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# MIXED $ZnS_xSe_{1-x}$ CRYSTALS AS A POSSIBLE MATERIAL FOR ALPHA-PARTICLE AND X-RAY DETECTORS

*A possibility to use $ZnS_xSe_{1-x}$ as a material for the detection of X-rays and alpha particles has been studied. The influence of the sulfur content on the properties of bulk $ZnS_xSe_{1-x}$ crystals is analyzed. Six specimens with different component contents were grown, by using the Bridgman–Stockbarger method: $ZnS_{0.07}Se_{0.93}$, $ZnS_{0.15}Se_{0.85}$, $ZnS_{0.22}Se_{0.78}$, $ZnS_{0.28}Se_{0.72}$, $ZnS_{0.32}Se_{0.68}$, and $ZnS_{0.39}Se_{0.61}$. The intensity of X-ray luminescence spectra of $ZnS_xSe_{1-x}$ crystals is found to increase with the sulfur content and reaches a maximum for the composition $ZnS_{0.22}Se_{0.78}$. The luminescence light yield of mixed $ZnS_xSe_{1-x}$ crystals is higher than that of commercial ZnSe(Te) and ZnSe(Al) crystals. The advantages of mixed crystals based on $ZnS_xSe_{1-x}$ over the ZnS(Te) and ZnSe(Al) crystals have been discussed.*

*K e y w o r d s*: scintillator, mixed crystals, $ZnS_xSe_{1-x}$, alpha detector, X-ray luminescence.

## 1. Introduction

Solid-state scintillation detectors containing scintillation crystals and silicon $p$–$i$–$n$ photodiodes are widely used in radiometers, dosimeters, and spectrometers, in technological equipment for customs and security control, medical diagnostics, environmental monitoring, and others [1]. In order to register radiation of various types, various scintillation detectors are currently used. For instance, ZnSe, ZnSe(Al), and ZnSe(Te) crystals are widely used for detecting X-rays and $\gamma$-radiation, whereas CsI(Tl), NaI(Tl), and ZnS(Ag) are the most widespread scintillators for detecting alpha particles.

However, all those crystals have a number of shortcomings. In particular, ZnSe crystals have a low light yield, and ZnSe(Al) ones a high thermal quenching factor [2]. The luminescence kinetics in ZnSe(Te) crystals is "slow": up to a hundred microseconds. Scintillators based on CsI(Tl) and NaI(Tl) are hygroscopic and require the additional moisture protection [3]. The shortcoming of ZnS(Ag)-based crystals consists in that they badly transmit photons of visible light and can only be used as thin layers [4].

A promising scintillator for alpha-particle and X-ray detectors is $ZnS_xSe_{1-x}$ [5–7]. Among the advantages of this material, we would like to distinguish its nonhygroscopicity, transparency with respect to the characteristic wavelength, and unlimited mutual solubility, which makes it possible to create materials with arbitrary component contents [8]. Furthermore, by increasing the bandgap width in $ZnS_xSe_{1-x}$, it is possible to considerably elevate the quenching temperature [9], which is very important for the creation of detectors. A lot of publications were devoted to the mixed $ZnS_xSe_{1-x}$ crystals [9–12, 14–18]. Most of

them describe crystals grown from the vapor phase, and only a few works concern crystals obtained by growing from the melt [8–10].

The methods of directional crystallization allow rather large mixed $ZnS_xSe_{1-x}$ crystals to be grown, which is of importance, if the latter are used as high-energy particle detectors. Currently, the properties of $ZnS_xSe_{1-x}$ crystals as high-energy particle detectors have not been studied enough, and their advantages over the classical ZnSe, ZnSe(Al), and ZnSe(Te) scintillators have not been proven yet. In this work, we studied the scintillation and optical properties of bulk $ZnS_xSe_{1-x}$ crystals taking their possible application as X-ray and alpha-particle detectors into account. A special attention is paid to the comparison of the properties of $ZnS_xSe_{1-x}$ and commercial ZnSe, ZnSe(Al), and ZnSe(Te) scintillators.

