Chalcogenide Letters Vol. 3, No. 12, December 2006, p. 125 – 132

PHOTOCONDUCTIVITY AND PHOTOLUMINESCENCE OF $PbGa_2Se_4$ CRYSTALS

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There were carried out complex researches of electrical conductivity, thermo-stimulated current, photoconduction and photoluminescence spectra and dependence on temperature of the stationary photoconductivity, in the range 100 ÷ 500 K for the ternary crystal $PbGa_2Se_4$. There were evidenced two types of slow recombination centres (r- and m-) and two capture centres, and their parameters were determined: concentration and position in the gap).

(Received November 21, 2006; accepted December 19, 2006)

Keywords: $PbGa_2Se_4$ single crystal, Photoconductivity, Photoluminescence, Recombination centres, Capture centres

1. Introduction

The preparation of new wide-gap semiconductors of complex composition, and the study of their structure and physical properties, represents one of the main direction of research in materials science. Among the physical properties of interest in technology, the photoconductivity is situated on the first places. The photoconductivity phenomenon lays at the basis of photoresistances, vidicons, memories and other devices. Many methods of research of physical properties of semiconductors are based on the photoconduction phenomenon.

For the photoelectric radiation receivers are necessary semiconducting materials that exhibit specific characteristics necessary for the optimized values of the working parameters of the devices: photo-sensitivity in a given spectral range, dark and photo- resistance, inertness, range of working temperatures, and so on. The transport parameters of the wide-gap semiconductors are determined mainly by the intrinsic and impurity point defects, that form the system of local centres in the forbidden gap. A good information on the recombination and capture centres can be collected by the investigation of the stationary and kinetic characteristic of the photoconductivity (PC) and photo-luminescence (PL) in a large temperature interval.

By considering the high photo-sensitivity of the binary lead selenide and gallium hexa-selenide, it is normal to suppose that photosensitivity exists also in the ternary crystal $PbGa_2Se_4$. The semiconducting compound $PbGa_2Se_4$ is situated on the quasi-binary section $PbSe\text{-}Ga_2Se_3$ of the system Pb-Ga-Se for the component ratio 1:1, as a result of the di-cationic interaction (AC+BC). The lead seleno-gallate melts congruently at 1053±2K [1].

In the last years this compound was not studied intensively. There are data on the crystal growth [4, 5], investigation of their structure [1, 2, 6, 7] and fundamental absorption edge [8]. The first research on the photoconduction in these crystals confirmed their high photosensitivity [2, 3].

In this paper are given the results of complex research on the stationary characteristics of the photoconductivity, on thermo-stimulated current (TSC) and photoluminescence of the $PbGa_2Se_4$ crystal, achieved with the methods developed for wide-gap semiconductors [9, 10].

2. Experimental

The synthesis of the ternary compound $PbGa_2Se_4$ has been carried out by direct melting of the corresponding quantities of very pure elementary components in quartz ampoules evacuated down to 10^{-3} Pa with the application of vibrational movements. The maximum synthesis temperature was 1200 K. For getting the polycrystalline alloys, that are used later for growing crystals, the melts are cooled with the rate of of 0.2 K/s. The $PbGa_2Se_4$ have been grown by directional crystallization from the melt (vertical Bridgman method) in evacuated quartz ampoules. The temperature gradient in the crystallization region was 20 ÷30 K/cm, and the speed of movement of the crystallization front was 0.2÷0.3 mm/h. The crystals have been grown as cylinders with the diameter of 18÷20 mm and length of 50 mm and easily cleaves along the cleavage plane (100) with the formation of a mirror surface. With the help of X-ray diffraction was established that the obtained crystal exhibits rhombic structure with the lattice parameters: a = 21.37 Å, b = 21.47 Å, c = 12.73 Å and belongs to the spatial group D_{2h}^{24} [1, 6]. According to the microphase analysis data the homogeneity of the single crystals along the length is high, and this speaks in favour of the keeping of the initial chemical composition.

For the study of the electrical and photoelectrical properties on freshly cleaved surfaces of the samples there were added aquadag co-planar contacts. The investigations of the dark conductivity and photoconductivity have been carried out in a cryostat evacuated at 10^{-3} Pa, that permits to change the temperature from 100 to 500 K. For the stabilization of the temperature it was used an industrial regulator VRT-3 that ensures an accuracy of ±0.01 K. The resistivity has been measured by the ammeter-voltmeter method with the application of a protection ring for the diminishing of the surface currents. The current has been measured by an electrometric amplifier U 5-9.

