STRUCTURE AND PHOTO-ELECTRIC PROPERTIES OF CRYSTALS $PbGa_2S_4$ AND $PbGa_2Se_4$

D. I. Bletskan, Yu.V. Voroshilov, L.M. Durdinets, V. M. Kabacij,

V.M. Holovey

Uzhgorod State University, 294000, Uzhgorod, Voloshin st., 54

Optically homogeneous bulk crystals of $PbGa_2S_4$ and $PbGa_2Se_4$ were obtained by the Bridgmen-Stocbarger technique X- ray difraction study confirmed them to belong rhombotedral syngony. The basic structural units of $PbGa_2S_4$ and $PbGa_2Se_4$ are $[GaX_4]$ tetrahedra and tetrahonal antiprisms $[PbX_8]$ (where X=S, Se).

Complex study of electric conductivity, thermally stimulated conductivity, PC spectra, temperature dependence of photoconductivity of wide-band triple crystals of $PbGa_2X_4$ have been conducted for the first time. This allowed to reveal and to determine the main parameters of trapping centers and recombination centers.

Introduction

Among physical properties of semiconductors, used in an engineering, one of principal places takes photoconductivity. Operation of various types of photoresistors, vidicons, memories and many other is based on this phenomena. The importance of numerous methods of examining of physical properties based on use of photo-conductivity.is also great for semiconductors.

In the present work outcomes of study of a structure and complex research of photoconductivity (PC) and thermally stimulated conductivity of crystals $PbGa_2S_4$ and $PbGa_2Se_4$ are considered; research were carried out with the help of well developed methods for wide-band semiconductors [1]. The principal attention is concentrated on a problem of deep centers, which influence the photosensitivity directly as recombination's centers or indirectly (according to electrical neutrality condition) as trapping t-centers of the minority and majority charge carriers.

Obtaining of crystals and preparation

In accordance with the equilibrium state diagrams in systems PbS - Ga_2S_3 and PbSe - Ga_2Se_3 triple compaunds of $PbGa_2S_4$ and $PbGa_2Se_4$ are formed with the melting temperature 1148±5K and 1053±2K, accordingly [2-4].

The most simple method of obtaining the triple substances of $PbGa_2S_4$ (Se_4) is direct synthesis from components, taken in stichiometric relation, in evacuated to 0,013 Pa quartz ampoules. Single crystals $PbGa_2S_4$ and $PbGa_2Se_4$ were grown from a melt by a method of verticaly oriented crystallization. It is experimentally established, that optimum conditions for growth of monocrystals of $PbGa_2S_4$ (Se_4) are temperature gradient in crystallization zone $(2\div3)\times10^{-3}$ K/m, maximum melting temperature 1100 K, speed of movement of crystallization front $2{,}8\times10^{-5}$ m/s. For more details of the conditions of the substance synthesis and crystals growth see [5].

The identification of the compounds obtained was carried cut by the methods of X- ray phase analysis and vibrational spectroscopy. According to the results of X-ray studies the triple compounds of $PbGa_2S_4$ and $PbGa_2Se_4$ crystallize in rhombic syngony, with the space group Fddd-D_{2h}^{24}. The lattice periods are : a=21,37 Å, b=21,47 Å with c=12,73 Å for crystals $PbGa_2Se_4$ [6] and a=20,380 Å, b=20,706 Å, with c=12,156 Å for $PbGa_2S_4$ [7]; Z=32.

