

## Research Article

# Light Sum Accumulation in ZnSe Crystals at X-Ray Excitation

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This paper presents the results of the dose dependencies of the light sum accumulation in ZnSe single crystals at a different X-ray excitation at 85 K. The values of light sum accumulation at different deep traps were determined from the thermally stimulated luminescence and conductivity curves. It was confirmed that the accumulated light sum is uniquely determined by the dose of radiation only, that is, the product of the intensity of excitation by the time of X-ray exposure. The same result is also given by the theoretical consideration of the kinetics of the light sum accumulation on deep traps for a multicenter model of crystal phosphors.

## 1. Introduction

Zinc selenide (ZnSe) belongs to wide-bandgap materials of  $A^{II}B^{VI}$  type and is a well-studied material [1–3]. ZnSe is widely used in the creation of semiconductor electronic devices and information display systems [4]. Over the last decade, another promising direction for ZnSe application has been developed: as detectors of an indirect ionizing radiation [4–6] and direct high-energy conversion of radiation into electric current [7]. Relatively high value of the effective atomic number  $Z_{ef} = 32$  and a band gap width  $E_g = 2.7$  eV (at 300 K), as well as the technology for growing high-quality single crystals with low concentrations of uncontrolled impurities and high material resistivity at  $\sim 10^{10} - 10^{14}$  Ohm cm make zinc selenide a promising material for creating X-ray semiconductor detectors that do not require cooling [7]. It should be noted that the resistivity of  $\sim 10^{14}$  Ohm cm in ZnSe crystals means that the concentration of free electrons in the conduction band does not exceed  $10^3$  cm $^{-3}$  at room temperature.

The kinetics of luminescence and conductivity in the crystal phosphors substantially depend not only on the concentration of various luminescence centers but also on the concentrations of various traps. Therefore, when studying the kinetics of luminescence and conductivity, it is necessary to know the kinetics of accumulation of the charge carriers on deep traps and the kinetics of accumulation of recharge of the luminescence centers. The classical kinetic theories

of photoluminescence [8–10] and photoconductivity [11–13], which use the simplest model of crystal phosphors with one trap and one recombination center, show that the value of the maximum accumulated light sum intensity on the trap  $n_{\infty} \sim \sqrt{I_{ex}}$  (where  $I_{ex}$  – excitation intensity). Since real crystals, as a rule, contain a set of traps and several luminescence centers, it is necessary to verify this ratio experimentally.

Thus, there arises a need for a comprehensive study of the luminescent and electrical properties of ZnSe. This paper is devoted to the study of the features of the light sum accumulation in the ZnSe single crystals at different intensities and duration of X-ray excitation in order to verify the influence of the excitation intensity on the value of the maximum accumulated light sum. For comparison, it is also necessary to obtain a theoretical dependence for the light sum accumulation on deep traps for a multicenter model of crystal phosphors.

*1.1. Experimental Method.* A comprehensive experimental study of X-ray conductivity (XRC), X-ray luminescence (XRL), phosphorescence (Ph), and conduction current relaxation (CCR) was carried out; however the main focus was on the studies of thermally stimulated conductivity (TSC) and luminescence (TSL) and their dose dependencies at different intensities of X-ray excitation. ZnSe crystals were grown from a prepurified initial charge and were not specifically doped during their growth. For the study purpose, the samples were made in the form of parallelepipeds with dimensions: 18×9×2

mm<sup>3</sup>. By the method of thermo-EMF, it was found that the samples had n-type conductivity. It is also known [14] that the photoconductivity in ZnSe is due to free electrons.

