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# Ag CHALCOGALLATES FOR UNCOOLED AND VIRTUALLY INERTIALESS X-RAY-DETECTING DEVICES

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***Abstract:*** A technique is proposed for producing single crystals of silver thiogallates with high X-ray conductivity and sensitivity coefficients at room temperature. Single crystals of $AgGaSe_2$ grown by chemical transport reactions method in comparison with $AgGaS_2$ and $AgGaS_{2x}Se_{2-2x}$ had the highest X-ray sensitivity. At an effective radiation hardness of 30 keV and a dose rate of $E$ =10 R/min the coefficient of roentgen sensitivity $K$ = 5.4 × 10$^{-13}$ (A min)/(V R) for $AgGaS_2$ and $K$ = 15 × 10$^{-13}$ (A min)/(V R) for $AgGaSe_2$. The coefficient of X-ray conductivity $AgGaSe_2$ varies within 1.2–8.5 min/R at effective radiation hardness of $V_a$ = 25–50 keV and a dose rate of $E$ = 0.75–31.3 R/min. The obtained $AgGaS_{2x}Se_{2-2x}$ materials can be used in constructing various uncooled and virtually inertialess X-ray-detecting instruments and devices.

***Key words:*** $AgGaS_{2x}Se_{2-2x}$, single crystals, effective radiation hardness, dose rate, roentgen sensitivity.

Silver chalcogallats are promising materials for the construction of X-ray detectors, laser radiation converters of the intermediate IR range, and parametric quantum generators, which may find application in nonlinear optics, spectroscopy, and the communications industry [1, 2].

$AgGaS_2$ single crystals can be produced by the Bridgman–Stockbarger (BS) technique [3, 4]. This method was used to synthesize single crystals with an absorption coefficient of 0.1 cm$^{-1}$ in the wavelength range of 0.9–8.5 μm. The optical transparency of $AgGaS_2$ was enhanced either by rapid quenching in air from a temperature slightly below the melting point or by annealing in the presence of $Ag_2S$. However, the first method caused large thermal stresses that induced the formation and spreading of cracks, and annealing did not suppress absorption in the entire spectral transparency range. The obtained $AgGaS_2$ single crystals also possessed insufficient X-ray sensitivity. A method for producing optically homogeneous $AgGaS_2$ single crystals by directed crystallization from a stoichiometric composition melt and a melt with excess $Ag_2S$ under the pressure of gas inert to the sulfide melt was proposed in [4]. This method makes it possible to reduce the cooling rate of grown crystals and obtain single crystals of high optical quality with an absorption coefficient of 0.1 cm$^{-1}$. However, high pressures in the furnace, on the one hand, require cumbersome experimental equipment and, on the other hand, reduce the heater temperature accuracy, impairing the optical quality of single crystals.

The aim of this study was to obtain optically homogeneous based $AgGaS_2$ single crystals with high X-ray sensitivity. Single crystals were grown by the BS technique and also using the method of chemical transport reactions (CTR). $AgGaS_2$ was synthesized from its elementary components: Ag (high purity grade), Ga (5N grade), S (high purity grade, TU 609254677), and Se (TU 6-09-2521-77). The initial synthesis components were taken in a stoichiometric ratio. The synthesis was performed in a horizontal furnace with the temperature within it increasing at a rate of 50 K/h to 1275 K. The reaction between the components proceeded for 4 h. The synthesized material was transferred to an ampule into a dual chamber vertical furnace for growth. $AgGaS_2$ single crystals were grown using the BS technique [1]. The $AgGaS_2$ melting temperature was $T_m$ = 1271 ± 3 K. The thermal conditions in the furnace were maintained using VRT-3 high-precision temperature controllers. The VRT-2 system is designed for precise temperature control and is used in electrical, electronic, heat energy and other industries. The VRT-2 system consists of two instruments: a measuring unit and a regulating device. In the block, the thermocouple signal is compensated by the signal from the built-in sensor, and the difference in these signals is amplified by the amplifier. The amplified signal is fed to the input of the regulating device. The device converts the input signal into a unified DC signal of 0–5 mA. The range of controlled temperatures is 0–1600 °C. Accuracy of adjustment is ± 0.5 °C. The temperature gradient at the crystallization front in the furnace was 3 K/mm. The ampule with molten material was lowered vertically and cooled at a rate of 0.5 mm/h. Following crystallization, the furnace was turned off and cooled to room temperature together with the sample.

