

# PHOTO-, ROENTGEN-SENSITIVITY AND ROENTGENOAMPERE CHARACTERISTICS OF $TlIn_{1-x}Sb_xSe_2$ SYSTEM SINGLE CRYSTALS

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The influence of composition of  $TlIn_{1-x}Sb_xSe_2$  solid solutions on photosensitivity and roentgendosimetric parameters was investigated.  $TlIn_{0.999}Sb_{0.001}Se_2$  single crystals had the highest value of roentgen-sensitivity ( $K_o$ ): for example, at dose  $E=0.75$  R/min and "effective hardness"  $U_a=25$  keV  $K_o$  was equal to 0.278 min/R.

The study of roentgen-ampere characteristics of  $TlIn_{1-x}Sb_xSe_2$  single crystals showed that dependence of roentgen-current ( $\Delta J_{E,0}$ ) on dose of x-ray ( $E$ ) is as follows:  $\Delta J_{E,0} \sim E^\alpha$ . It was shown, that at In→Sb substitution the coefficient  $\alpha$  increases. For example, in  $TlIn_{0.999}Sb_{0.001}Se_2$   $\alpha=0.96 \pm 0.46$ , but in  $TlIn_{0.9955}Sb_{0.0045}Se_2$   $\alpha=1.70 \pm 0.60$  at  $U_a=25 \pm 50$  keV.

Obtained results show, that crystals of  $TlInSe_2$ - $TlSbSe_2$  system can be used for the production of roentgendetectors.

Search of new semiconductive materials is one of the cardinal problems of modern solid state physics and crystallochemistry. Revealing of new materials along with the extension of scientific knowledge opens the new prospects; as a rule new substances especially with chain-layered structure show new properties and promote to the solution of new technical problems.

Among chain-layered semiconductors of  $A^3B^3C_2^6$  (A-Tl; B-In, Ga; C-S, Se, Te) the  $TlInSe_2$  group is the most sensitive to visible and roentgen radiation. Their photoelectric and roentgendosimetric characteristics are described in [1-8].

In [1] there have been studied influence of Ag, Cu and Sn on photoelectric properties of  $TlInSe_2$  single crystals. In [2,4,5] results of intercalation influence by Li ions on photo- and roentgen conductivity of  $TlInSe_2$  have been presented.

The aim of present paper is to treat influence of partial substitution of In ions in  $TlInSe_2$  by Sb ions on their photo- and roentgendosimetric parameters.

$TlSbSe_2$  wide-band crystals are differed by high photosensitivity and because of character of chemical bond due to pronounced lamination are rather interesting objects for study [9-13].

$TlInSe_2$  and  $TlSbSe_2$  compounds are synthesized from initial materials of Tl-000; In-000; Sb-000; Se-000 by direct component melting taken in stoichiometric relation in evacuated up to  $1.3 \cdot 10^{-3}$  Pa and sealed quartz ampules. For  $TlSbSe_2$  production we increase furnace temperature up to 878K and hold melt for 5-6 hours with continuous vibration and further slow cool it up to annealing temperature. As  $TlSbSe_2$  compound undergoes structural phase transition at 653K it is annealed at 693K and 573K for 200 hours.

$TlInSe_2$ - $TlSbSe_2$  cutting alloys are prepared from preliminary synthesized compounds  $TlInSe_2$  and  $TlSbSe_2$  by heating in evacuated ampules not above 1123K with the use of vibration mixing. Annealing is carried out at  $693 \pm 773$ K for 240 hours.

Obtained samples have been studied by differential-thermal (DTA) and roentgenphase (RPA) analyses. There have been used Pt/Rh-30/6- thermocouple at DTA, temperature determination accuracy is  $\pm 5$ K. RPA has been carried out on DRON-3 installation in  $Cu_{K\alpha}$  radiation. There have been grown  $TlIn_{1-x}Sb_xSe_2$  single crystals by Bridgemen-Stochbarger method at  $x=0.001$ ; 0.003 and 0.0045. Grown compositions have high degree of monocrystalline and splitting along the direction (001) into thin needles.

Monocrystalline samples are used for study of photoresistive properties.  $TlIn_{1-x}Sb_xSe_2$  crystals have p-type conductivity. Contacts are applied by In melting on splitting surface and provide ohmage volt-ampere characteristics (VAC) up to electric intensity  $\leq 200$ V/cm. Indium contacts are differed by stability and provide high measurement accuracy of photoelectric parameters of  $TlIn_{1-x}Sb_xSe_2$  crystals. Electric field is applied along the direction (001), and nonmodulated radiation flow is headed perpendicular to spall plane. Measurements are carried out at 300K, and voltage is taken within linear (ohmic) section of VAC. After measurement of spectral characteristics of photocurrents there have been carried out a compensation of light flows in quantum number with graduated germanium photodiode.