The light source for photoelectric measurements was given by a lamp of the type SI-200 with a known spectral distribution of energy. The measurement of the photoconduction spectra has been performed with an automated device situated on the base of the monochromator DMP-4, with the use of both constant and modulated illumination of the sample. In the case of modulated illumination of the samples, the photocurrent, which changes with the modulation of the light frequency, determines the sharp decrease of the voltage on the load resistance R_H (connected in series with the sample), which is measured by the nanovoltmeter UNIPAN 232 B with the recording on a printer.

The thermo-stimulated current has been measured in the temperature range 100 ÷ 500 K. The heating rate was 0.1 ÷ 0.3 K/s. The excitation of the non-equilibrium conductivity was achieved by the light got from the spectrum of the lamp SI-200 with appropriate filters. The illumination of the samples has been achieved both in the cooling process and for low temperatures. For these regimes differences in the TSC have been not observed.

The spectra of the stationary photoluminescence have been measured in the spectral range 0.4 ÷ 1.2 μm and temperature interval 100 ÷ 300 K. The optical excitation has been achieved by irradiation with a luminescent diode with the photon energy hν = 2.33 eV (532 nm) and power of ~37 mW. With the purpose to eliminate the possible distortion of the radiation spectra on the account of self-absorption, the radiation has been recorded on the side of the sample, on which the excitation light was directed. The spectra were analysed with the monochromator MDR-12, having a resolution not worse than 0.1 MeV.

3. Results and their interpretation

3.1 Electroconductivity in direct current.

Due to high resistance of the $PbGa_2Se_4$ crystals the measurement of the electroconductivity in direct current has been carried out in the temperature range 300÷500 K. For T = 300 K the specific dark electroconductivity of the $PbGa_2Se_4$ single crystals is $\sigma_T = (2\div5) \times 10^{-11}$ $\Omega^{-1}cm^{-1}$. One of the possible causes of the high resistance of the crystals is the self-compensation of the donors and acceptors in the process of crystal growth. Really, the presence in the ternary crystals $PbGa_2Se_4$ of two types of cation sublattices allows for the appearance of multiple intrinsic point defects, mainly due to the deviation from the stoichiometry. As a consequence, during growth process are created simultaneously intrinsic point defects both of donor and acceptor type, i.e. is produced self-compensation, that produces semi-insulating crystals.

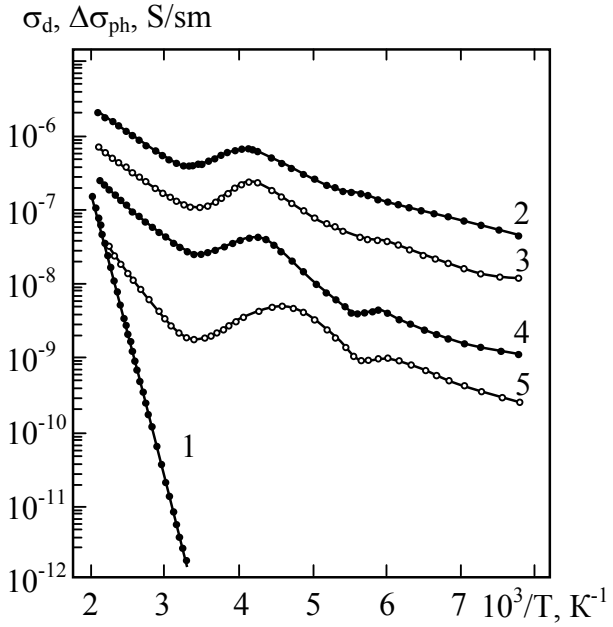

Fig. 1. The temperature dependence of the dark conductivity σ_d(1) and stationary photoconductivity $\Delta\sigma_{pc}$ (2-5) of the crystal $PbGa_2Se_4$, measured for the illumination, L: $2 - 10^{-4}$; $3 - 2.5 \times 10^{-3}$; $4 - 3.1 \times 10^{2}$; $5 - 78$.

