Research Article

Enhancing Roentgen Sensitivity of Gold-Doped CdIn$_2$S$_4$ Thiospinel for X-Ray Detection Applications

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The single crystals CdIn$_2$S$_4$(Au) were grown from preliminarily synthesized polycrystals by the method of chemical transport reactions in a closed volume with iodine used as a carrier. The influence of doping CdIn$_2$S$_4$ single crystals by gold (3 mol %) on their X-ray dosimetric parameters is studied. It is found that the X-ray sensitivity coefficients of CdIn$_2$S$_4$(Au) crystals increase 6–8 times compared with undoped CdIn$_2$S$_4$ at effective radiation hardness $V_a = 25–50$ keV and dose rate $E = 0.75–78.05$ R/min. Moreover, the persistence of the crystal characteristics completely disappears and the supple voltage of a CdIn$_2$S$_4$(Au) roentgen detector decreases threefold. The dependence of the steady X-ray-induced current in CdIn$_2$S$_4$(Au) on the X-ray dose is described by linear law. The studied crystals have a rather high room-temperature X-ray sensitivity ($K = 2 \cdot 10^{-9}–1.5 \cdot 10^{-8}$ (A-min)/(R·V)) and are attractive as materials for X-ray detectors.

1. Introduction

Single crystals of the CdIn$_2$S$_4$ compound belong to the class of wide-band-gap semiconductors [1] with a high specific resistance on the level of $\rho \sim 10^7$ Ohm-cm. The band gap of CdIn$_2$S$_4$ thiospinel is indirect, and values between 2.1 and 2.4 eV (between 2.5 and 2.7 eV for direct gap) have been reported by different authors [2]. According to [3, 4], the band gap of CdIn$_2$S$_4$ at room temperature is 2.62 eV. CdIn$_2$S$_4$ is a highly photosensitive semiconductor in the visible range of spectrum and may be used as active material for creation of solar cells and various optoelectronic devices [5–9]. Of interest is also the sensitivity of this material to X-rays. With time, more and more X-ray sensitive materials attract the attention of designers of X-ray detectors. The rather large values of the effective atomic number and the energy gap make CdIn$_2$S$_4$ a suitable material for the fabrication of X-ray detectors, which do not require being cooled. In our previous work [10], we reported the X-ray dosimetric properties of CdIn$_2$S$_4$ single crystals. It was shown that the X-ray sensitivity coefficient of CdIn$_2$S$_4$ is sufficiently high and ranged from $2.4 \cdot 10^{-10}$ to $2.4 \cdot 10^{-9}$ (A-min)/(R·V) at effective radiation hardness $V_a = 25–50$ keV and dose rate $E = 0.75–78.05$ R/min. But experimental data demonstrate that the photocurrent-dose curves of CdIn$_2$S$_4$ single crystals have some time lag: after X-rays are turned off, it takes several minutes for the current through CdIn$_2$S$_4$ to reach its dark level. Doping of CdIn$_2$S$_4$ single crystals with metals makes it possible to vary their roentgen dosimetric properties. Earlier, we reported the X-ray dosimetric properties of CdIn$_2$S$_4$ single crystals doped with Cu [11] and Fe [12]. For example, it was shown that the doping of CdIn$_2$S$_4$ single crystals with copper and iron substantially increases their coefficients of X-ray conductivity ($K_r$) and completely removes the inertia of X-ray-ampere characteristics.

It must be noted that in such kind of doped sulfide crystals a cationic disordering plays a principal role [13]. This in turn has a significant effect on the physical properties of these objects.

The aim of this work was to study the effect of doping CdIn$_2$S$_4$ single crystals with gold on their X-ray dosimetric characteristics. Therefore, the fabrication of CdIn$_2$S$_4$(Au)
crystals and the experimental studies of their X-ray conductivity at room temperature became our priority direction.