## 2. Experimental Part

Six specimens of $ZnS_xSe_{1-x}$ crystals with different sulfur contents $x$ were fabricated following the Bridgman–Stockbarger method. Mixed $ZnS_xSe_{1-x}$ crystals were grown from charges with various initial $x$-values: $x = 0.05$, 0.1, 0.15, 0.2, 0.25, and 0.3. Before growing, each charge was roasted in a quartz crucible at a temperature of 1220 K for 5 h in the hydrogen atmosphere in order to remove oxygen impurities. The specimens were grown by the Bridgman–Stockbarger method in graphite crucibles 25 mm in diameter and under the inert gas (Ar) pressure $P = 10^7 \div 10^9$ Pa. The speed of crucible drawing through the crystallization zone was 7 mm /h. The heater temperature was varied from 1870 to 2000 K, depending on the initial charge composition.

After the growing, the mixed crystals with the nominal compositions $ZnS_{0.05}Se_{0.95}$, $ZnS_{0.1}Se_{0.9}$, $ZnS_{0.15}Se_{0.85}$, $ZnS_{0.2}Se_{0.8}$, $ZnS_{0.25}Se_{0.75}$, and $ZnS_{0.3}Se_{0.7}$ were cut perpendicularly to the growth direction and polished. As a result, we obtained pellets 25 mm in diameter and 4 mm in thickness (see Fig. 1). One pellet of each of six $ZnS_xSe_{1-x}$ crystals was studied in detail. The properties of bulk $ZnS_xSe_{1-x}$ crystals were compared with those of ZnSe, ZnSe(Al), and ZnSe(Te) crystals obtained under similar conditions and described in more details in works [15, 16].

In order to determine the content of cationic impurities, as well as the actual composition of the crystals, a chemical analysis was carried out, which testified to six crystal compositions: $ZnS_{0.07}Se_{0.93}$, $ZnS_{0.15}Se_{0.85}$, $ZnS_{0.22}Se_{0.78}$, $ZnS_{0.28}Se_{0.72}$, $ZnS_{0.32}Se_{0.68}$, and $ZnS_{0.39}Se_{0.61}$. The specimens were annealed in a vapor of zinc ($T = 1223$ K, $P_{Zn} = 5 \times 10^7$ Pa, $t = 48$ h), which was also used for the final formation of luminescent centers, as well as for the suppression of non-radiating relaxation channels excited by charge carriers [15, 16]. Afterward, the specimens were ground and polished, by using a diamond powder. In Fig. 1, a photo of polished $ZnS_xSe_{1-x}$ crystals is exhibited.


***Fig. 1.*** Photo of mixed $ZnS_xSe_{1-x}$ crystals after their polishing

X-ray luminescence spectra were registered with a spectrophotometric complex KSVU-23. An X-ray apparatus REIS-I (Cu, $U = 10 \div 45$ keV) was used as an X-ray source. The relative light yield and the afterglow were measured with the help of an X-ray tube with a tungsten anode and a silicon photodiode PD-24 Smiths Heimann AMS-1. The mathematical processing of the measured data was carried out automatically.

The technical light yield of mixed $ZnS_xSe_{1-x}$ crystals was measured by the spectrometric method with the help of such sources of $\gamma$-quanta as $^{137}$Cs ($E_\gamma = 662$ keV) and $^{241}$Am ($E_\gamma = 59.5$ keV), and a source of alpha particles $^{239}$Pu ($E_\alpha = 5156$ keV). The working temperature was 294 K. A photomultiplier of the type R1307 was applied as a photodetector. GOST 17038.2-79 was used as a standard [2].

## 3. Results and Discussion

The final compositions of mixed $ZnS_xSe_{1-x}$ crystals grown by the Bridgman–Stockbarger method