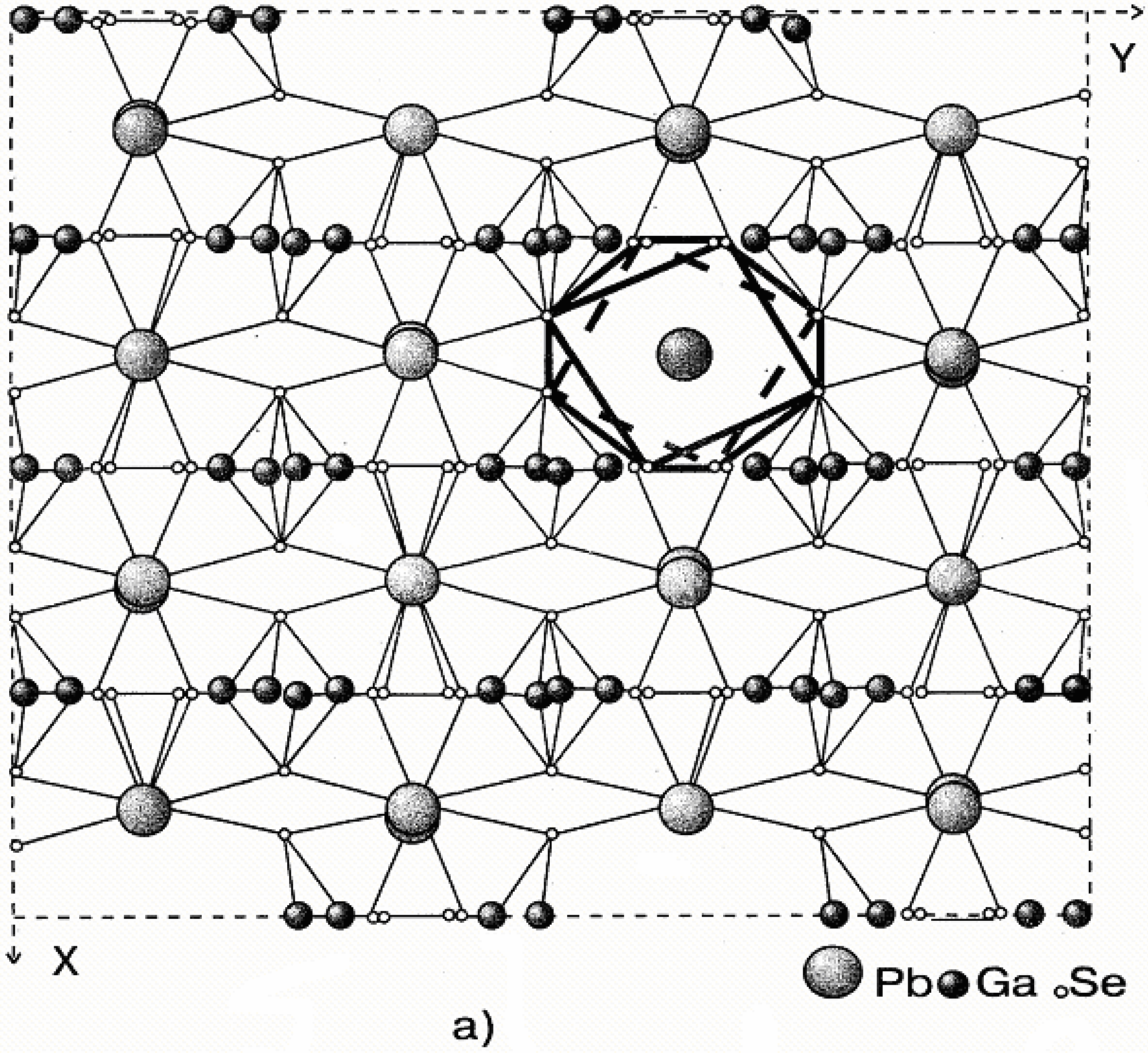


Fig. 1. Projections of an elementary cells of a crystalline structure of $PbGa_2Se_4$ on planes:

a) XY (coordination tetragonal antiprisms [$PbSe_8$] with the horizontal bases parallel to a plane a b are shown.