To examine conductivity, the electrical contacts in the form of two parallel strips of 1×5 mm<sup>2</sup> (at a distance of 5 mm from each other) were sprayed on the very surface of the single crystal samples. The conductors were then soldered to the contacts. In this work, we used such a contact geometry, in which the sprayed electrodes were located in the central part of the most polished surface of the sample. A constant stabilized voltage from 0 to 1000 V was applied to one electrode, and the other was connected to a nanoammeter to record the current. The magnitude of the conduction current was measured with an accuracy of 1% for the currents from 10 pA to 1 mA. For all values of the conduction current, the following condition was satisfied: the input impedance of the nanoammeter was by several orders of magnitude smaller than the electrical resistance of the ZnSe sample. The nanoammeter is a part of a specially designed measuring unit of I – V curve, which allows choosing different modes of voltage variations: manual, stepwise, and linear with various speeds.

To study the TSL and TSC, the sample was placed in a cryostat and was secured with a large polished surface (opposite to the surface with contacts) to a polished copper block to ensure good thermal contact of the sample with the cryostat's copper substrate. It is necessary to conduct temperature studies, as it ensures the minimum temperature gradient in the sample. Previously it was found that the maximum temperature difference in various parts of the sample does not exceed 0.3 K. During the studies, the sample was in a vacuum ( $p < 1$  Pa). The sample surface between the electrical contacts was irradiated with the integral radiation of the BHV-7 X-ray tube (Re, 20 kV, 5 mA ( $I_{1X} = 0.13$  mW/cm<sup>2</sup>) or 25 mA ( $I_{2X} = 0.64$  mW/cm<sup>2</sup>),  $L=130$  mm) through a beryllium window in a cryostat. The intensity of the X-ray excitation was changed by varying the anode current of the X-ray tube at a constant voltage. The shape of the emission spectrum of the X-ray tube remained unchanged, and the intensity was proportional to the magnitude of the anode current of the X-ray tube.

The luminescence spectra were recorded at 8, 85, and 295 K. The dose dependencies of TSL and TSC were measured after X-ray excitation for a fixed time  $\tau_X$  at a temperature of 85 K. After irradiation and relaxation of phosphorescence and conduction current (about 10 minutes), the sample was heated to 450 K using an electric furnace of 800 W embedded in the cryostat. The heating rate of the sample was  $0.40 \pm 0.02$  K/s. The cooling was made by liquid nitrogen. The radiation dose was changed by altering the time of exposure  $\tau_X$  at a constant intensity of the X-ray tube, using two operating modes: 20 kV, 25 mA, and 20 kV, 5 mA.

Two channels were used to record the luminescence: integral and spectral. The optical axes of the two recording systems were exactly in the middle between the electrical contacts and at an angle of 45° to the normal of the sample surface, which was uniformly irradiated by the X-ray quanta (Figure 1).

When using an integral channel, the luminescent radiation was focused using quartz lens onto the photocathode of a photoelectric multiplier PMT-106.

For the spectral registration the luminescent irradiation from the sample through a quartz condenser and a monochromator MDR-2 (600 lines/mm diffraction grating) was recorded either PMT-106 (in the spectral range of 350 – 820 nm) or cooled PMT-83 (in the range of 600 – 1200 nm). The accuracy of determining the intensity of X-ray luminescence was not worse than 3%, and TSL – 5% and was limited by the presence of the dark currents of the photomultiplier and the noises of the recording system. All luminescence spectra were corrected for the spectral sensitivity of the recording system.

## 2. Results of the Experimental Studies

*2.1. The Luminescence Spectra for X-Ray Luminescence of the ZnSe.* The characteristic XRL spectra for ZnSe single crystal ZnSe samples in the spectral region from 400 to 1200 nm at different temperatures (8 – 420 K) consist of two known [14–18] wide luminescence bands with maxima at 630 nm (1.92 eV) and 970 nm (1.28 eV). The spectra of different high-resistance samples differ only in the intensity ratio of these two main luminescence bands. Figure 2 shows the XRL spectra of two ZnSe samples, which were studied in detail for the dose dependencies of TSL and TSC. The edge luminescence and the luminescence of donor-acceptor pairs in high-resistance ZnSe samples were not found.