In Table 1 there have been presented values of resistance relation in darkness and light 200 lux for  $TlIn_{1-x}Sb_xSe_2$  single crystals ( $R_d/R_l$ ) at photon energy corresponding to photocurrent maximum ( $h\nu_{max}$ ), also average values of integral photosensitivity ( $S_{ph}$ ).

As it is seen from table 1 samples of mixed crystals have high sensitivity in intrinsic absorption band.

By increasing  $x$  from 0.001 up to 0.0045 the ration  $R_d/R_l$  increases from 1.8 up to 9.37. High values of integral photosensitivity ( $S_{ph}$ ) of studied crystals show prospects of their use as phototransducers of different purpose.

Table 1  
Average parameter values of photoresistors of  $TlIn_{1-x}Sb_xSe_2$ -based crystals.

$x$	$R_d/R_l$	$S_{ph}$ $\mu A \cdot lm^{-1}$	$h\nu_{max}$ $eV$
0	8.65	123.5	1.5
0.001	1.8	28.2	1.5
0.003	4.13	288.0	1.45
0.0045	9.37	110.5	1.4

It is of interest to reveal influence of partial substitution In→Sb on roentgendosimetric characteristics of crystals under study.

Roentgenconductivity and roentgendosimetric characteristics are taken for crystals of initial compound  $TlInSe_2$  as well as for crystals of solid solution on its base corresponding to the substitution In→Sb.

Electric intensity in samples is  $2.5 \pm 25$  V/cm. Source of roentgen radiation is the installation for roentgenstructural analysis of URS-55A-type with BSV-2 tube. Roentgen

radiation intensity is controlled by current variation in tube at each given value of accelerating potential in it during the measurement. Absolute values of roentgen radiation dose are measured by crystal dosimeter of DRGZ-2.

Roentgenconductivity coefficients characterizing roentgen-sensitivity of crystals under investigation are defined as relative change of conductivity under the effect of roentgen radiation on per-unit of dose, as:

$$K_{\sigma} = \frac{\Delta\sigma_{E,0}}{\sigma_0 \cdot E} = \frac{\sigma_E - \sigma_0}{\sigma_0 \cdot E} \left( \frac{\text{min}}{R} \right),$$

where  $\sigma_0$  - is a conductivity in the absence of roentgen radiation;  $\sigma_E$  is a conductivity under the effect of radiation with  $E$  (R/min) dose intensity.

Values of certain above-mentioned characteristic coefficients of roentgenconductivity of crystals as initial compound  $TlInSe_2$  as solid solutions on its base corresponding to substitution  $In \rightarrow Sb$  are given in table 2 for different values of accelerating voltage ( $V_a$ ) in tube and corresponding doses of roentgen radiation.

As it follows from the experimental data, the coefficients of roentgenconductivity  $K_{\sigma}$  in all investigated crystals decrease regularly with a dose increase as well with the rise of value of accelerating voltage  $V_a$  in roentgen tube. Drop of roentgenconductivity coefficient  $K_{\sigma}(E, V_a)$  is especially in the range of comparatively low values of accelerating voltage and roentgen radiation dose. Above  $V_a=30\div35$ keV and  $E=10\div15$  R/min the change of  $K_{\sigma}(E, V_a)$  at subsequent rise of " $V_a$ " and " $E$ " is slight. One of the possible reasons of the observed regularities can be as follows: in investigated crystals especially at comparatively low accelerating voltages the roentgenconductivity appears to be due predominantly to radiation absorption in oversurface layer. And with the rise of

radiation intensity there have been initiated to prevail a mechanism of surface-square recombination that leads to observed decrease of roentgenconductivity coefficient. As the accelerating potential increases the "effective hardness" of roentgen radiation rises by virtue of which the depth of its penetration into the crystal increases as a result of this the absorption-generation of free photo(roentgeno) carriers in volume predominantly occurs and proportion of incident radiation on crystal passing through it increases. Namely by this reason probably as values of accelerating potential increase the observed decrease of roentgenconductivity coefficient and its dependence on radiation dose takes place.