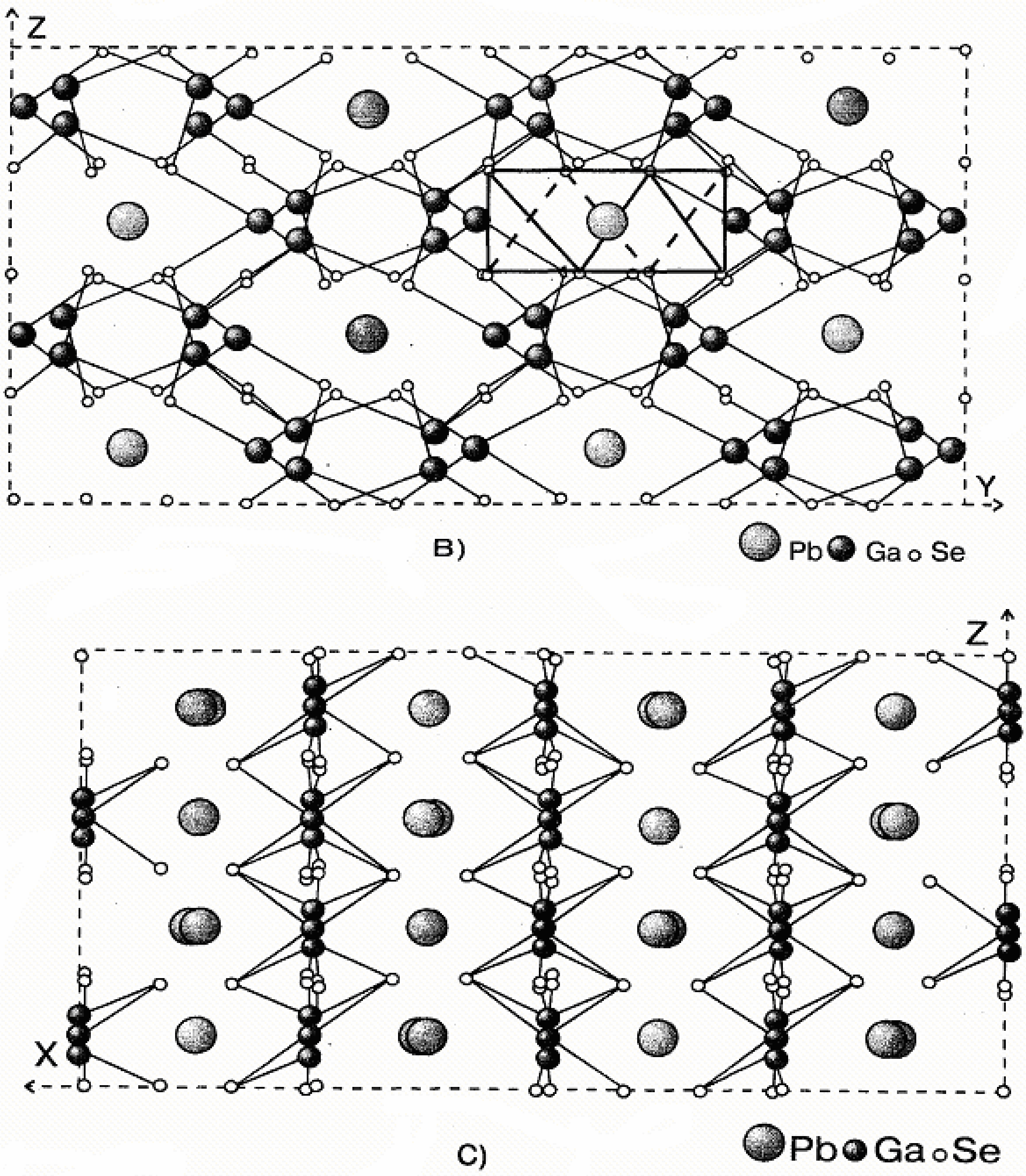


Fig. 1. Projections of an elementary cell of a crystalline structure of $PbGa_2Se_4$ on planes:

b) ZY (one antiprism [$PbSe_8$] among joined [$GaSe_4$] tetrahedra are shown;

c) XZ (are allocated infinite chain joine of [$GaSe_4$] tetrahedra.

The structure of crystals belongs to a structural type of $SrIn_2Se_4$, derivative from TlSe. In all three directions X, Y and Z packing of chalcogen atoms is four-layered (fig.1). Between the chalcogen layers the layers of Pb and Ga atoms are placed, all Ga atoms being placed in YZ planes every 1/4 cells aleng the X axis , and Pb atoms in XY planes every 1/4 along the an Z and YZ axes in 1/4 along the X axis (fig.1). Coordination of Pb atoms is tetragonal-antiprismatic, like in Tl^{1+} ions in TlSe compound. The interatomic distances Pb-Se in tetragonal antiprisms [$PbSe_8$] are 3,06÷3,29Å. All antiprisms to a certain degree are deformed, so that half of Pb atoms (I and II sort) have only two values of interatomic distances with Se atoms 3,17Å and 3,28Å and the other half of the atoms (III sort) - four 3,06Å; 3,10Å ; 3,25Å and 3,29Å, that is close the sum of their ionic radi (1,26 + 1,93=3,19Å).

In X direction the antiprisms [PbX_8] are connected in infinite chains by lateral edges, 4 in a cell. The intervals between these chains are filled with coordination tetrahedrons of Ga [GaX_4], also connected by the edges or apexes. Interatomic distances in Ga-Se are 2,33 ÷ 2,53Å, that corresponds to a sum of covalent radii (1,26 + 1,14=2,40Å). Thus, the structure of compounds of $PbGa_2X_4$ is chain-layered with obviously expressed ion-covalent character of bonds, derivative from the structure of galium selenide (T_2^{1+}, T_2^{3+}, Se_4), in which Tl^{3+} ions are replaced by Ga atoms , and Tl^{1+}ions Pb^{2+} ions in the ratio 2:1.

