 diode laser ($\lambda = 980$ nm, $P = 150$ mW). Electric transport measurements were performed using a Keithley 6430 Sub-Femtoamp SourceMeter electrometer.

## 3. Crystallographic features of the $AgCd_2GaS_4$ structure

The crystal structure of the $AgCd_2GaS_4$ compound may be presented as the packing of the tetrahedra of sulfur atoms surrounding Ga atoms, while Ag and Cd atoms are located in the voids between these tetrahedra (Fig. 1a). The cuboctahedral second coordination surrounding (SCS) [26] of $GaS_4^{5-}$ anions (Fig. 2) confirms the close packing of these anions. Ag atom 4s occupy tetrahedral voids within the SCS, while Cd atoms take octahedral voids.

The solid solution range of $AgCd_2GaS_4$ at the $AgGaS_2$–CdS

**Fig. 1.** Photo of the studied $AgCd_2GaS_4$ single crystal.