RESPONSE OF SILVER CHALCOGALLATES TO X-RAYS

S.M. ASADOV [1*], S.N. MUSTAFAEVA [2], V.F. LUKICHEV [3]

[1]Nagiev Institute of Catalysis and Inorganic Chemistry, ANAS, Baku, Azerbaijan.
salim7777@gmail.com
[2]Institute of Physics, ANAS, Baku, Azerbaijan. solmust@gmail.com
[3]Institute of Physics and Technology of RAS, Moscow, Russia icic.lab6@yandex.ru

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 an effective radiation hardness of V_a = 25–50 keV and a dose rate of E = 0.75–31.3 R / min.

Keywords*:* X-ray, $AgGaS_{2x}Se_{2-2x}$, single crystals, effective radiation hardness, chemical transport reactions
PACs: 61.05.–a, 61.43

$AgGaS_2$ single crystals can be produced by the Bridgman-Stockbarger (BS) technique [1-3]. 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.

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. 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 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. 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 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 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:

$$K_\sigma = \frac{\sigma_E - \sigma_0}{\sigma_0 \cdot E} \quad (1)$$

where σ_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 σ_0 is the dark electric conductivity of a single crystal. The X-ray sensitivity (A min)/(V R) of a single crystal was calculated as

$$K = \frac{\Delta I_{E,0}}{U \cdot E} \quad (2)$$

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.

Fig. 1 shows the dependences of the X-ray sensitivity coefficient on the X-ray dose for an $AgGaS_2$ single crystal at T = 300 K and U = 60 V. It can be seen that the X-ray sensitivity of $AgGaS_2$ varied from 1.3 × 10^{-11} to 1.4 × 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

131 H.Javid ave, AZ-1143, Baku
ANAS, G.M.Abdullayev Insttute of Physics
E-mail: jophphysics@gmail.com

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 dependence of X-ray conductivity coefficient K_σ of $AgGaS_2$ single crystals.

Single crystals of $AgGaSe_2$ grown by CTR 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 $K = 5.4 \times 10^{-13}$ (A min)/(V R) for $AgGaS_2$ and $K = 15 \times 10^{-13}$ (A min)/(V R) for $AgGaSe_2$ (Figs. 2 and 3). The coefficient of X-ray conductivity $AgGaSe_2$ varies within 1.2–8.5 min/R an effective radiation hardness of V_a = 25–50 keV and a dose rate of E = 0.75–31.3 R / min. It was found that the X-ray sensitivity coefficient of $AgGaS_{2x}Se_{2-2x}$ 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 dependence of K_σ of $AgGaS_{2x}Se_{2-2x}$ single crystals.

The X-ray ampere characteristics of $AgGaS_{2x}Se_{2-2x}$ 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:

$$I_r = \Delta I_{E,0} = I_E - I_0 \sim E^\alpha .$$

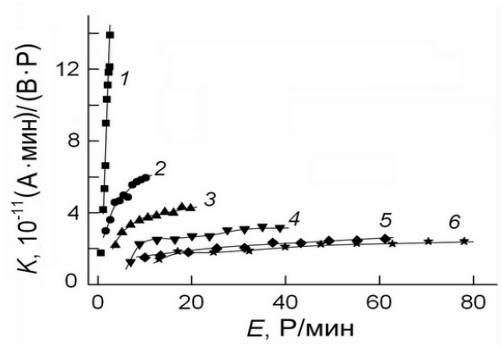

Fig. 1. Dependences of X-ray sensitivity coefficient on irradiation dose rate for $AgGaS_2$ (BS method) single crystal (T = 300 K and U = 60 V) at various accelerating voltages V_a (keV) applied to tube: 25 (1), 30 (2), 35 (3), 40 (4), 45 (5), and 50 (6).

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 studied single crystals tended toward linearity (α→ 1) at higher V_a values. This is important from a practical standpoint. We also investigated the X-ray current in the $AgGaS_{2x}Se_{2-2x}$ samples and found that the dark current in the samples, in contrast to $CdIn_2S_4$ and $CdGa_2S_4$ single crystals [2, 3], reached a steady state value almost immediately after the X-ray radiation was turned off.

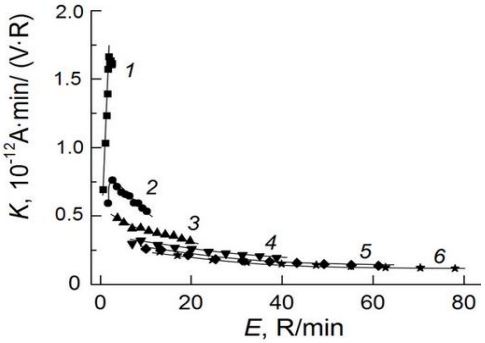

Fig. 2. Dependences of X-ray sensitivity coefficient on irradiation dose rate for $AgGaS_2$ (CTR method) single crystal (T = 300 K and U = 60 V) at various accelerating voltages V_a (keV) applied to tube: 25 (1), 30 (2), 35 (3), 40 (4), 45 (5), and 50 (6).

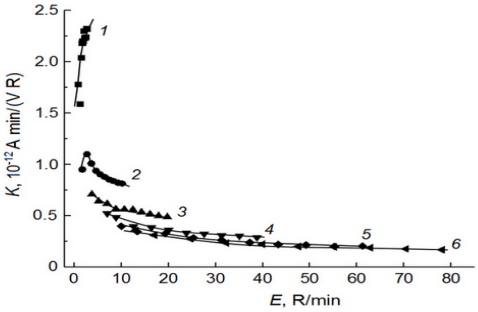

Fig. 3. Dependences of X-ray sensitivity coefficient on irradiation dose rate for AgGaSSe (CTR method) single crystal (T = 300 K and U = 60 V) at various accelerating voltages V_a (keV) applied to tube: 25 (1), 30 (2), 35 (3), 40 (4), 45 (5), and 50 (6).

Thus, the obtained single crystals can be recommended as active materials for the creation on their basis of uncooled and practically non-inertial X-ray recording devices.

ACKNOWLEDGMENT: Research has been supported by the SDFAR (grant № EIF-BGM-3-BRFTF-2+/2017-15/05/1), (grant № EİF-BGM-4-RFTF-1/2017) and grant № RFFI AzRus 1. «Аз_а». 2018.

[1] *S.N. Mustafaeva, M.M. Asadov, D.T. Guseinov,* X-Ray Dosimetric Properties of Vapor-Grown $CdGa_2S_4$ Single Crystals // Inorganic Materials. 2010. V. 46. № 6. P. 587-589

[2] *S.N. Mustafaeva, M.M. Asadov, D.T. Guseinov* X-Ray Electric Properties of $CdIn_2S_4$ Monocrystal // Inorganic Materials: Applied Research. 2010. V. 1. № 4. P. 293-296

[3] *T. Uematsu, T. Doi, T. Torimoto, S.Kuwabata* Preparation of Luminescent $AgInS_2$-$AgGaS_2$ Solid Solution Nanoparticles and Their Optical Properties // J. Phys. Chem. Lett. 2010. V.1. № 22. P. 3283