The growth of $AgGaS_{2x}Se_{2-2x}$ ($x$ = 0; 0.5 и 1.0) single crystals was performed by the CTR method. $AgGaX_2$ (X – S, Se) are taken together with the transporting agent iodine in the ampoule for the crystal growth [1]. They react to form the gaseous binary iodides and selenium at high temperature. All these gaseous species diffuse to the colder growth zone due to the drop in temperature. At the growth zone they react back to form the ternary chalcogenide with the release of iodine. The iodine liberated diffuses back to the source end to form the metal iodides once again. The chemical reaction for $AgGaSe_2$ may be given as

$$AgGaSe_2 \text{ (solid)} + 2I_2 \text{ (gas)} \leftrightarrow AgI \text{ (gas)} + GaI_3 \text{ (gas)} + Se_2 \text{ (gas)} \leftrightarrow AgGaSe_2 \text{ (solid)} + 2I_2 \text{ (gas)}$$

The main advantage of growing single crystals using the CTR method is the ability to conduct the process at lower temperatures and pressures.

The results of X-ray studies at room temperature showed that single crystals based on the $AgGaS_2$ compound crystallize in the chalcopyrite structure with the lattice parameters $a$ = 5.7571–5.7572 Å and $c$ = 10.3110–10.3036 Å for $AgGaS_2$ and $a$ = 5.992; $c$ = 10.883 Å for $AgGaSe_2$.

The contacts for X-ray dosimetry studies were created in the fabrication of $AgGaS_{2x}Se_{2-2x}$ samples by alloying indium onto the lateral sides of single crystals. X-ray radiation was directed at the intercontact region of the prepared samples during measurements. X-ray apparatus for structural analysis (URS-type setup) with a BSV-2(Cu) tube served as the source of X-ray radiation used to study the X-ray dosimetric characteristics of the obtained $AgGaS_{2x}Se_{2-2x}$ single crystals. The X-ray radiation intensity was adjusted by varying the current in the tube at each given value of the accelerating potential applied to it. The absolute doses of X-ray radiation were measured by a DRGZ-02 X-ray dosimeter. The variation of current strength in the studied samples under the action of X-ray radiation was measured in the regime of small load resistance $R_l << R_c$ using a U5-9 electrometric amplifier. The amplifier is based on the principle of measuring weak currents in terms of the voltage drop across a known load resistance $R_l$. This resistance is the input impedance of the amplifier. The amplifier has three operating sub-ranges input impedances: $10^{12}$, $10^{10}$ and 5.1× $10^6$ Ohm. Measuring the values of $U_l$ and knowing $R_l$, we can determine the value of the current through the load resistance $R_l$, and also through the sample $R_{cr}$: $I_{cr} = I_l = U_l / R_l$. The resistance of the sample at a given electric voltage (($U - U_l$) was determined from the formula: $R_{cr} = (U - U_l)/ I_{cr}$.

The error in measuring the current averaged 5-6%. The results of analyzing the X-ray dosimetry properties of $AgGaS_{2x}Se_{2-2x}$ single crystals are detailed below. All measurements were conducted at $T$ = 300 K. The studied $AgGaS_{2x}Se_{2-2x}$ single crystals exhibited high sensitivity to X-ray radiation. The X-ray conductivity coefficient (relative change in electric conductivity of crystal due to X-ray radiation at a given dose) of a sample was determined by the following equation:

$$K_\sigma = \frac{\sigma_E - \sigma_0}{\sigma_0 \cdot E} \tag{1}$$

where $\sigma_E$ is the sample electric conductivity ($Ohm^{-1}cm^{-1}$) under the action of X-ray irradiation with a dose rate of $E$ (R/min) and $\sigma_0$ is the dark electric conductivity of a single crystal. The X-ray sensitivity (A min)/(V R) of a single crystal was calculated by the following equation:

$$K = \frac{\Delta I_{E,0}}{U \cdot E} \tag{2}$$

where $\Delta I_{E,0} = I_E - I_0$; $I_E$ is the current strength in the sample at an X-ray dose rate of $E$ (R/min), $I_0$ is the dark current, and $U$ is the external voltage applied to the sample. The X-ray sensitivity coefficients of $AgGaS_2$ single crystals were determined in accordance with the equation (2) at various accelerating potentials ($V_a$) applied to the tube and the corresponding X-ray doses.