The primitive part of an lattice cell contain fragments of [GaX_4] chains, alternating with antiprisms [PbX_8], 8 Pb, 16 Ga and 32 X in all. The factor-group analysis of an vibration spectrum of crystals gave the following expansion of normal modes by the irreducible representations of the factor - group D_{2h}:

$$\Gamma=19A_{1g} + 22B_{1g} + 22B_{3g} + 19A_u + 22B_{2u} + 21B_{3u}.$$

In Raman spectrum 84 oscillatory modes are active, in IR absorption - 81 .

Alongside with the X-ray methods of identification of a structure of crystal compaunds can successfully be used non-destructive express - method – Raman-spectroscopy. In fig. 2 non-polarized spectra of crystals $PbGa_2S_4$ (curve 1) and $PbGa_2Se_4$ (curve 2) are presented. Similarity of Raman spectra shows their isostructurallity.

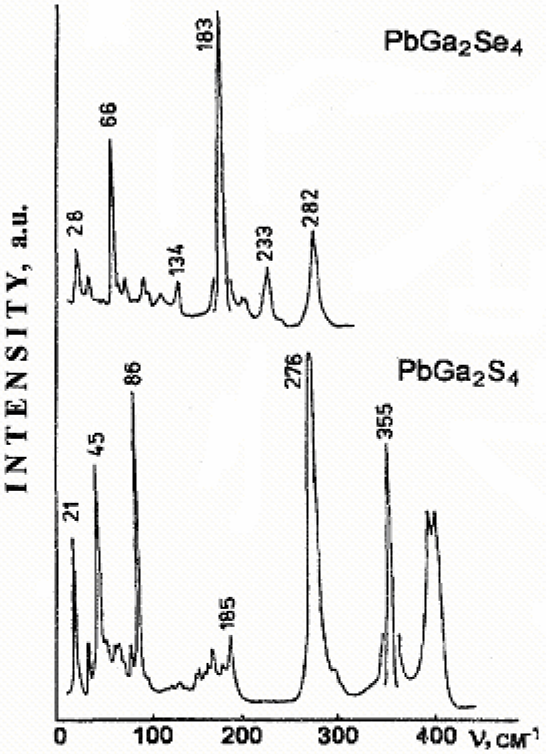
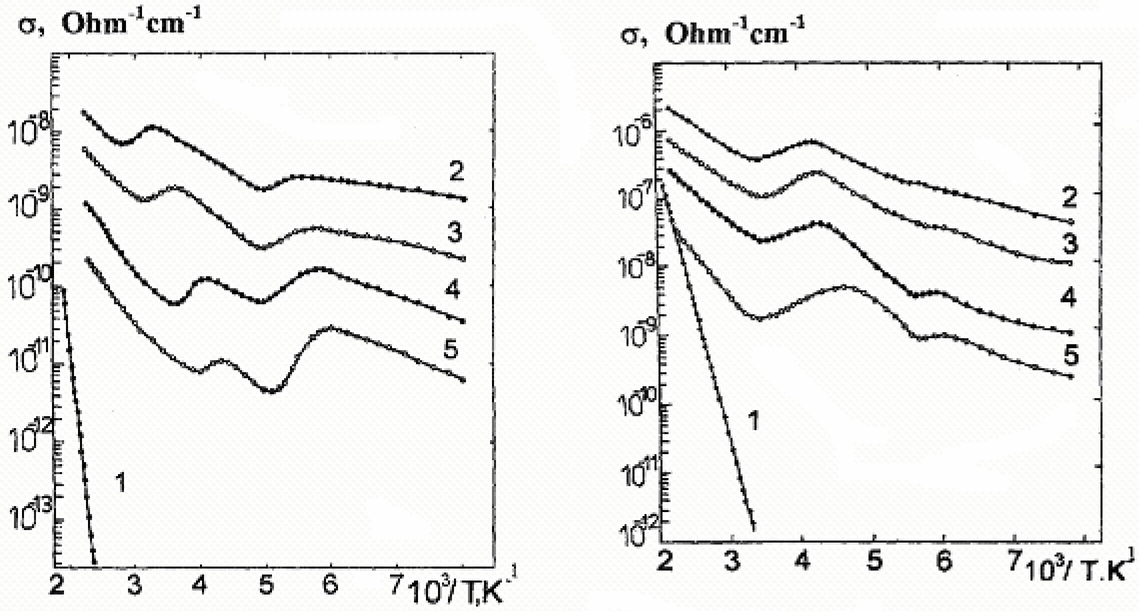


Fig. 2. Non-polarized Raman spectra of $PbGa_2S_4$ and $PbGa_2Se_4$ crystals.

Direct-current electrical conductivity

In crystals $PbGa_2S_4(Se_4)$ brightly expressed cleavage planes on (100) are available, on which they are easily cleaved, that allows to prepare samples of necessary thickness with natural smooth faces without additional processing. On the samples examined the aquadag contacts were deposited; this allows to apply electric field along the cleavage planes (100).