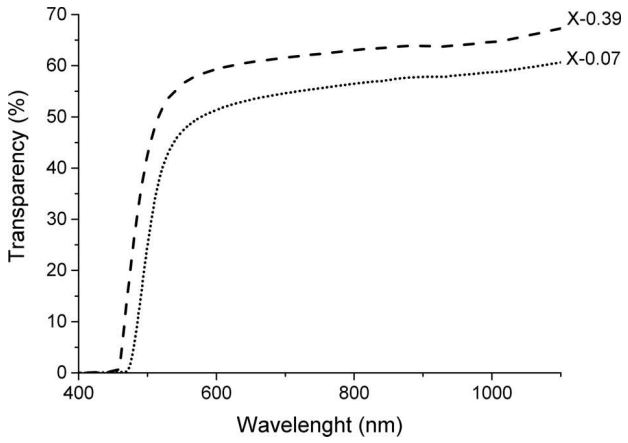


***Fig. 2.*** Transparency of $ZnS_xSe_{1-x}$ crystals

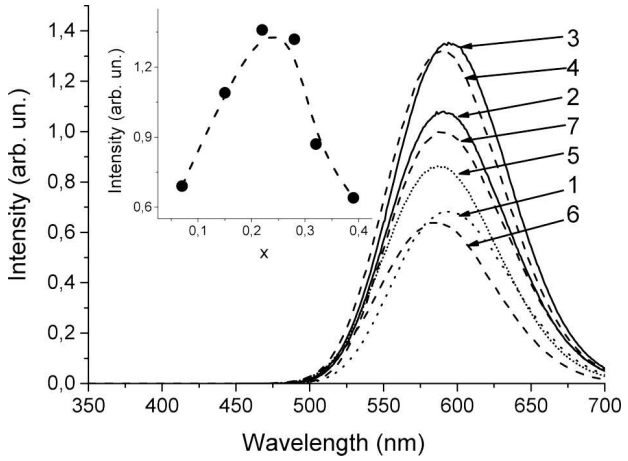


***Fig. 3.*** Normalized X-ray luminescence spectra for bulk $ZnS_xSe_{1-x}$ crystals after their annealing in Zn vapor: $ZnS_{0.07}Se_{0.93}$ (*1*), $ZnS_{0.15}Se_{0.85}$ (*2*), $ZnS_{0.22}Se_{0.78}$ (*3*), $ZnS_{0.28}Se_{0.72}$ (*4*), $ZnS_{0.32}Se_{0.68}$ (*5*), $ZnS_{0.39}Se_{0.61}$ (*6*), and ZnSe(Al) (*7*). The dependence of the luminescence band intensity on the composition of bulk $ZnS_xSe_{1-x}$ crystals is shown in the inset

were found to equal $ZnS_{0.07}Se_{0.93}$, $ZnS_{0.15}Se_{0.85}$, $ZnS_{0.22}Se_{0.78}$, $ZnS_{0.28}Se_{0.72}$, $ZnS_{0.32}Se_{0.68}$, and $ZnS_{0.39}Se_{0.61}$. For comparison, ZnSe(Te) and ZnSe(Al) crystals were also fabricated under the same conditions.

The optical research was carried out at room temperature for $ZnS_xSe_{1-x}$ specimens with different contents of their components. The transmittance spectra of bulk $ZnS_xSe_{1-x}$ crystals are shown in Fig. 2. The corresponding values measured at $\lambda = 1100$ nm were found to change from 61% for $ZnS_{0.07}Se_{0.93}$ to 67% for $ZnS_{0.39}Se_{0.61}$, which testifies to a high optical quality of the crystals.

The light generation in $ZnS_xSe_{1-x}$ crystals takes place owing to the transformation of the energy of X-rays or $\gamma$-quanta at the structural defects. Those defects can be identified with the help of X-ray luminescence. The normalized experimental X-ray luminescence spectra of $ZnS_xSe_{1-x}$ crystals with different component ratios are shown in Fig. 3. The luminescence spectra of mixed $ZnS_xSe_{1-x}$ crystals demonstrate a broad band with a maximum that changes its position from 584 to 591 nm. Higher sulfur contents $x$ give rise to a shift of the luminescence band maximum toward shorter waves. This is a result of the band gap growth with increasing the sulfur concentration [13].

The positions of the X-ray luminescence bands in ZnSe(Al) and $ZnS_xSe_{1-x}$ crystals coincide and correspond to the glow of the triple complex $V_{Zn}Zn_iO_{Se}$. Hence, the mechanism of radiative transitions in those crystals is identical [18–20]. The normalized intensity of X-ray luminescence increases with the sulfur content and reaches a maximum for the composition $ZnS_{0.22}Se_{0.78}$. This occurs owing to the formation of an optimal number of triple complexes $V_{Zn}Zn_iO_{Se}$ in those crystals (see the inset in Fig. 3). A further increase of the sulfur content leads to a decrease in the intensity of X-ray luminescence due to an increase of the defect concentration in bulk $ZnS_xSe_{1-x}$ crystals.