We also studied roentgenampere characteristics of  $TlInSe_2$ ,  $TlIn_{0.9955}Sb_{0.0045}Se_2$ ,  $TlIn_{0.999}Sb_{0.001}Se_2$  crystals at different "effective hardnesses" of radiation. From these data analysis it follows that a dependence of stationary roentgencurrent  $\Delta J_{E,0}$  on roentgen radiation ( $E$ ) has exponential character, i.e.

$$\Delta J_{E,0} = J_E - J_0 \sim E^{\alpha}$$

Exponent of a given dependence is defined graphically from roentgenampere characteristics as tangent of an angle of dependence slope  $lg \Delta J_{E,0}$  on  $lg E$ .

Along with above-mentioned general regularities from the data in the Table 2 the regular increase of exponent function value  $\Delta J_{E,0} \sim E^{\alpha}$  " $\alpha$ " under other equal conditions as the partially substitution of three-valent indium cations for corresponding Sb cations is traced. As it substitutes there have been shown tendency to decrease of roentgenconductivity coefficient ( $K_{\sigma}$ ), especially in the range of low intensities of soft (low  $V_a$ ) roentgen radiation. Revealed empirical regularities can be very useful in the development of crystalline roentgendetectors on the base of crystals of a given system.

Table 2.  
Roentgendosimetric characteristics of  $TlIn_{1-x}Sb_xSe_2$  single crystals

Crystal composition	$V_a$ keV	Dose intensity $E$ , R/min	$K_{\sigma}$ , min/R	$\alpha$
$TlInSe_2$	25	0.75÷2.73	0.32±0.2	0.68
	30	1.75÷10.22	0.143±0.063	0.56
	35	3.75÷19.74	0.090±0.044	0.54
	40	7.0÷38.8	0.064±0.029	0.52
	45	10÷61.2	0.056±0.021	0.50
	50	13.5÷78.0	0.048±0.020	0.48
$TlIn_{0.999}Sb_{0.001}Se_2$	25	0.75÷2.73	0.278±0.221	0.96
	30	1.75÷10.22	0.179±0.082	0.58
	35	3.75÷19.74	0.1111±0.517	0.55
	40	7.0÷38.8	0.0744±0.0322	0.52
	45	10÷61.2	0.0604±0.0238	0.48
	50	13.5÷78.0	0.0525±0.0211	0.46
$TlIn_{0.9955}Sb_{0.0045}Se_2$	25	0.75÷2.73	0.129±0.142	1.70
	30	1.75÷10.22	0.111±0.05	0.71
	35	3.75÷19.74	0.073±0.0425	0.67
	40	7.0÷38.8	0.051±0.27	0.65
	45	10÷61.2	0.0484±0.022	0.62
	50	13.5÷78.0	0.038±0.020	0.60

- [1] E.M. Kerimova, S.N. Mustafaeva, A.B. Magerramov. Nonorganic materials. 1997, v. 33, №11, pp. 1325-1326.
- [2] S.N. Mustafaeva. Nonorganic materials. 1994, v. 30, №8, pp. 1033-1036.
- [3] A.Z. Abasova, E.M. Kerimova, G.A. Muradova, A.M. Pashaev. Ionizing irradiation of photoresistors and diode structures on the base of  $TlGaSe_2$  and  $TlInSe_2$  single crystals. Institute Phys. Conf. Ser. №152 : Section H : single crystals and thin film devices. 1998. IOP publishing LTD. p.983-988.
- [4] S.N. Mustafaeva, M.M. Asadov, V.A. Ramazanade. Roentgen-ampere dosimetric characteristics of lithium-intercalated  $TlGa(In)Se_2$  single crystals. Materials of the Conf. on Ternary and Multinary Compounds. Salford, United Kingdom. 8-12<sup>th</sup> Sept. 1997, pp.1.71.
- [5] S.N. Mustafaeva, M.M. Asadov, V.A. Ramazanade. Nonorganic materials. 1995, v. 32, 31, pp. 318-320.
- [6] O.Z. Alekperov, M.A. Aljanov, E.M. Kerimova. Turkish Journal of Physics. 1998, v. 22, p.1.6.
- [7] E.M. Kerimova, S.N. Mustafaeva, R.N. Kerimov, G.A. Gadzhieva. Nonorganic materials. 1999, v. 35, №10, pp. 1-2.
- [8] E.M. Kerimova, S.N. Mustafaeva, E.F. Bagirzade, D.A. Huseynova. Roentgendetectors. Mater. Of PPMSS 99 Chernivtsi, Ukraine. Sept., 7-11, 1999, p. 279.
- [9] D.V. Gitsu, I.N. Grincheshen, N.S. Popovich. Phys. Stat. Sol. (a) 1982, v.72, №1, p. K113-K116.
- [10] D.V. Gitsu, I.N. Grincheshen, N.S. Popovich. Phys. Stat. Sol. (a) 1983, v.76, №1, p. K5-K7.
- [11] I.N. Grincheshen, N.S. Popovich, A.A. Shtanov. Phys. Stat. Sol. (a) 1984, v.85, №1, p. K85-K88.
- [12] I.N. Grincheshen, N.S. Popovich. Fizika tekhnika polupr. 1985, v.19, №2, pp.230-233.
- [13] G.I. Stepanov, I.V. Votgros, B.S. Chinik and others. Fizika tverdogo tela. 1975, v.17, №1, pp. 166-169.