The 630 nm band, according to [14, 15], is due to the complex center which contains a zinc vacancy, and the band with a maximum at 970 nm is due to the complex center with a selenium vacancy [16, 17]. Both XRL bands are due to the luminescence recombination mechanism since they are observed in the phosphorescence and TSL [18]. The spectral maxima of these bands [19] vary little with temperature change, which allows recording them at a fixed wavelength at different temperatures. In all luminescence studies for the 970 nm band, the registration was carried out at a wavelength of 953 nm, since at this length the maximum luminescence of this band is observed without taking into account the spectral sensitivity of the recording system.

*2.2. Thermally Stimulated Luminescence and Conductivity ZnSe.* The TSL and TSC curves are intense enough to register, and they indicate a significant level of stockpiling of the charge carriers at the traps. For convenience, we will denote TSL curves when registering in the 630 nm band as TSL-630 and TSL-970, when registering in the 970 nm band. Figures 3 and 4 show the characteristic TSL-630, TSL-970, and TSC curves for two samples of ZnSe single crystal at high and low radiation doses. It should be noted that the ratio of the intensities of the TSL and TSC peaks vary for different samples, which indicates a different concentration of various traps in different ZnSe crystals.

Most of the charge carriers are thermally delocalized from the traps when heated to a temperature of 250 K, which indicates the dominance of the concentration of traps which

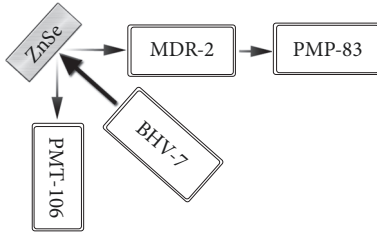


FIGURE 1: Geometry of XRL and TSL spectra registration.

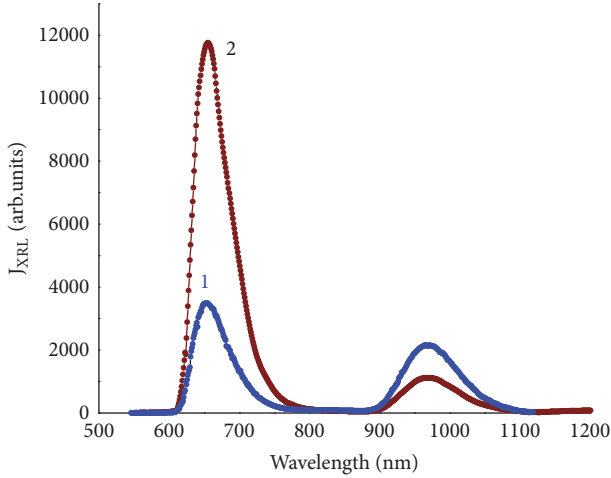


FIGURE 2: XRL spectra of the first (1) and the second (2) ZnSe samples at 85 K.

are not deep-level traps in the test material. The most high-temperature maximum (very weak) is observed at  $T_m = 292$  K on the TSC curves.

In the TSL and TSC curves for each ZnSe sample the same peaks are observed. Thus, for the first sample, the dominant peaks are  $T_m \sim 129$  K, 170 K, 184 K, 211 K, and 238 K. For the second sample, the dominant peaks on the TSL and TSC curves are  $T_m \sim 143$  K, 170 K, 184 K, and 224 K and a weak peak at 292 K, which is not visible in the TSL due to the temperature luminescence extinction of 630 nm and 970 nm bands. Let us note that although the temperature position of one and the same TSL and TSC peak do not coincide (and should not coincide), but the temperature difference between them does not exceed 2-3 K, which is significantly less than the temperature difference between adjacent peaks [20] ( $\Delta T_m = 13.6$  K).

The similarity between the TSL curves when registering at two recombination centers TSL-630 and TSL-970 and TSC curves means that the delocalization of charge carriers from any trap leads to the appearance of free carriers in the zone (TSC peak) and their subsequent recombination at the recharged luminescence centers of both samples (630 and 970 nm), the TSL peaks. It also indicates that we have a similar electronic recombination mechanism at the luminescence centers, which determine the 630 and 970 nm bands.