The light yield is one of the most important parameters of scintillators, which determines its capability as a detector. In order to obtain more accurate results, the light yield of mixed $ZnS_xSe_{1-x}$ crystals was measured by two methods: the X-ray excitation method and the spectrometric one. In the case of X-ray excitation, the light yield of bulk $ZnS_xSe_{1-x}$ crystals was at the level of ZnSe(Te) crystals or higher. In particular, the light yield of the $ZnS_{0.22}Se_{0.78}$ specimen was 1.6 times as high as that of the reference ZnSe(Te) crystal (see Table 1).

The afterglow characterizes not only the scintillator inertia, but also the dynamic range of recorded signals. The afterglow of mixed $ZnS_xSe_{1-x}$ crystals was about 0.02% after 15 ms, except for the $ZnS_{0.39}Se_{0.61}$ specimen. So, it was rather short in comparison with that for the known fluorescent materials such as ZnS, CsI(Tl), and $Lu_2SiO_5:Ce$ [21–23] (see Table 1). The light yield of polished zinc-annealed ZnSe(Al) and

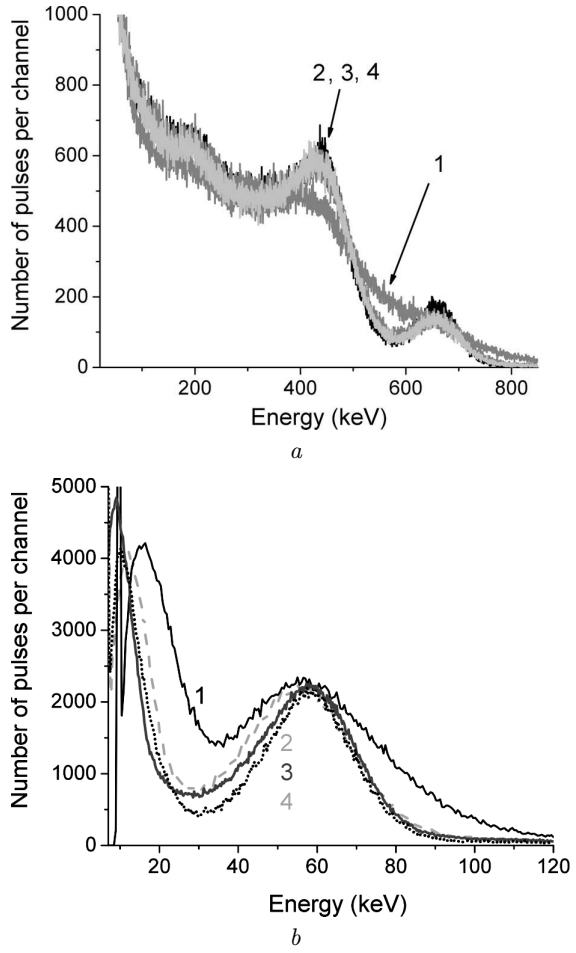


***Fig. 4.*** Amplitude spectra of $ZnS_{0.15}Se_{0.85}$ (*1*), $ZnS_{0.22}Se_{0.78}$ (*2*), $ZnS_{0.39}Se_{0.61}$, (*3*), and ZnSe(Al) (*4*) crystals obtained with $\gamma$-rays from (*a*) $^{137}$Cs and (*b*) $^{241}$Am sources