The dependences of the X-ray sensitivity coefficient on the X-ray dose for an $AgGaS_2$ single crystal (BC) at $T$ = 300 K and $U$ = 60 V show that the X-ray sensitivity of $AgGaS_2$ varied from $1.3 \times 10^{-11}$ to $1.4 \times 10^{-10}$ (A min)/(V R). It was found that the X-ray sensitivity coefficient of $AgGaS_2$ increased with increasing radiation dose. The value of K increased fairly rapidly at $V_a$ = 25 keV. At higher values of effective hardness of X-ray radiation, the $K(E)$ dependence flattened; the X-ray sensitivity depended only weakly on $E$ at $V_a$ = 50 keV. Similar patterns were observed in the case of the dose dependences of X-ray conductivity coefficient $K_\sigma$ of $AgGaS_2$–based single crystals (Table).

***Table***

*Coefficients of roentgenconductivity of $AgGaS_{2x}Se_{2-2x}$ (x = 0; 0.5 u 1.0) single crystals at $T$ = 300K*

| $E$, R/min | $K_\sigma$, min/R | | | $V_a$, keV | $E$, R/min | $K_\sigma$, min/R | | | $V_a$, keV |
|---|---|---|---|---|---|---|---|---|---|
| | $x$ = 1 | $x$ = 0.5 | $x$ = 0 | | | $x$ = 1 | $x$ = 0.5 | $x$ = 0 | |
| 1.68 | 2.68 | 6.55 | 6.94 | 25 | 8.89 | 0.62 | 1.46 | 1.76 | 40 |
| 2.03 | 3.20 | 6.90 | 8.54 | | 12.60 | 0.56 | 1.19 | 2.04 | |
| 2.73 | 3.11 | 6.96 | 8.30 | | 16.38 | 0.52 | 1.16 | 1.97 | |
| 3.64 | 1.37 | 3.02 | 3.39 | 30 | 10.00 | 0.50 | 1.20 | 1.23 | 45 |
| 6.44 | 1.24 | 2.64 | 3.99 | | 25.34 | 0.36 | 0.87 | 1.28 | |
| 8.33 | 1.14 | 2.52 | 3.72 | | 31.29 | 0.34 | 0.80 | 1.25 | |
| 8.82 | 0.79 | 1.70 | 2.53 | 35 | 13.05 | 0.46 | 1.07 | 1.16 | 50 |
| 10.64 | 0.75 | 1.69 | 2.73 | | 17.01 | 0.41 | 0.94 | 1.31 | |
| 12.46 | 0.72 | 1.68 | 2.59 | | 24.64 | 0.34 | 0.81 | 1.31 | |

The X-ray ampere characteristics of $AgGaS_2$–based single crystals were also studied. It follows from the results of these studies that the dependence of the steady X-ray current on the X-ray radiation dose is a power law one:

$$I_r = \Delta I_{E,0} = I_E - I_0 \sim E^{\alpha} \qquad (3)$$

The values of α for the studied single crystals varied depending on the effective hardness of X-ray radiation from 2–2.5 at $V_a$ = 25 keV to 1.2–1.3 at $V_a$ = 30–50 keV. The X-ray ampere characteristics of $AgGaS_2$ single crystals tended toward linearity (α→ 1) at higher $V_a$ values. This is important from a practical standpoint. From the dosimetric data for single crystals obtained by chemical transport reactions it was found that single crystals of $AgGaSe_2$ had the highest X-ray sensitivity.