The temperature dependence of the dark electroconductivity is represented in Fig. 1. As evident from this dependence the electroconductivity raises with the increase of the temperature after an exponential law $\sigma_T = \sigma_o exp(E_a/kT)$ with the activation energy $E_a = 0.9 \pm 0.05$ eV. Because the obtained value of the activation energy of electroconductivity of the studied crystals is essentially lower than the value of the width of the forbidden gap $E_g = 2.44$ eV, then the activation of the electroconductivity must be related to the ionization of the impurity states.

3.2. The photoconductivity spectra

The single crystal $PbGa_2Se_4$ obtained from melt exhibits significant photosensitivity without additional thermal processing or any special activation. During illumination with integral light (illumination: $L = 10^4$ lx) the conductivity increases by several orders of magnitudes. The multiplicity of the photo-response to the integral light $K = \sigma_\Phi/\sigma_T$ (σ_Φ is the conductivity under

light) essentially depends on the sample temperature and reaches $10^2 \div 10^3$ at T = 293 K and $\sigma_\Phi/\sigma_T = 10^5 \div 10^6$ at T =100 K.

In the Fig. 2 are represented the photoconductivity spectra of the crystals $PbGa_2Se_4$, measured at different temperatures. In the photoconduction spectra are observed three maxima, whose energy positions at T = 100 K correspond to $h\nu_{max1}$=2.47 ±0.02 eV, $h\nu_{max2}$=2.22±0.02 eV and $h\nu_{max3}$=1.46±0.02 eV. By comparing the photoconductivity spectra with the absorption edges [8] it follows that the high energy maximum $h\nu_{max1}$=2.47 eV is situated in the range of the fundamental absorption edge and is conditioned by the direct band-band transition, i.e. is intrinsic. The values of the width of the forbidden gap in $PbGa_2Se_4$ at T = 100 K, determined after the position of the long wavelength half-height intrinsic photoconductivity (according to Moss criterium), is equal to E_g=2.43 ± 0.01 eV and is in good agreement with the value E_{gd}=2.440±0.005 eV, obtained in [8] from the analysis of the intrinsic absorption edge.

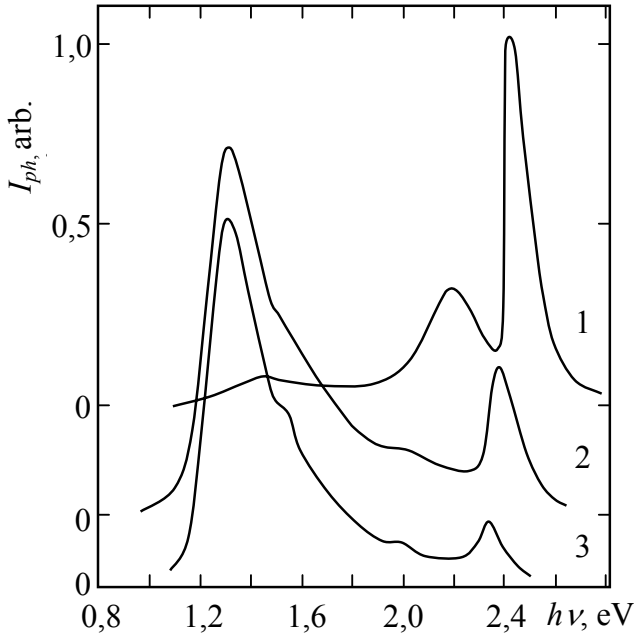

Fig. 2. The photoconduction spectra of the crystal $PbGa_2Se_4$ measured at various temperatures, T, K: 1 – 100, 2 – 293, 3 – 350.

The second maximum $h\nu_{max2}$=2.22 eV in the low-temperature photoconductivity spectra is also intrinsic and is related to the generation of electron-hole pairs due to indirect optical transitions (according to [8] the width of the forbidden gap for indirect transitions is E_{gi}=2.234 eV at T = 112 K).

Excepting intrinsic maxima in the photoconduction spectra of the $PbGa_2Se_4$ crystals one observes still one band at long wavelengths, with the maximum at $h\nu_{max3}$= 1.446 eV. Considering that not intentional doping of crystals has been made, the nature of the impurity bands is conditioned by the intrinsic point defects of the lattice.