An analysis of the temperature position of the TSL and TSC peaks in ten different samples of ZnSe single crystals at  $\beta = 0.40$  K/s shows that peaks from the same set are observed, and their intensities vary significantly in different samples. That is, for ZnSe single crystals, there is a certain set of traps and various samples differing only in the concentration ratio. Moreover, this set of traps corresponds to the data [20] and obeys the formula of a harmonic oscillator.

The temperature position of the TSL and TSC peaks practically does not alter with a change in the dose of X-ray irradiation ( $D = I_X \cdot \tau_X$ ) from the minimum ( $D_{\min}$ ) to the maximum ( $D_{\max}$ ), while  $D_{\max}/D_{\min} = 10,000$ . Since the TSL and TSC peaks from neighboring traps noticeably overlap, firstly the temperature position of peaks was determined for the resulting experimental maxima, depending on the X-ray irradiation dose. Once it was verified that the temperature situation remains unchanged within a few degrees, the next step was to decompose the TSL and TSC curves into its components. In this case, the theoretical forms of the peaks of the TSL and TSC curves, given in [19], were used. It was verified that the temperature positions of the maxima of these components also remain practically unchanged at various doses of irradiation. It indicates that the probability of relocalization to the same trap is much less than the total probability of recombination at different luminescence centers and localization to the deeper traps. But the accumulation rate for traps of different depths is different, and therefore the TSL and TSC curves (Figures 3 and 4), obtained at different doses of X-ray irradiation, differ.

At high temperatures ( $T > 350$  K) in all ZnSe samples, we observe conductivity appearance, while the current magnitude does not depend on the X-ray dose received. Reheating without irradiation repeats this dependence of the current magnitude on temperature. It clearly indicates that at  $T > 350$  K the dark conductivity grows in these ZnSe samples.

Referring to papers that have been previously published, the way how to determine trap concentrations sometimes has been used a *thermostimulated conductivity (TSC) technique* [21, 22]. However, with this method, the filling of the trap levels could not be more accurately determined and does not consider the spatial distribution of localized charge carriers on traps.

### 3. The Light Sum Accumulation in ZnSe Single Crystals

The classical kinetic theories of luminescence and conductivity are not suitable for determining the kinetics of charge carrier accumulation on deep traps since they use a model of crystal phosphors with one type of traps and one luminescence center. In real crystals, several traps are always observed (several peaks on the TSL and TSC curves). Let us consider the light sum accumulation on deep traps within multicenter model of crystal phosphor, in which at excitation temperature  $T_0$  the following are present: several types of shallow traps, phosphorescent trap, and several types of deep traps for electrons, and at least two kinds of luminescent centers with

