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ELECTRICAL AND PHOTOELECTRIC PR0PIRTIES OF SOLID SOLUTIONS $In_{1-x}Er_xSe$

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***Abstract**: The results of experiments on the temperature dependencies of the electrophysical properties of* $In_{1-x}Er_xSe$ *single crystals are explained using energy spectrum data. The introduction of Er atoms into InSe leads to an increase in its photosensitivity and an appearance of residual conductivity. Analysis of the current-voltage characteristics of the irradiated* $In_{0.9993}Er_{0,0007}Se$ *and* $In_{0.9991}Er_{0,0009}Se$ *crystals showed that the current flow mechanism in them is due to the monopolar injection.*

***Keywords**: electrical conductivity, monopolar injection, photoconductivity, radiation*

Introduction:

Indium monoselenide belongs to the semiconductor layered compounds of the A^3B^6 group. InSe single crystals are very promising for developing efficient solar energy converters [1,2], optical [3] and X-ray [4] radiation detectors, etc. To extend the working range and increase the sensitivity of this compound, various methods are used: introduction of impurities [5], irradiation with γ-rays and neutrons [6], pressure [7]. For the same purpose, we synthesized some compounds of the InSe-ErSe system, the state diagram of which was first obtained in [8], their single crystals were grown, and the electrophysical and photoelectric properties of these compounds were studied.

The doping of indium selenide with the rare-earth element erbium has attracted rather wide attention of researchers. In [9–12], the optical absorption edge and the influence of an external electric field on InSe and InSe<Er> were studied in a wide temperature range. The analysis of the tail of absorption, interpreted as the tail of Urbach-Martienssen, is carried out, and the value of the effective mass of current carriers is calculated.

In [13], the magnetoresistance and the Hall effect were measured in InSe and InSe<Er> in the temperature range 10–340 K. It was found that the electrical conductivity in InSe and InSe<Er> decreases with increasing temperature at $T\gtrsim60$ and $T\gtrsim100K$, respectively.

The authors of [14] experimentally investigated the dependences of electrophysical parameters on temperature in pure and weakly doped with rare earth elements (gadolinium, holmium and dysprosium) n-InSe crystals. The inconsistency of the values of electrophysical parameters obtained in various works, as well as on various samples, and of the course of their temperature dependences in n-InSe single crystals is associated by the authors with the presence of large-scale chaotic defects in those crystals.

It is known from [8], that at room temperature there is a solubility region reaching up to 2.5 mol% ErSe in InSe-based solution. InSe-based substitution solid solutions crystallize in the hexagonal system.

Experimental results and discussion:

We synthesized the crystals of solid solutions $In_{1-x}Er_xSe$ (x = 0; 0.01; 0.03; 0.05; 0.07; 0.09 mol%) by fusing the corresponding components, taken in a stoichiometric ratio, in graphitized quartz ampoules, evacuated to the residual pressure $1.3\cdot10^{-2}$Pa, in a two-temperature furnace with the use of vibration-based mixing [15].

To study the electrophysical properties in the temperature range of 300-800 K, single-crystal samples grown by the Bridgman method were cut out with a diamond disc. Their typical sizes were about 1×2×6 mm. Indium was used as a contact material for the samples. The magnetic field strength during the measurement of the Hall effect was 40 kE. The strength of the current was limited by the region of the ohmicity of the current-voltage characteristic and was ~10–15 μA.

Figures 1a and 1b, respectively, show the temperature dependences of the specific conductivity and the Hall effect of the $In_{1-x}Er_xSe$ crystals (x = 0; 0.01; 0.03; 0.05; 0.07 mol%). At an ErSe concentration of 0.01 mol%, the conductivity increases in comparison with pure InSe, and with a further increase in the concentration of impurities, it begins to decrease. The decrease in the hole concentration is associated with the compensation of the ionized state of its own acceptor. It can be seen, that when temperature grows to ~500 K, electrical conductivity increases ~2.5 times. Temperature dependence of electrical conductivity obeys the exponential law $\sigma = \sigma_0\cdot e^{-\Delta E/\kappa T}$.