In view of large high-resisivity of crystals $PbGa_2S_4$ and $PbGa_2Se_4$ the measurements of electrical conductivity in a direct current mode are carried out in temperature range 300÷500K. At T=400K specific dark electrical conductivity of single crystals $PbGa_2S_4$ is $\sigma=(1\div3)10^{-15}Ohm^{-1}cm^{-1}$, and of single crystals $PbGa_2Se_4$ – $\sigma=(2\div5)\cdot10^{-9}Ohm^{-1}cm^{-1}$. One of the probable reasons of large high-resistancy of researched crystals is the process of self-compensation of the donors and acceptors during growth of crystals. The temperature dependences of dark electrical conductivity of crystals $PbGa_2S_4$ and $PbGa_2Se_4$ are given in fig.3 a,b, curves 1. As it is seen from these dependences, electrical conductivity grows exponentially with increase of temperature under the law $\sigma=\sigma_o \exp(E_a / kT)$ with activation energy $E_a = 1.6 \pm 0.05$ eV for crystals $PbGa_2S_4$ and $E_a = 0,9 \pm 0,05$ eV for crystals $PbGa_2Se_4$. As the obtained values of the activation energy of electrical conductivity of crystals are considerably lower than those of the forbidden bandwidths the activation of electrical conductivity is due to ionization of impurity states.



a b

Fig. 3. Temperature dependences of dark conductivity (1) and photoconductivity (2-5) of $PbGa_2S_4$ (a) and $PbGa_2Se_4$ (b) crystals, measured at illumination L (*l*x): 2- 104; 3- 2,5×10³; 4- 3,1×10²; 5- 78.

The stationary characteristics of photoconductivity

Measurements of photoconductivity have been carried out at stationary excitation in conditions of a direct current. Illumination of a sample is realized from a lamp with a tape spiral by a potency of 400 W with a passage of light through a water filter. The monocrystals $PbGa_2S_4(Se_4)$, obtained from a melt, have significant(sizeable) photosensitivity without additional heat treatment or any special activation. At illumination by integrated light (light exposure $L=10^4$ *l*x) the conductivity increased on by several orders. A multiplicity of the photoanswer to integrated light $K=\sigma_{ph}/\sigma$ (where σ_{ph} – the conductivity on light) depends on σ and temperature and reaches $10^{-4}\div10^{-5}$ at T=293K and $\sigma_{ph}/\sigma = 10^{-7} \div 10^{-8}$ at T=100K, for crystals $PbGa_2S_4$ and on the average is smaller by two orders for crystals $PbGa_2Se_4$.

Basic characteristic of any photoconductor is spectral distribution of photosensitivity. In fig. 4, a and b the PC spectra of crystals $PbGa_2S_4$ and $PbGa_2Se_4$, measured at various temperatures are presented. From the comparison of a PC spectrum (fig..4, a) and fundamental absorption edge of thyogallat of lead, given in work [7], it is seen, that the sharp increase of a signal of photoconductivity takes place in the region of a fundamental absorption due to the increase of absorption. At photon energy, close to the band gap - curve reaches a maxima $h\nu_{max1} = 2,88 \pm 0,01$ eV at T=293K, and then decreases in strong absorptions. The value of the band gap, determined by the position of the long-wave half-drop of the intrinsic photoconductivity (using a criterion Moss) $E_g=2,83\pm0,02$ eV and is in a good agrement with value $E_g^{op} = 2,840\pm0,005$ eV, obtained in [7] in the analysis of an edge intrinsic absorption. Thus, it is possible to conclude, that the most high-energy maxima in PC spectrum of crystals $PbGa_2S_4$ at T=293K ($h\nu_{max1} = 2,88 \pm 0,01$ eV) is in the range of fundamental absorption edge and is stipulated by band-to-band bipolar generation of free charge. Increase of temperature of a sample results in broadening of an intrinsic PC band and it is displaces in a leg of smaller energies. The temperature variation E_g, evaluated by the shift of the intrinsic maximum PC, has appeared equal to $dE / dT = 5 \times 10^{-4}$ eV/K, wich agrees well with the data of the research of the intrinsic absorption edge [7].

In PC spectra of investigated crystals $PbGa_2S_4$ in addition to intrinsic band one more clearly expressed impurity band is observed with the maximum of photon $h\nu_{max2} = 2,55$ eV and red boundary of the photoanswer at responce photon energy $E_{red} = 2,3$ eV (T=293K). With increase of a sample temperature the intensity of impurity PC band crystals $PbGa_2S_4$ grows with simultaneous shift of a maxima to the smaller photon energies (curves 1 and 2 in fig. 4, a).