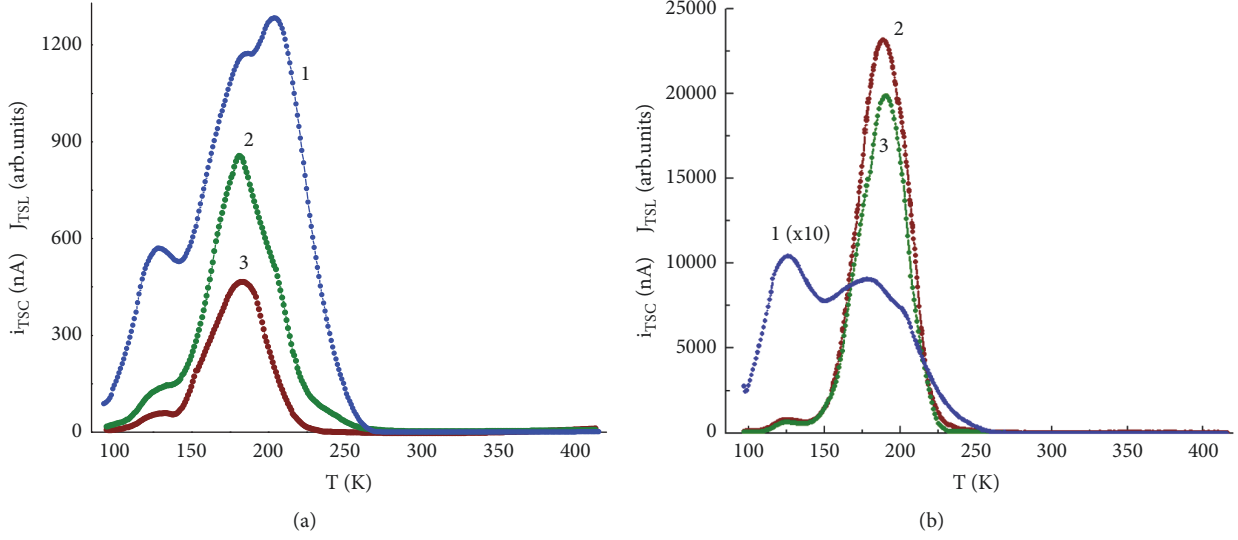


FIGURE 3: TSC (1), TSL-630 (2), and TSL-970 (3) curves of ZnSe sample #1: at a low dose of radiation ( $D_X = 7.8 \text{ mJ/cm}^2$ ) (a) and at a high dose of radiation ( $D_X = 4608 \text{ mJ/cm}^2$ ) (b).

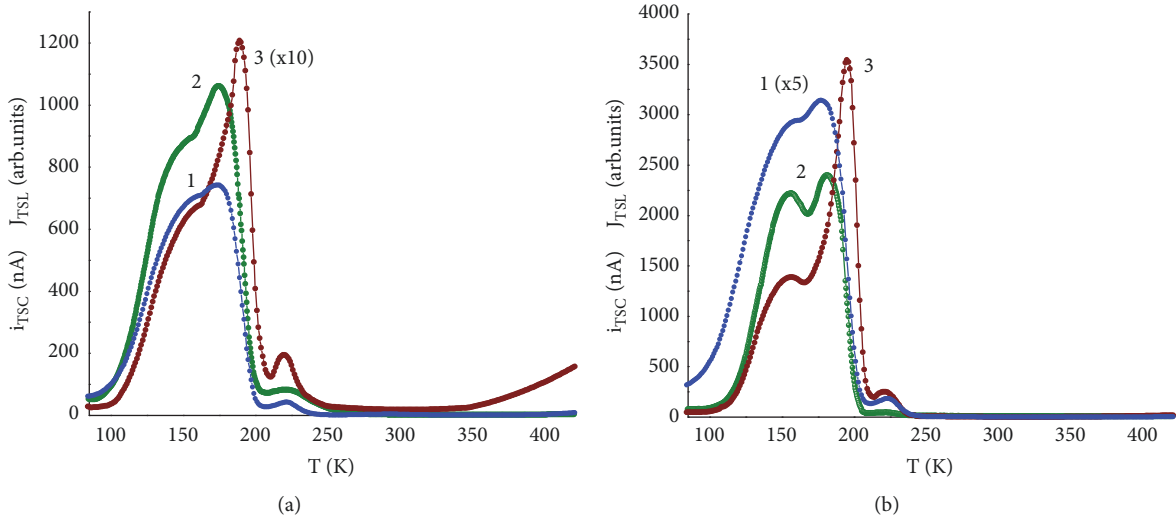


FIGURE 4: TSC (1), TSL-630 (2), and TSL-970 (3) curves of ZnSe sample #2: at a low dose of radiation ( $D_X = 7.8 \text{ mJ/cm}^2$ ) (a) and at a high dose of radiation ( $D_X = 4608 \text{ mJ/cm}^2$ ) (b).

electronic recombination mechanism (deep traps for holes). Shallow traps do not significantly affect the luminescence kinetics since electrons on them are in a localized state for a very short time ( $< 1 \text{ s}$ ).