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### **TlInSe<sub>2</sub>-TlSbSe<sub>2</sub> SİSTEMİ MONOKRİSTALLARININ FOTO- VƏ RENTGEN HƏSSASLIĞI VƏ RENTGENAMPER XARAKTERİSTİKALARI**

$TlIn_{1-x}Sb_xSe_2$  bərk məhlulunun tərkibinin onların foto- və rentgendozimetrik parametrlərinə təsiri öyrənilmişdir. Bütün öyrənilən tərkiblərdən  $TlIn_{0.999}Sb_{0.001}Se_2$  monokristallarının rentgen keçirmə əmsalı ( $K_\sigma$ ) qismən böyük qiymətə malikdir, məsələn: "effektiv sərt" şüalanmanın  $U_\gamma=25keV$  və dozanın gücü  $E=0.278 R/dəq$  qiymətlərində  $K_\sigma=0.278dəq/R$ .

$TlIn_{1-x}Sb_xSe_2$  kristalının rentgenamper xarakteristikası göstərir ki, stasionar rentgen cərəyanı ( $\Delta J_{E,0}$ ) rentgenşüalanmanın dozasından asılılığı üstlü xarakter daşıyır:  $\Delta J_{E,0} \sim E^\alpha$ .  $In \rightarrow Sb$  qismən əvəzlənməsi və  $x$ -in artırılması nəticəsində  $\alpha$  qiyməti artır. Belə ki,  $U_\gamma=25 \div 50keV$  qiymətlərində  $TlIn_{0.999}Sb_{0.001}Se_2$  üçün əgər  $\alpha=0.96 \div 0.46$ ,  $TlIn_{0.9955}Sb_{0.0045}Se_2$  üçün isə  $\alpha=1.70 \div 0.60$  olur. Alınan nəticələr göstərir ki,  $TlInSe_2$ - $TlSbSe_2$  sistemin rentgendefektorların hazırlanması üçün istifadə oluna bilər.

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### **ФОТО-И РЕНТГЕНОЧУВСТВИТЕЛЬНОСТЬ И РЕНТГЕНОАМПЕРНЫЕ ХАРАКТЕРИСТИКИ МОНОКРИСТАЛЛОВ СИСТЕМЫ TlInSe<sub>2</sub>-TlSbSe<sub>2</sub>**

Изучено влияние состава твердых растворов  $TlIn_{1-x}Sb_xSe_2$  на фоточувствительность и рентгенодозиметрические параметры. Из изученных составов наибольшее значение коэффициента рентгенопроводимости  $K_\sigma$  имели монокристаллы  $TlIn_{0.999}Sb_{0.001}Se_2$ , так например  $K_\sigma=0.278$  мин/Р при "эффективной жесткости" излучения  $U_\gamma=25$  кэВ и мощности дозы  $E=0.278$  Р/мин. Изучение рентгеноамперных характеристик кристаллов  $TlIn_{1-x}Sb_xSe_2$  показало, что зависимость стационарного рентгено-тока ( $\Delta J_{E,0}$ ) от дозы рентгеновского излучения ( $E$ ) носит степенной характер:  $\Delta J_{E,0} \sim E^\alpha$ .

По мере частичного замещения  $In \rightarrow Sb$ , т.е. с увеличением  $x$ , прослеживается увеличение величины показателя  $\alpha$ . Так, если для  $TlIn_{0.999}Sb_{0.001}Se_2$   $\alpha=0.96 \div 0.46$ , то для  $TlIn_{0.9955}Sb_{0.0045}Se_2$   $\alpha=1.70 \div 0.60$  при  $U_\gamma=25 \div 50$ кэВ. Полученные результаты показали, что кристаллы системы  $TlInSe_2$ - $TlSbSe_2$  могут быть использованы для создания рентгенодетекторов.