One can observe that with the increase of the temperature of the sample, takes place a strong scattering of the intensities of the intrinsic and impurity bands in the photoconduction spectra. The dominant intrinsic band at T = 100 K (band with $h\nu_{max1}$=2.47 eV) in the photoconduction spectra (Fig. 2, curve 1), exhibits with the raising temperature an essential decrease, and, in the same time, the intensity of the impurity band ($h\nu_{max1}$=1.46 eV) sharply increases down to room temperature, thereafter remains practically unchanged. Thus, both intrinsic and impurity maxima, with the increase of the sample temperature shift towards the long wavelength domain of the spectrum. Above the room temperature the energetical position of the maximum of the impurity band in the photoconduction spectrum remains practically unchanged

($h\nu_{max3}$=1.33 eV), and on its high energy roof appears a peculiar feature as a shoulder at $h\nu \approx 1.55$ eV. The temperature coefficient of the change of E_{gd} of the crystal $PbGa_2Se_4$ estimated from the shift of the intrinsic photoconduction maximum is $\Delta E_{gd}/dT \sim -5 \times 10^{-4}$ eV/K that is in good agreement with the research data on the temperature behaviour of the intrinsic absorption: -4.75×10^{-4} eV/K [7].

3.3. Photoluminescence spectra

In the spectra of $PbGa_2Se_4$ crystals have been observed two bands of intrinsic recombination radiation (Fig. 3). For T = 100 K the positions of the maxima in the photoluminescence spectra correspond to the energies: $h\nu_{max1}$=2.1 eV and $h\nu_{max2}$=1.43 eV. When the temperature increases both bands vanish. The temperature dependence of the radiation intensity in the maxima of the bands is described by the exponential law:

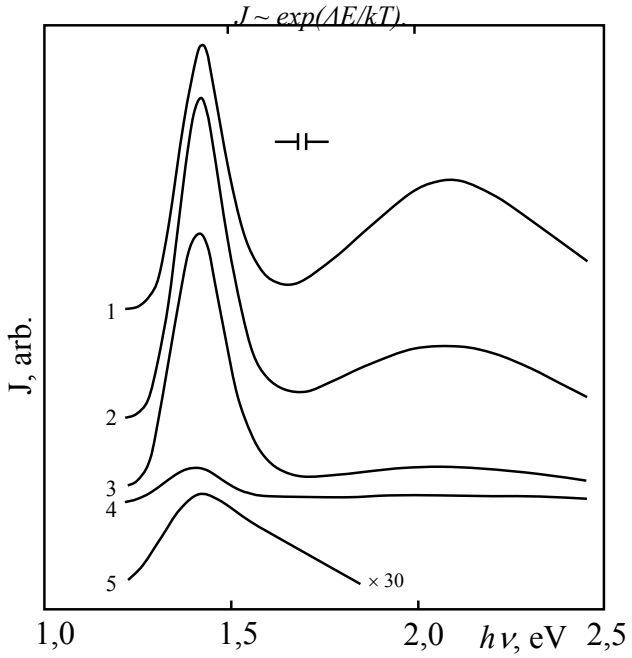

Fig. 3. The photoluminescence spectra of the $PbGa_2Se_4$ crystal, measured or various temperatures T, K: 1 – 100, 2 – 140, 3 – 180, 4 – 220, 5 – 300.

It is remarkable the correlation between the temperature dependencies of the intensities of the impurity bands in the photoluminescence and photoconduction spectra. The vanishing with temperature of the intensity of the bands $h\nu_{max2}$ = 1.43 eV in the photoluminescence spectra is accompanied by the increase of the intrinsic band $h\nu_{max3}$=1.46 eV in the photoconduction spectrum. It is important to observe the very close values of the activation energies of these two processes. Consequently, the coverage of the above shown recombination channel leads to the increase of the non-equilibrium charge carriers, and this determines the activation of the stationary photoconduction (Fig. 1, curves 2 – 5).

The second important particularity of the temperature dependence of the intensity of the intrinsic photoluminescence ($h\nu_{max2}$=1.43 eV) consists in the fact that the activation energy ΔE_{PL} indicates that the radiation is not related to the trapping of the free carriers on an impurity centre, but is a result of an internal centre transition or a transition between impurity levels. If it is correct to admit that the high-resistance of the $PbGa_2Se_4$ crystal is determined by the self-compensation of the donor and acceptor states, then, in the frame of this model it is preferable to relate the photoluminescence band $h\nu_{max2}$=1.43 eV to the transition of the carriers inside the donor-acceptor

complex. The presence of the impurity bands in the PC and PL of the investigated crystals indicates that, as in the major part of the wide-band semiconductors, in the forbidden gap of the $PbGa_2Se_4$ exist many deep local centres, whose photo-ionization determines the impurity PC. The most complete information on the process of capture and recombination of the non-equilibrium charge carriers in wide-band semiconductors is given by the measurements of the temperature dependence of the PC, thermo-stimulated conduction, mobility and of lux-ampere characteristics (LAC).