One of the probable mechanisms that shape the patterns observed in the $K$ ($E$, $V_a$) dependences is as follows. At relatively small accelerating potentials, the X-ray conductivity of the studied single crystals is induced primarily by the radiation absorption by the near surface layer. The effective hardness of X-ray radiation increases at higher accelerating potentials, and the depth of penetration of this radiation into the crystal increases accordingly. I.e., the absorption and production of X-ray carriers occurs largely in the bulk, and the fraction of radiation that passes through the crystal increases. As a result, the X-ray sensitivity coefficient is reduced and becomes less dependent on the radiation dose at higher accelerating potentials.

We also investigated the X-ray current in the $AgGaS_2$-based samples and found that the dark current in the samples, in contrast to $CdGa_2S_4$ and $CdIn_2S_4$ single crystals [5-7], reached a steady state value almost immediately after the X-ray radiation was turned off. This offers the opportunity to use the obtained $AgGaS_2$ single crystals as active elements of virtually inertia less X-ray detectors that do not require cooling and have a high X-ray sensitivity coefficient.

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## ХАЛЬКОГАЛЛАТЫ СЕРЕБРА ДЛЯ НЕОХЛАЖДАЕМЫХ И БЕЗИНЕРЦИОННЫХ ДЕТЕКТОРОВ РЕНТГЕНОВСКОГО ИЗЛУЧЕНИЯ

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***Резюме:*** Предложена технология получения монокристаллов халькогаллатов серебра с высокими коэффициентами рентгенопроводимости и рентгеночувствительности при комнатной температуре. Монокристаллы $AgGaSe_2$, выращенные методом химических транспортных реакций, имели наибольшую рентгеночувствительность по сравнению с $AgGaS_2$ и $AgGaS_{2x}Se_{2-2x}$. При эффективной жесткости X-излучения $V_a$ = 30 кэВ и мощности дозы E = 10 Р/мин коэффициент рентгеночувствительности составлял $K = 5.4 \times 10^{-13}$ (А мин)/(В Р) для $AgGaS_2$ и $K = 15 \times 10^{-13}$ (А мин)/(В Р) для $AgGaSe_2$. Коэффициент рентгенопроводимости $AgGaSe_2$ составлял 1.2 – 8.5 мин /Р при $V_a$ = 25 – 50 кэВ и $E$ = 0.75 – 31.3 Р/мин. Полученные материалы $AgGaS_{2x}Se_{2-2x}$ могут быть использованы для создания неохлаждаемых и практически безинерционных детекторов X-излучения.

***Ключевые слова:*** $AgGaS_{2x}Se_{2-2x}$, монокристаллы, эффективная жесткость излучения, мощность дозы, рентгеночувствительность.

## ĞÜMÜŞ XALKOGALATLARI ƏSASINDA SOYUDULMAYAN VƏ İNERSİYASIZ RENTGEN DETEKTORLARI

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***Xülasə:*** Otaq temperaturunda yüksək rentgen keçiriciliyi və həssaslıq əmsalları ($K$) olan gümüş xalkogallatların monokristalları kimyəvi nəqletmə reaksiyaları (KNR) üsulu ilə alınmışdır. $AgGaS_2$ və $AgGaS_{2x}Se_{2-2x}$ ilə müqayisədə KNR metodu ilə yetişdirilən $AgGaSe_2$-in monokristalları ən yüksək rentgen həssaslığa malikdir. Müqayisə etdikdə effektiv radiasiya sərtliyi $V_a$ = 30 keV və doza dərəcəsi $E$ = 10 R/dəq $AgGaS_2$ üçün $K = 5.4 \times 10^{-13}$ (A dəq)/(V R) və $AgGaSe_2$ üçün isə $K = 15 \times 10^{-13}$ (A dəq)/(V R) olur. $V_a$ = 25-50 keV və $E$ = 0.75-31.3 R/dəq olduqda $AgGaSe_2$-nin rentgen keçiriciliyi əmsalı 1.2-8.5 dəq/R intervalda dəyişir. Alınan $AgGaS_{2x}Se_{2-2x}$ materiallar soyudulmayan və inersiyasız işləyən rentgen detektorların hazırlanması üçün istifadə edilə bilər.

***Açar sözlər:*** $AgGaS_{2x}Se_{2-2x}$, monokristallar, radiasiya sərtliyi, doza dərəcəsi, rentgen həssaslığı.