We can determine the levels of deep traps' maximum filling ( $r_e$ ) based on their kinetic equations (for example, for  $m$ - and  $k$ -type traps) for the stationary state:

$$\begin{aligned} \frac{\partial n_m}{\partial t} &= N^- u^- \sigma_m^- (v_m - n_m) - w_m n_m - P^+ u^+ \sigma_m^+ n_m = 0 \\ \frac{\partial n_k}{\partial t} &= N^- u^- \sigma_k^- (v_k - n_k) - w_k n_m - P^+ u^+ \sigma_k^+ n_k = 0 \end{aligned} \quad (1)$$

and kinetic equations for free electrons ( $N^-$ ) and holes ( $P^+$ )

$$\begin{aligned} \frac{\partial N^-}{\partial t} &= G - \sum N^- u^- \sigma_m^- (v_m - n_m) - \sum w_m n_m \\ &\quad - \sum N^- u^- \sigma_j^- p_j = 0 \\ \frac{\partial P^+}{\partial t} &= G - \sum P^+ u^+ \sigma_j^+ (v_{p_j} - p_j) - \sum w_j p_j \\ &\quad - \sum P^+ u^+ \sigma_m^+ n_m = 0 \end{aligned} \quad (2)$$

using the notation:  $n$  and  $p$  are the concentrations of the localized electrons and holes;  $u^-$  and  $u^+$  are the thermal velocity of free charge carriers;  $\sigma$  is localization cross sections

(the superscript is the sign of the charge of the free carrier; subscript is a type of the local center);  $\nu$  is concentrations of local centers;  $w$  is the probability of thermal delocalization of charge carriers;  $G$  is the generation rate of free charge carriers (proportional to the excitation intensity  $I_x$ ).

Since the probability of thermal delocalization from deep traps is very small ( $w_m, w_k, w_j \approx 0$ ), this process can be neglected. As a result, the maximum concentration of localized electrons ( $n_{m\infty}, n_{k\infty}$ ) will be determined by the competition of two processes: the localization of free electrons and the recombination of free holes with localized electrons. From (2), it is possible to obtain stationary concentrations of free electrons and holes, which are determined by the intensity of generation of free charge carriers ( $G$ ) and their lifetime in the zones ( $\tau^-, \tau^+$ ) [19]:

$$\begin{aligned} N^- &= G\tau^- = \frac{G}{\sum u^- \sigma_m^- \nu_m}, \\ P^+ &= G\tau^+ = \frac{G}{\sum u^+ \sigma_j^+ \nu_{pj}} \end{aligned} \quad (3)$$

When a steady state is reached, if we consider that the ratio of the cross sections of holes localization to the electron's localization  $\sigma_m^+/\sigma_m^-$  should not vary much for each of the deep traps, then for the maximum level of deep traps filling we get

$$\begin{aligned} \frac{n_{m\infty}}{\nu_m} &= \frac{1}{1 + (\sigma_m^+/\sigma_m^-) (\sum \nu_d \sigma_d^- / \sum \nu_p \sigma_p^+)} \approx \frac{n_{k\infty}}{\nu_k} \\ &= \frac{1}{1 + (\sigma_k^+/\sigma_k^-) (\sum \nu_d \sigma_d^- / \sum \nu_p \sigma_p^+)} = r_e \end{aligned} \quad (4)$$

For two types of luminescence centers ( $j=1,2$ ), which are deep traps for holes, it is also logical to introduce the level of their recharge ( $r_h$ ). For them, the corresponding kinetic equations will be

$$\begin{aligned} \frac{\partial p_1}{\partial t} &= P^+ u^+ \sigma_1^+ (\nu_{p1} - p_1) - N^- u^- \sigma_1^- p_1 = 0 \\ \frac{\partial p_2}{\partial t} &= P^+ u^+ \sigma_2^+ (\nu_{p2} - p_2) - N^- u^- \sigma_2^- p_2 = 0 \end{aligned} \quad (5)$$