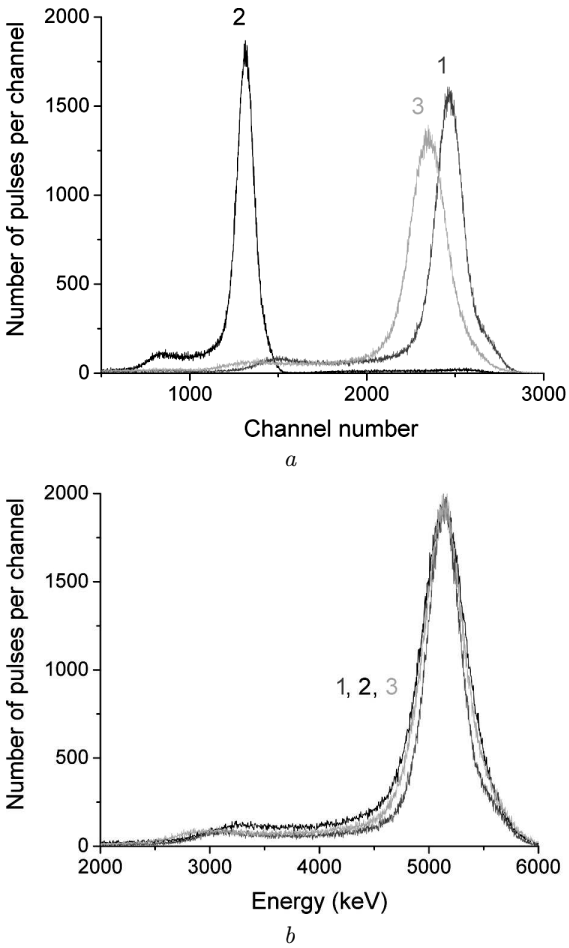


***Fig. 5.*** Amplitude (*a*) and energy (*b*) spectra of $ZnS_{0.22}Se_{0.78}$ (*1*), ZnSe(Te) (*2*), and ZnSe(Al) (*3*) crystals obtained for $\alpha$-particles from a $^{239}$Pu source

*Table 1.* **Experimental light yield of mixed $ZnS_xSe_{1-x}$ crystals excited with X-ray radiation**

| Specimen | Relative light yield, % | Afterglow, % | | |
|---|---|---|---|---|
| | | 5 ms | 15 ms | 25 ms |
| $ZnS_{0.07}Se_{0.93}$ | 98 | 0.24 | <0.02 | <0.02 |
| $ZnS_{0.15}Se_{0.85}$ | 84 | 0.15 | <0.02 | <0.02 |
| $ZnS_{0.22}Se_{0.78}$ | 159 | 0.40 | <0.02 | <0.02 |
| $ZnS_{0.28}Se_{0.72}$ | 122 | 0.54 | <0.02 | <0.02 |
| $ZnS_{0.32}Se_{0.68}$ | 103 | 0.37 | <0.02 | <0.02 |
| $ZnS_{0.39}Se_{0.61}$ | 136 | 0.46 | 0.07 | <0.02 |
| ZnSe(Te) | 100 | 0.30 | 0.17 | <0.02 |
| ZnSe(Al) | 95 | 0.40 | <0.02 | <0.02 |
| ZnS | 75 | 58.04 | 39.74 | 31.77 |

$ZnS_xSe_{1-x}$ crystals was measured by the spectrometric method and with the use of $^{241}$Am and $^{137}$Cs radiation sources. In $ZnS_{0.22}Se_{0.78}$ crystals excited by both sources, a satisfactory separation was observed (Fig. 4), which confirms the high efficiency of low-energy quantum registration by the examined scintillators.

The light yield of $ZnS_{0.22}Se_{0.78}$ specimens amounted to 116.6% with respect to that of ZnSe(Al), if the $^{137}$Cs source was used in the measurements, and to 130% in the case of the $^{241}$Am source (see Table 2). The mixed $ZnS_{0.15}Se_{0.85}$ and $ZnS_{0.39}Se_{0.61}$ crystals (Table 2) demonstrated worse spectrometric parameters in comparison with the $ZnS_{0.22}Se_{0.78}$ specimen, analogously to the measurements of light

*Table 2.* **Experimental light yield of mixed $ZnS_xSe_{1-x}$ crystals measured in the spectrometric regime**

| Scintillator | $^{137}Cs - E_g = 662$ keV | | $^{241}Am - E_g = 59.5$ keV | |
|---|---|---|---|---|
| | $V_{max}$, keV | $I_1/I_2$, % | $V_{max}$, keV | $I_1/I_2$, % |
| ZnSe(Al) | 649 | 100.0 | 47 | 100.0 |
| $ZnS_{0.15}Se_{0.85}$ | 443 | 68.3 | 33 | 70.7 |
| $ZnS_{0.22}Se_{0.78}$ | 756 | 116.6 | 61 | 129.9 |
| $ZnS_{0.39}Se_{0.61}$ | 606 | 93.4 | 46 | 98.8 |

yield for those specimens subjected to the X-ray irradiation (see Table 1).