2. Experiment

The gold-doped (3 mol%) CdIn$_2$S$_4$ (Au) compound was prepared using the method of high-temperature synthesis by alloying high-purity (no lower than 99.999%) constituents in an evacuated quartz ampoule. CdIn$_2$S$_4$ (Au) crystals were grown from synthesized pellets by the chemical transport technique with iodine as a carrier gas. Crystal thus obtained had an octahedral shape with clear-cut faceting and a high optical transparency. X-ray studies showed that CdIn$_2$S$_4$ (Au) crystals have a normal-spinel-like cubic structure and their dark specific conductivity is $\sigma = 2 \times 10^{-7}$ Ohm$^{-1}$-cm$^{-1}$ at $T = 300$ K.

Ohmic contacts to CdIn$_2$S$_4$ (Au) samples were made by firing indium into the end faces. The contact spacing, which was exposed to X-ray radiation, was 0.1 cm.

A URS X-ray setup with a BSV-2 tube (Cu radiation) was used as an X-ray source. The X-ray intensity was controlled by varying the current in the tube at each value of the applied accelerating voltage ($V_a$). The absolute X-ray dose was measured with a DRGZ-02 X-ray dosimeter. The sample to be examined was placed in a light-tight X-ray chamber. An X-ray-induced change in the current through the sample was detected by U5-9 electrometric amplifier using a low-value load resistor. During the measurements, the effective radiation hardness was $V_a = 25-50$ keV and interval of dose rate $E = 0.75-78.05$ R/min. All measurements were taken at $T = 300$ K.

3. Experimental Results

The X-ray conductivity coefficient characterizing the X-ray sensitivity of crystals is defined as a relative X-ray-induced change in the conductivity per unit dose rate:

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

(1)

where $\sigma_E$ is the conductivity of a crystal subjected to X-ray radiation with dose rate $E$ and $\sigma_0$ is the dark conductivity at 300 K.

The X-ray sensitivity coefficient was determined by the formula

$$K = \frac{I_E - I_0}{U \cdot E},$$

(2)

where $I_E$ is the current through the sample subjected to X-ray radiation with dose rate $E$, $I_0$ is the dark current, and $U$ is the applied voltage.

Experimental values of X-ray conductivity coefficients $K_\sigma$ obtained for CdIn$_2$S$_4$ (Au) crystals at different values of accelerating potential $V_a$ across the tube and dose rates are listed in Table 1. Associated values of $K_\sigma$ for undoped CdIn$_2$S$_4$ single crystal are also given in Table 1 for comparison. The values of $K_\sigma$ for CdIn$_2$S$_4$ (Au) are seen to far exceed $K_\sigma$ for CdIn$_2$S$_4$.

![Figure 1: Dose dependence of the X-ray sensitivity coefficient for the gold-doped (3 mol%) CdIn$_2$S$_4$ single crystal for accelerating voltage $V_a = (1)25$, (2)30, (3)35, (4)40, (5)45, and (6)50 keV. $U = 0.8$ V; $T = 300$ K.](image)

Figure 1 plots X-ray sensitivity coefficient $K$ calculated by formula (2) versus the X-ray dose rate for the CdIn$_2$S$_4$ (Au) crystal at $T = 300$ K and $U = 0.8$ V. It is seen that X-ray sensitivity of the CdIn$_2$S$_4$ (Au) crystal varies between $2 \times 10^{-3}$ and $1.5 \times 10^{-3}$ (A-min)/(V-R). These values of $K$ for CdIn$_2$S$_4$ (Au) exceed $K$ by 6–8 times for undoped CdIn$_2$S$_4$ [10]. It must be noted that X-ray sensitivity coefficients of studied CdIn$_2$S$_4$ (Au) crystals exceed also values of $K$ for CdIn$_2$S$_4$ single crystals doped with Cu [11] and Fe [12]. These values of $K$ for CdIn$_2$S$_4$ single crystals undoped and doped with Fe, Cu, and Au are listed in Table 2 for comparison.

From experimental data (Figure 1), it follows that the $K(E)$ dependence for CdIn$_2$S$_4$ (Au) at low dose rates is an increasing function (curve 1, Figure 1). Curves 2–6 first increase with the dose rate and then decrease starting from certain $E$; at $E > 30$ R/min, X-ray sensitivity coefficient becomes almost independent of $E$.

Figure 2 shows the roentgen-ampere characteristics of the CdIn$_2$S$_4$ (Au) crystal at different radiation hardness. With an increase in $V_a$, the roentgen current through the sample decreases whatever the dose rate $E$ is.