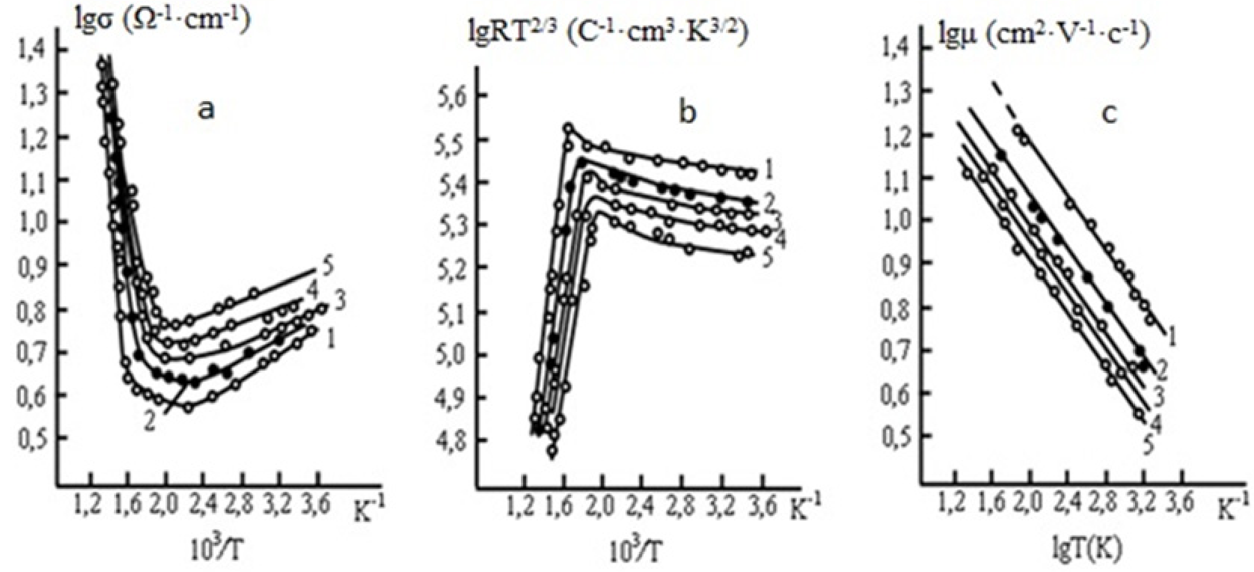

Fig. 1. Temperature dependences for solid solutions $In_{1-x}Er_xSe$ single crystals: a - electrical conductivity, b - Hall coefficient, c - Hall mobility. x: 1 – 0; 2 – 0.07 mol%; 3 – 0.05 mol%; 4 – 0.03 mol%; 5 - 0.01 mol%.

The temperature dependence of the Hall coefficient (R) is more complex. It can be assumed that the change in the Hall factor R with temperature is due to the change in the band gap E_g. In this approximation, estimates of the temperature dependence of E_g on the I and II sectors lead, respectively, to the values $\partial Eg_1/\partial T = -2.7\cdot10^{-4}$ eV/K and $\partial Eg_2/\partial T = -1.3\cdot10^{-4}$ eV/K.

From Fig. 1c, it can be seen that the mobilities of current carriers for $In_{1-x}Er_xSe$ single crystals increase with x. The increase in mobility for these compounds correlates with a decrease in the band gap and an increase in the melting point. It has been established that a change in the mobility of current carriers with temperature follows the law $\mu=f(T^{-3/2})$, which corresponds to their scattering on longitudinal acoustic phonons.

With increasing Er content, the value of carrier concentration increases from $9.1\cdot10^{16}$ cm^{-3} for InSe to $8.76\cdot10^{20}$ cm^{-3} for compositions with a maximum Er content.

It was established by thermo-emf measurements (Fig. 2) that the InSe compound, and the solid solutions based on it have p-type conductivity. Thermo-emf in $In_{1-x}Er_xSe$ alloys increases with temperature rise up to ~500 K, and then decreases. This can be explained by the fact that when In is replaced by Er, the chemical bond is metallized, resulting in decrease of the ionic component of the chemical bond.