In PC spectra of crystals $PbGa_2Se_4$ (fig. 4, b) three brightly expressed maxima are observed, energetic positions of which at T=100K are $h\nu_{max1} = 2,47 \pm 0,02$ eV and $h\nu_{max2} = 2,22 \pm 0,02$ eV and $h\nu_{max3} = 1,46 \pm 0,02$eV. In view of a lack in literature the data on the research of the edge absorption of these crystals we conducted on the same samples the measurements of PC spectra and the edge absorption, that allowed to carry out the identification of the observed PC maxima. From comparison of PC spectra and the edge absorption spectra if follows, that the high-energy maximum $h\nu_{max1} = 2,47 \pm 0,002$ eV is due to band-to-band transitions, i.e. is intrinsic. It is worth noting strong dependence of the intensity of both the intrinsic and impurity maxima on the temperature of a sample. If at T=100K the intrinsic band in PC spectra of crystals $PbGa_2Se_4$ is dominating (curve 1 on fig.4, b), with increase of a sample temperature of the intrinsic intensity ($h\nu_{max1} = 2,47$ eV) and the high-energy impurity ($h\nu_{max2} = 2,22$ eV) bands sharply decreases, at the same time intensity of the most long-wave impurity

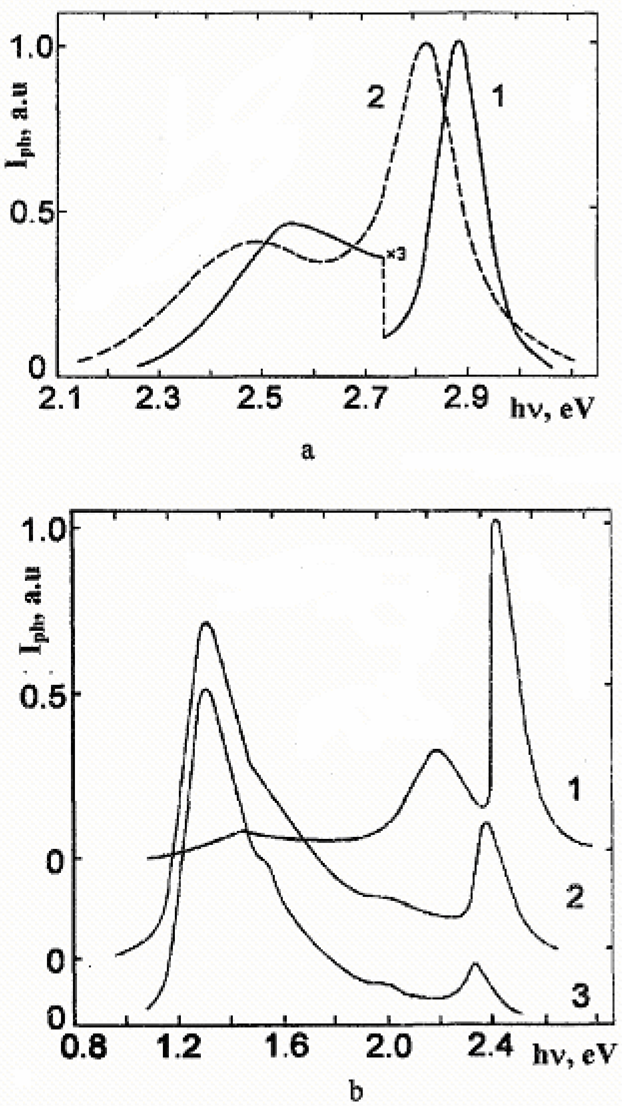


Fig. 4. Photoconductivity spectra of of $PbGa_2S_4$ (a) and $PbGa_2Se_4$ (b) crystals measured at various temperatures T, K: a) 1- 293; 2- 380 and b) 1- 100; 2- 293; 3- 350.

($h\nu_{max1}$ = 1,46 eV) band sharply grows in the same way up to room temperatures, and then remains practically constant. Both the intrinsic and the two impurity maxima with increase of temperature of a sample are shiffed to the long-wave part of the spectrum. Above the room temperatures, the energetic position of maximum of the most long-wave impurity band in spectra remains practically constant ($h\nu_{max3}$ = 1,33 eV), and on its high-energy dip an additional peculiarity is observed as a shoulder at $h\nu \approx 1{,}55$ eV. Temperature coefficient of E_g variotion for crystal of $PbGa_2Se_4$, evaluated by the shift of the intrinsic maximum, is equal $dE_g / dT = 7\times10^{-4}$ eV / K. The presence of impurity band in PC spectra the crystals studied testifies that as well as in majority of wide-band semiconductors, in a forbidden zone of $PbGa_2S_4(Se_4)$ deep local centers are present, the photoionization of which is the cause of the impurity by PC.