Figure 3 plots the roentgen current versus the radiation hardness for CdIn$_2$S$_4$ (Au) at $E = 10$ R/min. When $V_a$ rises from 30 to 50 keV, $\Delta I_{E,0} = I_E - I_0$ linearly drops.

The roentgen-ampere characteristics of the CdIn$_2$S$_4$ (Au) crystal for all values of $E$ (except for the initial points) and $V_a$ were almost linear; that is,

$$\Delta I_{E,0} \sim E.$$

(3)

Linear dosimetric characteristics are most suitable for practical use.

Figure 4 illustrates dose dependence of resistance of the CdIn$_2$S$_4$ (Au) crystal at various radiation hardness values. Dark resistance of studied sample was equal to 10 MOhm.
As it is seen from Figure 4 at all radiation hardness values, the CdIn$_2$S$_4$⟨Au⟩ resistance drops when $E$ rises from 0.75 to 78.05 R/min. For example, at $V_a = 50$ keV, the value of the CdIn$_2$S$_4$⟨Au⟩ resistance decreases from 10 to 2.2 MΩhm.

Earlier [10], when studying the X-ray dosimetric characteristics of undoped CdIn$_2$S$_4$ single crystals, we found that when X-ray radiation is switched off, the dark current reaches a steady-state value within 5-6 min rather than at once. Doped CdIn$_2$S$_4$⟨Au⟩ crystals compare favorably with undoped ones in that the roentgen current in them does not relax with time. When X-ray radiation is switched off, the dark current is established almost at once. In addition, the supply voltage of a CdIn$_2$S$_4$ X-ray detector is 24 V/cm, while 8 V/cm is sufficient for a CdIn$_2$S$_4$⟨Au⟩ detector. The values of supply voltage for CdIn$_2$S$_4$ crystals undoped and doped with Fe, Cu, and Au are listed in Table 2. It must be noted that roentgen dosimetric characteristics of studied CdIn$_2$S$_4$⟨Au⟩ single crystals were well reproduced.

### Table 1: X-ray conductivity coefficients of CdIn$_2$S$_4$ and CdIn$_2$S$_4$⟨Au⟩ crystals at 300 K.

| Dose rate $E$, R/min | $K_\sigma$, $10^{-2}$ min/R | $V_a$, keV | Dose rate $E$, R/min | $K_\sigma$, $10^{-2}$ min/R | $V_a$, keV |
|----------------------|----------------------------|------------|----------------------|----------------------------|------------|
| CdIn$_2$S$_4$        | 26.7                       | 7.0        | CdIn$_2$S$_4$        | 0.93                       | 5.72       |
| CdIn$_2$S$_4$⟨Au⟩    | 2.4                        | 1.04       | CdIn$_2$S$_4$        | 1.00                       | 7.15       |
|                      | 29.8                       | 1.10       | CdIn$_2$S$_4$        | 2.20                       | 7.34       |
|                      | 30.3                       | 2.09       | CdIn$_2$S$_4$        | 3.40                       | 7.23       |
|                      | 29.5                       | 23.8       | CdIn$_2$S$_4$        | 3.80                       | 7.25       |
|                      | 29.0                       | 16.38      | CdIn$_2$S$_4$        | 4.50                       | 7.19       |
|                      | 29.3                       | 20.09      | CdIn$_2$S$_4$        | 5.10                       | 7.13       |
|                      | 29.2                       | 27.58      | CdIn$_2$S$_4$        | 5.70                       | 7.10       |

### Table 2: X-ray sensitivity coefficients at $E = 0.75$–78.05 R/min and $V_a = 25$–50 keV and the supply voltages of CdIn$_2$S$_4$ specimens undoped and doped with Fe, Cu, and Au ($T = 300$ K).