In order to study the properties of $ZnS_xSe_{1-x}$ crystals as alpha-particle detectors, a rectangular piece $10 \times 10 \times 2$ mm$^3$ in dimensions was cut out from the $ZnS_{0.22}Se_{0.78}$ crystal, which was preliminary annealed in a Zn vapor. For the sake of comparison, ZnSe(Al) and ZnSe(Te) crystals with the same dimensions and also annealed in a Zn vapor were used. The light yield of ZnSe(Al), ZnSe(Te), and $ZnS_xSe_{1-x}$ thin crystalline specimens was measured, by using the spectrometric method and the $^{239}$Pu alpha-particle source.

The energy position of registered peaks (Fig. 5, *a*) testifies that the mixed $ZnS_{0.22}Se_{0.78}$ crystal has a higher light yield in comparison with that of the ZnSe(Al) and ZnSe(Te) crystals. The $ZnS_{0.22}Se_{0.78}$ crystals also demonstrate a satisfactory separation (Fig. 5, *b*) at an energy of 5156 keV, which confirms the high efficiency of alpha-particle registration by the examined scintillators.

## 4. Conclusions

Bulk $ZnS_xSe_{1-x}$ crystals with the parameter $x$ within the interval $x = 0.07 \div 0.39$ were grown by the Bridgman–Stockbarger method. The grown crystals had a good transparency, with a transmittance higher that 61% at the wavelength $\lambda = 1100$ nm. The scintillation properties of $ZnS_xSe_{1-x}$ crystals were shown to depend on the sulfur content $x$. The dependence of the X-ray fluorescence intensity on the sulfur content was nonmonotonic, by reaching a maximum for the composition $ZnS_{0.22}Se_{0.78}$. Our researches showed that the bulk $ZnS_xSe_{1-x}$ crystals can be used as highly effective X- and gamma-ray detectors. Our researches also testify to the promising application of mixed $ZnS_xSe_{1-x}$ crystals as alpha-particle detectors, with the $ZnS_{0.22}Se_{0.78}$ crystals having the best light yield and energy separation in the case where $^{239}$Pu is applied as a source of alpha particles.

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ЗМІШАНІ КРИСТАЛИ $ZnS_xSe_{1-x}$
ЯК МОЖЛИВІ МАТЕРІАЛИ ДЛЯ ДЕТЕКТОРІВ
АЛЬФА ТА РЕНТГЕНІВСЬКОГО ВИПРОМІНЮВАННЯ

Р е з ю м е

Вивчено можливість використання матеріалу $ZnS_xSe_{1-x}$ як детектора для рентгенівського та альфа випромінювання. Досліджено вплив вмісту сірки на властивості об'ємних кристалів $ZnS_xSe_{1-x}$. Об'ємні кристали $ZnS_xSe_{1-x}$ були вирощені методом Бриджмена–Стокбаргера. Отримано шість сполук з різним вмістом компонентів: $ZnS_{0,07}Se_{0,93}$, $ZnS_{0,15}Se_{0,85}$, $ZnS_{0,22}Se_{0,78}$, $ZnS_{0,28}Se_{0,72}$, $ZnS_{0,32}Se_{0,68}$, $ZnS_{0,39}Se_{0,61}$. Було виявлено, що інтенсивність спектрів рентгенолюмінесценції кристалів $ZnS_xSe_{1-x}$ зростає зі збільшенням вмісту сірки і досягає максимуму для складу $ZnS_{0,22}Se_{0,78}$. Світловихід змішаних кристалів $ZnS_xSe_{1-x}$ вище, ніж у комерційних кристалів ZnSe(Te) і ZnSe(Al). Показані переваги змішаних кристалів на основі $ZnS_xSe_{1-x}$ в порівнянні з кристалами ZnSe(Te) і ZnSe(Al).