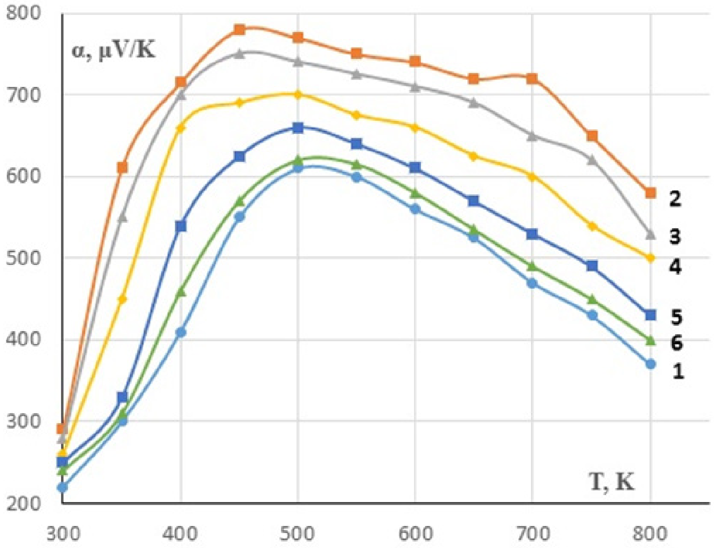

Fig. 2. Temperature dependences of thermo-emf of solid solutions $In_{1-x}Er_xSe$ single crystals; 1 - x=0; 2 - x=0.0001; 3 - x=0.0003; 4 - x=0.0005; 5 - x=0.0007; 6 - x=0.0009.

Treating indium selenide as a direct-gap crystal [16], one can qualitatively explain the temperature dependences R(T), σ(T) and charge carrier mobility μ(T) for $In_{1-x}Er_xSe$ solid solutions.

According to [16], the bottom of the indirect gap (point M of the Brillouin zone) is located 10–15 meV above the direct gap (point Γ). With increasing temperature in the sector I, the change in concentration is due to the change in the width of the direct forbidden gap. When the temperature reaches ~500 K, the indirect gap creeps into the direct gap, and the rate of change of concentration in sector II is determined by the rate of change of the width of the indirect forbidden gap. The kink in the dependence of the electrophysical parameters on temperature for pure crystals can be explained by the difference in the effective masses of the carriers in the direct and indirect gaps. The effective mass of carriers in the indirect gap is more than in the direct gap [16]. With an increase of the ErSe content, the transition boundary from the direct to the indirect gap shifts to the high-temperature region. These phenomena are of interest for the creation of devices based on indium selenide.

Our research has shown that the partial substitution of indium for erbium in an InSe compound substantially changes its photoelectric parameters. Compared to the original crystals, crystals with rare-earth ions have a rather high photosensitivity at relatively low values of dark resistivity (ρ_d). The integral photosensitivity of InSe with rare-earth Er ions is $K=10^{-8}$-10^{-7} A·m/(lm·V) ($\rho_d = 10^2$ Ω·m), and for the original crystals $K=10^{-9}$-10^{-8} A·m/(lm·V) ($\rho_d = 10^3$-10^5 Ω·m), that is, an order of magnitude more than the original crystals with the same thickness, the same area of the receiving window, and the same amount of power obtained in the same mode from the same components.

An additional photosensitivity region (P_1 = 1.15 eV) was found in the photoconductivity spectra of samples of InSe crystals doped with Er, apparently due to the erbium impurity states [8]. Figure 3 shows the spectral dependences of the photoconductivity of the original and Er^{3+} doped InSe crystals. At 77K, the absorption edge shifts towards short wavelengths. Peak P_3 can be explained by the presence of surface states.

Studies have shown that residual conductivity (RC) occurs in the entire photosensitivity area. The condition of the RC remains for approximately 12 hours. When heated, the sample RC decreases to a certain value. The recording of the spectral dependence of the photocurrent after reaching the level of the dark current completely coincides with the initial one. Thus, the above results convincingly demonstrate that the introduction of Er atoms into InSe leads to an increase in photosensitivity and the appearance of RC, which persists for 12 hours. This is of interest for creation of instruments with an optical memory.