In wide-band semiconductors, to which belong also $PbGa_2S_4(Se_4)$ the photosensitivity is determined mainly by the system of energy levels, formed by local centers of a various energy nature. At the description of recombination process it is necessary to take into account, that in complex multicomponent photoconductors the spectrum impurity states is rather broad, and all types of centers to a certain extent influence the photosensitivity either directly as recombination centers or indirectly as the adhesion centers. For the definition of parameters of local centers and the definition of electronic passages in wide-band semiconductors complex of stationary and kinetic methods of PC research is used [1]. The most complete information on processes and recombinations of nonequilibrium charge carriers given the measurements of a temperature dependence of PC, termally stimulated conductivity, mobility and lux-ampere characteristics (LAC).

In majority photosensitive semiconductors either the temperature quenching of PC or increase (thermal activation) with growth of temperature [1] is observed. The family of PC temperature dependences PC crystal $PbGa_2S_4(Se_4)$, measured at various levels of a constant illumination the intrinsic integrated light, is shovn in fig. 3, a, b curves 2-5. From these figures it is seen, that in the temperature interval 100÷400K on a general background of thermal activation PC two regions temperature quenching of photoconductivity are observed, that testiqiest to the existence in a band gap of the crystals studied of two types of sensitising r- and m- of recombination centers.

The beginning of temperature quenching of PC depends on intensity of excitation, moving at its increase to the higher temperatures. The quenching ratio also depends on the intensity of excitation. Most clearly it is expressed in the low-temperature region of T-quenching.

It is known [1-9], that the temperature quenching of PC, being one of basic attributes of two-centers model of recombination, arises at thermal exchange of charge carriers betwen the centres and the valence band (v- band). The condition of transition from high sensitivity to smaller one both with increase of temperature at fixed light intensity, and with a diminution of light intensity at fixed temperature is expressed [9]:

$$\ln n_{max} = \ln (N_c S_p / S_n) - E_{rc}/kT_{max}, \qquad (1)$$

where n_{max}– the number of free electrons, corresponding to a maximum of T-quenching, N_c- effective density of states in c- band, S_p and S_n- of ections of holes capture by thesensitizing r- centers, E_{rc}- depth of occurrence of the sensitizing centers, T_{max}- temperature, corresponding to maximum T- quenching.

Using a set of curves on fig. 3 and expression (1) we determined the depth of occurance of sensitizing r- and m- of recombination centers: E_{rc} = 0,65 eV and E_{mc} = 0,43 eV for crystals $PbGa_2S_4$ and E_{rc} = 0,94 eV and E_{mc} = 0,51 eV for $PbGa_2Se_4$.

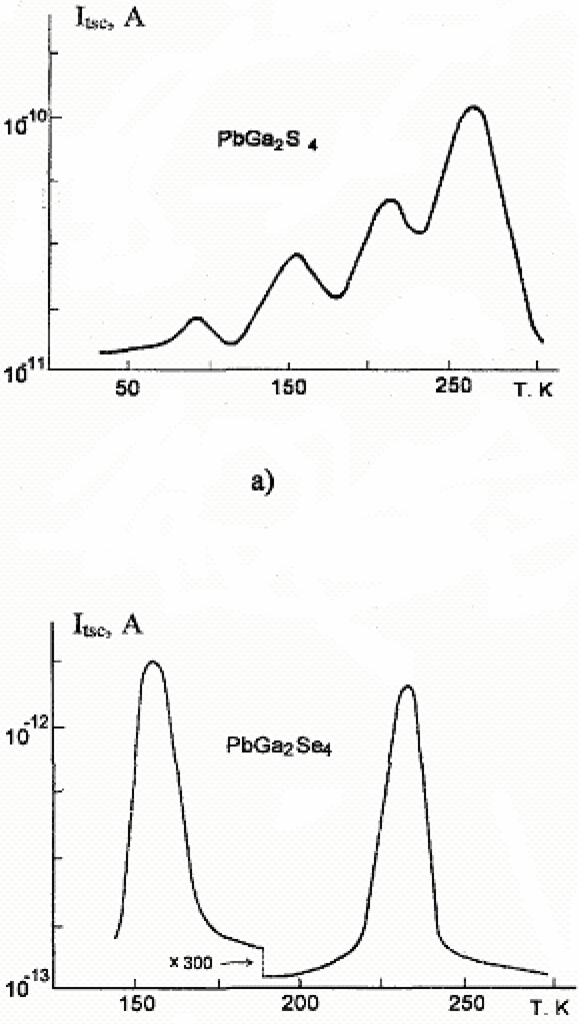
Thus, in assotiations $\sigma_f = f(T)$ crystals $PbGa_2S_4(Se_4)$ two competing processes are present: thermal activation and the thermal quenching of photoconductivity according to