3.4. The temperature dependence of the stationary photoconduction

The family of the curves of temperature dependency of FC of crystalline $PbGa_2Se_4$, measured for different levels of constant illumination with integral light, is given in Fig. 1, curves 2 – 5. As opposite to the majority of the photosensitive semiconductors, where one observes the vanishing with temperature of the photocurrent, or its increase (thermo-activation) with the increasing temperature [10, 12], for the lead seleno-gallate. On the general ground of the photoconduction thermo-activation there are observed two domains of temperature vanishing of the photoconduction. Firstly the vanishing with temperature of PC depends on the intensity of excitation, and shifts with its increase on the side of higher temperatures. The multiplicity of the vanishing PC depends also on the excitation intensity. This is most clearly evidenced for the low-temperature domain (first one).

The temperature vanishing of the PC takes place when the hole demarcation level for the sensitive centres coincides with the level corresponding to these centres. The transition from high sensitivity to lower one both with the increase of the temperature for fixed light intensity, and with the diminishing of the light intensity for fixed temperature is governed by the expression [11]:

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

where n_{max} is the number of free electrons, corresponding to the maximum of the vanishing, N_c is the effective density of states in the c-band, the cross-sections S_p and S_n correspond to trapping the holes and electrons achieved by the sensitive *r*-centres, E_{rc} is the depth of the sensitive centres, T_{max} is the temperature corresponding to maximum temperature of vanishing.

The presence of two temperature domains of vanishing PL indicates the existence in the forbidden gap of the investigated crystals of two types of "sensitive" *r* and *m* recombination centres. By analyzing the family of curves represented in Fig. 1, by taking into account the relation (1) it is possible to determine the depth of "sensitive" *r* and *m* recombination centres: E_{cr}=0.94 eV, E_{cm}=0.51 eV for $PbGa_2Se_4$.

Thus, in the dependencies σ_Φ = f(T) of the $PbGa_2Se_4$ crystals appear two congruent processes: thermo-activation and vanishing with temperature of the photoconductivity. The activation of the PC can be conditioned by temperature changes of the mobility of the basical carriers (in the case of the impurity mechanism of scattering), on their cross-section of capture on the recombination centres, on the quantum output of the photo-effect for the complex mechanism of generation (e.g. exciton mechanism) and, finally, trapping of the basical charge carriers. Due to the multitude of causes for the activation of the PC, for there are needed additional data for the correct interpretation of the results. The analysis of the temperature dependence of the PC in a large row of wide-band semiconductors shows convincingly that in the major part of cases the PC activation is determined by the presence of capture centres of basical carriers (t-centres). In this case the phenomenon of temperature activation of PC is given by the thermal redistribution of the charge between the trapping centres of the non-equilibrium charge carriers (donors) and their recombination centres (acceptors). With the aim to confirm the validity of the application of the above model for the explanation of the activation of PC in $PbGa_2Se_4$, there are necessary data that support the presence of the trapping centres.

3.5. Thermo-stimulated conduction

For evidencing the trapping centres in the $PbGa_2Se_4$ crystals and for the determinatiojn of their fundamental parameters, depth E_{ct} and concentration N_t, has been carried out thermo-stimulated current measurements (TC). As visible in Fig. 4, in the temperature domain 100 ÷ 300 K on the TC curve exist two current maxima, due to the presence of two trapping levels.

For the determination of the energy of the trapping levels by using the TC curve there was applied the analysis method not-depending on the recombination type (monomolecular or bimolecular) and on the charge carriers in crystals: the method of *starting raising* [12]. For the application of this method it is necessary the thermal cleaning of the peaks [13]. The TC analysis with the method of "thermal cleaning" has shown that for the observed peaks were responsible the states with a distribution near to discrete one. The first part (up to the maximum) of the TC curves, independently of the trapping levels (rapid, with the capture of the carriers from the band, or slow, without capture) is described by the expression $I_{TCT} = const \times exp(-E_t/kT)$. In the coordinates $I_{TCT} \sim T^{-1}$ these parts of the TS curves represent straight lines, and, from the slope of the straight lines is possible to get the energy positions of the trapping levels: E_{t1} = 0.23±0.02 eV; E_{t2} = 0.52 ± 0.02 eV.