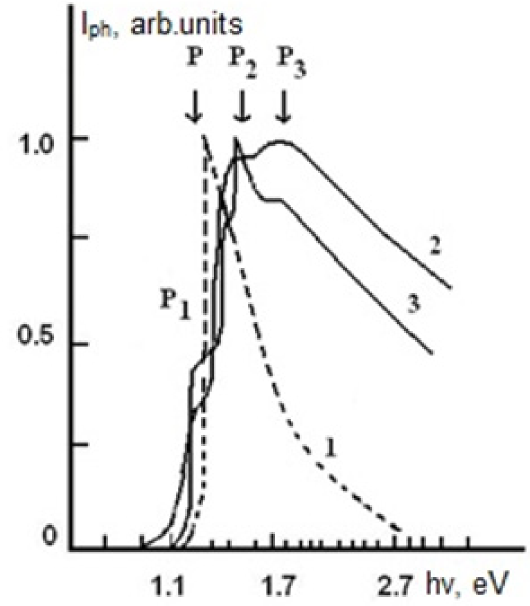

Fig. 3. The spectral dependences of the photoconductivity of solid solutions InSe-ErSe single crystals (1 - InSe at 300K; 2, 3 - 0.09 mol% ErSe) at 300 and 77K, respectively.

The spectral sensitivity of InSe crystals ranges from short wavelengths up to soft X-rays, which makes them promising for creating effective X-ray detectors. Therefore, it is of interest to look for opportunities to improve the X-ray dosimetric characteristics of this compound. For this purpose, InSe single crystals with Ag and Ge impurities were previously obtained [17]. The detectors made from them make it possible to measure radiation doses in the range $1.0\cdot10^{-5}$-$1.0\cdot10^{3}$ R/min with a higher X-ray sensitivity, which remains almost unchanged within 20-88°C. These detectors do not lose their X-ray-sensitive properties under the action of UV and γ-radiation, and their dosimetric characteristics are stable.

It should be noted that recently chalcogenide semiconductors doped with rare-earth elements have been intensively studied. Doping of such semiconductor materials with rare-earth elements gives them photoconductive and luminescent properties, increasing their radiation resistance [17-18]. A^3B^6 type layered semiconductor compounds are promising as detectors of hard electromagnetic radiation [19]. Therefore, we studied the effect of γ-irradiation on the current-voltage characteristics (IVC) of $In_{0.9993}Er_{0,0007}Se$ and $In_{0,9991}Er_{0,0009}Se$ single crystals. Contact phenomena play a significant role in the electrical properties of such compounds. Even though the main current carriers in InSe are holes, injected electrons contribute to the electrical and photoelectric properties of this semiconductor. For this reason, the study of injected currents and electron capture levels in it is of great interest.

Samples of $In_{0.9993}Er_{0.0007}Se$ and $In_{0.9991}Er_{0.0009}Se$ single crystals for electrical measurements were made in a sandwich variant, so that an external constant electric field was applied across the layers, i.e. along the C-axis of the single crystal. Silver paste was the contact material for the samples. The thickness of single-crystal samples reached 300 μm, and the contact area was $\sim2\cdot10^{-2}$ cm^2.

The samples were irradiated with a continuous radiation from a Co_{60} source with an energy of 1.25 MeV and a radiation flux density of $1.4 \cdot 10^{11}$ quantum/s·cm^2. Samples were irradiated at room temperature as described in [19].

Figure 4 shows the IVC of $In_{0.9993}Er_{0.0007}Se$ single crystals at room temperature before irradiation (curve 1) and after irradiation with a dose of D_γ=0.5 Gy (curve 2). The IVC for samples from $In_{0.9991}Er_{0.0009}Se$ single crystals has a similar form; therefore, we present curves for only one composition. At low voltage there is a linear dependence corresponding to Ohm's law, when a certain voltage is reached, the dependence I(U) takes the form $I \sim U^2$. The first section corresponds to Ohm's law, the second section is quadratic or "trap", the third (sharp growth) corresponds to a space charge limited current (SCLC). The saturation of the currents was not observed up to the current density $j \sim 10^{-3}$ A/cm^2. The obtained IVC has the form typical for SCLC in semiconductors with traps [20].