| Crystal              | $K_V$, (A/min)/(R-V) | $U$, V/cm |
|----------------------|---------------------|-----------|
| CdIn$_2$S$_4$        | 2.4 · $10^{-10}$–2.4 · $10^{-9}$ | 24        |
| CdIn$_2$S$_4$⟨Fe⟩ (3 mol%) | 2.0 · $10^{-12}$–2.2 · $10^{-11}$ | 500       |
| CdIn$_2$S$_4$⟨Cu⟩ (3 mol%) | 10 · $10^{-9}$ | 5         |
| CdIn$_2$S$_4$⟨Au⟩ (3 mol%) | 2 · $10^{-9}$–1.5 · $10^{-8}$ | 8         |

As it is seen from Figure 4 at all radiation hardness values, the CdIn$_2$S$_4$⟨Au⟩ resistance drops when $E$ rises from 0.75 to 78.05 R/min. For example, at $V_a = 50$ keV, the value of the CdIn$_2$S$_4$⟨Au⟩ resistance decreases from 10 to 2.2 MΩhm. Earlier [10], when studying the X-ray dosimetric characteristics of undoped CdIn$_2$S$_4$ single crystals, we found that when X-ray radiation is switched off, the dark current reaches a steady-state value within 5-6 min rather than at once. Doped CdIn$_2$S$_4$⟨Au⟩ crystals compare favorably with undoped ones in that the roentgen current in them does not relax with time. When X-ray radiation is switched off, the dark current is established almost at once. In addition, the supply voltage of a CdIn$_2$S$_4$ X-ray detector is 24 V/cm, while 8 V/cm is sufficient for a CdIn$_2$S$_4$⟨Au⟩ detector. The values of supply voltage for CdIn$_2$S$_4$ crystals undoped and doped with Fe, Cu, and Au are listed in Table 2. It must be noted that roentgen dosimetric characteristics of studied CdIn$_2$S$_4$⟨Au⟩ single crystals were well reproduced.
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Δ/E,0 (10−8 A)

4
3
2
1
0
30 35 40 45 50
Va (keV)

Figure 3: Roentgen current through the gold-doped (3mol%) CdInS4 single crystal versus the X-radiation hardness at dose rate $E = 10$ R/min.

Figure 4: Dose dependence of CdInS4(Au) resistance for effective radiation hardness $V_a = (1)25$, (2)30, (3)35, (4)40, and (5)50 keV.

4. Conclusions
The gold-doped (3 mol%) CdIn$_2$S$_4$(Au) compound was prepared by high-temperature synthesis. CdIn$_2$S$_4$(Au) single crystals were grown from synthesized pellets by the chemical transport technique with iodine as a carrier gas. X-ray studies showed that CdIn$_2$S$_4$(Au) crystals have a normal-spinel-like cubic structure. Comparative analysis shows that values of X-ray conductivity coefficient ($K_x$) and X-ray sensitivity coefficient ($K$) for CdIn$_2$S$_4$(Au) far exceed $K_x$ and $K$ for CdIn$_2$S$_4$. The roentgen current in CdIn$_2$S$_4$(Au) crystals does not relax with time, and their roentgen-ampere characteristics are linear. Thus, it can be concluded that gold-doped (3 mol%) CdIn$_2$S$_4$ single crystals are highly sensitive to X-rays and can be used for fabrication of low-power fast-response X-ray detectors, which do not require cooling.

Conflict of Interests
The authors declare that there is no conflict of interests regarding the publication of this paper.

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Radiation hardness prepared by high-temperature synthesis. CdIn

The gold-doped (3mol%) CdIn$_2$S$_4$(Au) compound was prepared by high-temperature synthesis. CdIn$_2$S$_4$(Au) single crystals were grown from synthesized pellets by the chemical transport technique with iodine as a carrier gas. X-ray studies showed that CdIn$_2$S$_4$(Au) crystals have a normal-spinel-like cubic structure. Comparative analysis shows that values of X-ray conductivity coefficient ($K_x$) and X-ray sensitivity coefficient ($K$) for CdIn$_2$S$_4$(Au) far exceed $K_x$ and $K$ for CdIn$_2$S$_4$. The roentgen current in CdIn$_2$S$_4$(Au) crystals does not relax with time, and their roentgen-ampere characteristics are linear. Thus, it can be concluded that gold-doped (3 mol%) CdIn$_2$S$_4$ single crystals are highly sensitive to X-rays and can be used for fabrication of low-power fast-response X-ray detectors, which do not require cooling.