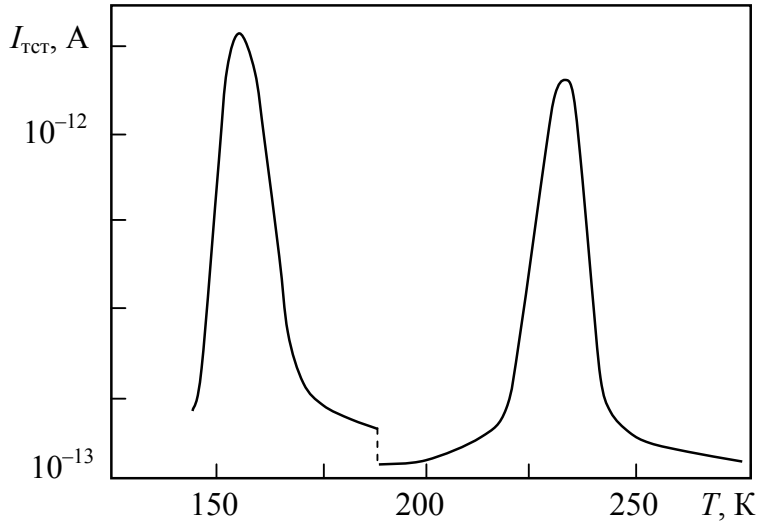

Fig. 4. The curves of thermo-stimulated currents in the $PbGa_2Se_4$ crystals measured for the heating rate of the sample: 0.45 K/s.

The concentration of the traps has been obtained from the area under the TS peaks and are: $N_{t1} = (1\text{-}2)\times10^{16}$ and $N_{t2}=(7\text{-}8)\times10^{15}$ cm^3. Necessary for such calculation, τ_n, has been determined from the stationary photocurrent, and its value was close to the value of the TS current and to the known number of quanta of the exciting light, that impinges on the sample. The use of $\tau_{nstat.}$ is due to the fact that in the investigated samples for recombination of the non-equilibrium carriers it is realized the so-called case χ = 1 [14], that has been demonstrated by LAC researches and investigations of the curves of relaxation of the photo-current for illumination of the samples with the pulses of the exciting or vanishing infrared light on the ground of own illumination [15].

It is to observe that the change of the concentration of the trapping centres in crystals is related to the multiplicity of the activation of PC for fixed illumination of the sample, and, also, determines the temperature for which the PL activation is stopped.

By considering that a special doping in the process of crystal growth has been not made, and has been not made the thermal processing in various media, the logical conclusion is that electrical, photoelectrical and luminescence properties of the ternary semiconductor crystal $PbGa_2Se_4$ are determined by the intrinsic point defects. The explanation of the nature of the donor and acceptor levels in $PbGa_2Se_4$ crystals represent a complex problem because even the

consideration of the simplest point defects of the crystalline structure, and, in particular, the vacancies of the interstitial atoms and substitutional atoms leads to 12 types of point defects, each of which can form electrically and optically active levels in the forbidden gap of this semiconductor.

4. Conclusions

By the Bridgman method there were grown optically homogeneous bulk crystals $PbGa_2Se_4$. The X-ray diffraction investigation of this crystal allowed to assign it to the rhombic simetry. The photo-sensitivity of the $PbGa_2Se_4$ crystal is observed in a large domain of the optical spectrum, that comprises both inter-band and impurity ranges, and strongly depends on the temperature.

The presence of the impurity bands in the PL and PC spectra, of two domains of thermo-activation and temperature vanishing PC, two peaks on the TS curves and superlinear LAC in the range of temperature vanishing of PC is indicative of the fact that in the trapping and recombination processes of the non-equilibrium charge carriers in the $PbGa_2Se_4$ crystals act two trapping levels and several types of recombination centres, conventionally noted *m*, *r* and *s* centres (*m*, *r* centres of slow recombination and *s*-centres of rapid recommendation).

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