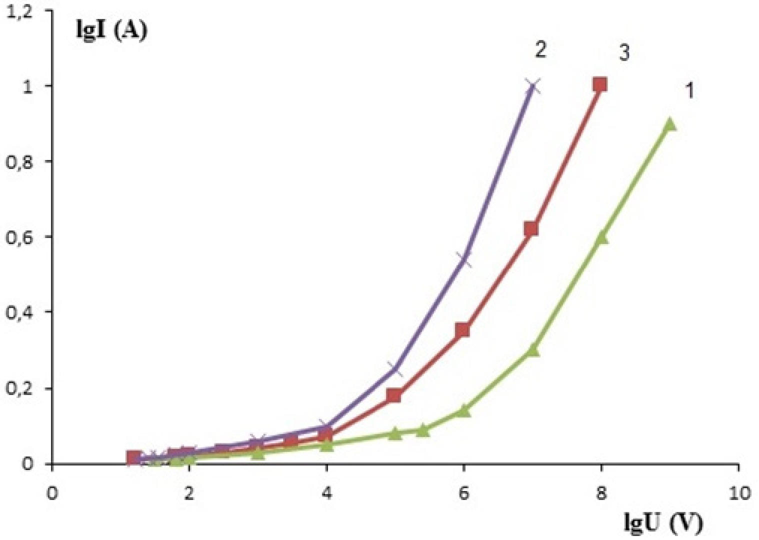

Fig. 4. Volt-ampere characteristic of the structure Ag-$In_{0.9993}Er_{0.0007}Se$-Ag: 1-not irradiated, 2-irradiated with a dose of D_γ = 0.5 Gy, 3- irradiated with a dose of D_γ = 1 Gy.

This is further confirmed by studies of the dependence of the current density on the sample thickness at various voltages (T=const). It was found that the current density depends on the sample thickness according to the power law $j = d^{-3}$. This fact indicates that in an erbium-doped indium selenide crystal, SCLC are occurring, and this allows us to obtain information about local states in the forbidden gap and explain the shape of the IVC. The SCLC model [21] applied to the data we obtained for $In_{0.9993}Er_{0.0007}Se$ single crystals made it possible to calculate the parameters given in Table 1, where D_γ is the radiation dose, $N_{t,\ CM}^{-3}$ is the concentration of traps, $P_{0,\ CM}^{-3}$ is concentration of equilibrium carriers, and θ is the degree of trap filling.

Table 1. Electrical parameters in $In_{0.9993}Er_{0.0007}Se$ single crystals.

D_γ, Gy	N_t, cm^{-3}	P_0, cm^{-3}	$\theta \cdot 10^{-1}$
0	$8.8 \cdot 10^{10}$	$6.12 \cdot 10^{9}$	2.7
0.5	$1.18 \cdot 10^{11}$	$5.31 \cdot 10^{9}$	2.6
1	$1.1 \cdot 10^{10}$	$5.5 \cdot 10^{8}$	2.68

When irradiated with a dose of 0.5 Gy (curve 2), the concentration of equilibrium carriers decreases, which is associated with a change of the Fermi quasi-level position. The decrease in the voltage of the transition from the linear section of the IVC to the quadratic under irradiation confirms our assumption that deep trap states begin to play the main role, which leads to an increase in the concentration of traps and a decrease in the degree of their filling.

An increase in the irradiation dose to 1 Gy leads to the disintegration of complexes formed as a result of irradiation at low doses, and an accumulation of point defects is observed, leading to a decrease in the hole concentration (curve 3) [22]. The appearance of such a type of disturbances in semiconductors was observed when irradiating them with neutrons [20], as well as fast electron beams [23].

Based on the analysis of the IVC of γ-irradiated layered $In_{0.9993}Er_{0.0007}Se$ and $In_{0.9991}Er_{0.0009}Se$ single crystals, it was shown that the current flow mechanism in them is due to a monopolar injection.

Conclusion:

When measuring the electrophysical properties of solid solutions $In_{1-x}Er_xSe$ single crystals, it was found that at high temperatures from ~500K, when the impurities are completely ionized, their own conductivity occurs. Thermo-emf of these crystals increases on the temperature interval from room temperature to 500 K, and decreases at T> 500 K, which is caused by a change in the concentration and effective mass of current carriers with a change in temperature. The introduction of Er atoms into InSe leads to an increase in its photosensitivity and the appearance of RC.

Under γ-irradiation of $In_{0.9993}Er_{0,0007}Se$ and $In_{0.9991}Er_{0,0009}Se$ single crystals with a dose of 0.5 Gy, in contrast to unirradiated crystals, a decrease in the concentration of equilibrium charges and an increase in the concentration of traps is observed, along with a decrease in their filling. Increasing the radiation dose to 1 Gy leads to a decrease in the hole concentration. Analysis of the IVC of irradiated $In_{0.9993}Er_{0,0007}Se$ and $In_{0.9991}Er_{0,0009}Se$ crystals showed that the current flow mechanism in them is due to the monopolar injection.

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