[10] the phenomenon of temperature activation of PC is due to thermal recharge between the main non-equilibrium charge carriers donors and their recombination centers. With the aim of confirmation of the validity of application of the mentioned model to the explanation of PC activation in crystals of $PbGa_2S_4(Se_4)$ we need, the data corfirming the presence of the trapping centers.

For the revealing of the of centers of an adhesion and determination of their basic parameter - depth E_t- of accurance of the - research of thermally stimulated current TSC in crystals of $PbGa_2S_4$ and $PbGa_2Se_4$ was carried out (fig.5). As it is obvious from fig.5, a in the range of temperatures 100÷300K in a TSC curve of $PbGa_2S_4$ there observed four current maxima, caused by presence of four trapping levels. With increase of heating rate of a sample the maxima shifted to higher temperatures with simultaneous increase current peak maxima. In TSC curve of $PbGa_2Se_4$ crystal (fig.5, b), there are observed only two maxima, that testifiles to the presence in a of two band gap centers.

To determine the energy location of levels, TSC curves was applied the method of analysis, in dependent of the recombinations type (monomolecular or bimolecular) and charge carriers in crystals - a method of initial rise [11]. To apply this method "thermal clearing " of the peaks [12] is necessary. The initial part (up to the maximum) of TSC curves (independently fast or slow retrapping), is described by the expression $I_{tsc} = \text{const} \times \exp(-E_t / kT)$. In coordinates $\ln I_{tsc} - T^{-1}$ these part of TSC curves are represented by the straight lines, by the slope of the curve of which energy depthes of occurance of levels were determined: $E_{t1} = 0{,}16 \pm 0{,}02$ eV; $E_{t2} = 0{,}21 \pm 0{,}02$ eV; $E_{t3} = 0{,}34 \pm 0{,}02$ eV; $E_{t4} = 0{,}45 \pm 0.02$ eV for $PbGa_2S_4$ and $E_{t1} = 0{,}23 \pm 0{,}02$ eV; $E_{t2} = 0{,}52 \pm 0{,}02$ eV for $PbGa_2Se_4$.

We should note in conclusion that the experimental available on the study of electrical conductivity, TSC and stationary PC characteristics are not satficient yet for a final construction of the diagram of electron state in a band gap of $PbGa_2S_4$ and $PbGa_2Se_4$crystals. For this purpose, at least, additional data on photoluminesce and temperature dependence of driff mobility are needed.



a)

b)

Fig. 5. Curves of termally stimulated current in $PbGa_2S_4$ (a) and $PbGa_2Se_4$ (b), crystals (heating rate is 0,45 K/s).

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СТРУКТУРА І ФОТОЕЛЕКТРИЧНІ ВЛАСТИВОСТІ КРИСТАЛІВ $PbGa_2S_4$ І $PbGa_2Se_4$

Д.І. Блецкан, Ю.В. Ворошилов, Л.М. Дурдинець, В.М. Кабацій, В.М. Головей

Ужгородський державний університет, 294000, Ужгород вул. Волошина, 54

Методом Бріджемена-Стокбаргера одержані оптично однорідні кристали $PbGa_2S_4$ і $PbGa_2Se_4$, рентгеноструктурні дослідження яких підтвердили належність їх до ромбічної структури. Основними структурними елементами будови $PbGa_2S_4$ і $PbGa_2Se_4$ є тетраедри [GaX_4] і тетрагональні антипризми [PbX_8] (де X = S, Se). Структура кристалів належить до структурного типу $SrIn_2Se_4$, похідного від TlSe.

Проведено комплексне дослідження електропровідності, термостимульованої провідності, спектрів фотопровідності і температурної залежності фотопровідності широкозонних потрійних кристалів $PbGa_2X_4$, що дозволило виявити та визначити основні параметри центрів прилипання та рекомбінації. В спектрах фотопровідності проявляються як власні так і домішкові смуги, енергетичне положення та інтенсивність яких істотно змінюється із зміною температури. Заміщення S на Se в потрійних сполуках $PbGa_2X_4$ супроводжується збільшенням електропровідності і зменшенням ширини забороненої зони.