Similarly, as for electrons, we get

$$\begin{aligned} \frac{p_{1\infty}}{\nu_{p1}} &= \frac{1}{1 + (\sigma_1^-/\sigma_1^+) (\sum \nu_{pj} \sigma_{pj}^+ / \sum \nu_d \sigma_d^-)} \approx \frac{p_{2\infty}}{\nu_{p2}} \\ &= \frac{1}{1 + (\sigma_2^-/\sigma_2^+) (\sum \nu_{pj} \sigma_{pj}^+ / \sum \nu_d \sigma_d^-)} = r_h \end{aligned} \quad (6)$$

if the ratio of the cross sections of the localization of electrons and holes  $\sigma_j^-/\sigma_j^+$  is not very different for various recombination centers.

At excitation in crystal phosphors at each moment of time, the charge conservation law must be satisfied; that is, the balance equation must be satisfied

$$p_1 + p_2 = \sum n_d \implies r_h (\nu_{p1} + \nu_{p2}) = r_e \sum \nu_d \quad (7)$$

The number of electrons localized in the traps should correspond to the number of localized holes. As a result, the following equation should be satisfied:

$$\begin{aligned} \frac{r_e}{r_h} &= \frac{\sum \nu_p}{\sum \nu_d} = \frac{1 + (\sum \nu_p \sigma_p^+ / \sum \nu_d \sigma_d^-) (\sigma_j^- / \sigma_j^+)}{1 + (\sum \nu_d \sigma_d^- / \sum \nu_p \sigma_p^+) (\sigma_m^- / \sigma_m^+)} \\ &\cong \frac{\sum \nu_p \sigma_p^+ \sigma_j^-}{\sum \nu_d \sigma_d^- \sigma_j^+} \end{aligned} \quad (8)$$

Equation (8) will be valid for all crystal phosphors, in which the ratio of localization cross sections for electrons and holes is not very different for various traps and for various luminescence centers.

By using (8), which we substitute in (4) and (6), we obtain simple relations for the filling levels of the deep traps and the recharge level of the luminescence centers:

$$\begin{aligned} r_e &= \frac{n_{m\infty}}{\nu_m} = \frac{n_{k\infty}}{\nu_k} = \frac{1}{1 + \sum \nu_d / \sum \nu_{pj}} = \frac{\sum \nu_{pj}}{\sum \nu_d + \sum \nu_{pj}} \\ r_h &= \frac{p_{1\infty}}{\nu_{p1}} = \frac{p_{2\infty}}{\nu_{p2}} = \frac{1}{1 + \sum \nu_{pj} / \sum \nu_d} = \frac{\sum \nu_d}{\sum \nu_d + \sum \nu_{pj}} \end{aligned} \quad (9)$$

Thus, the maximum recharge levels for the deep traps and luminescence centers are determined by the relation of concentrations, while the following is performed:  $r_e + r_h = 1$ .

For such a multicenter model of crystal phosphorus, it is possible to determine the kinetics of electron accumulation on deep traps by integrating the differential equation (1) with the initial condition: at  $t = 0$  all  $n_m = 0$ .

$$\begin{aligned} \frac{\partial n_m}{\partial t} &= N^- u^- \sigma_m^- (\nu_m - n_m) - P^+ u^+ \sigma_m^+ n_m \implies \\ &\frac{dn_m}{n_m - (N^- u^- \sigma_m^- / (N^- u^- \sigma_m^- + P^+ u^+ \sigma_m^+)) \nu_m} \\ &= -(N^- u^- \sigma_m^- + P^+ u^+ \sigma_m^+) dt \\ n_m(t) &= n_{m\infty} \left\{ 1 - \exp \left[ - \left( \frac{\sigma_m^-}{\sum \nu_d \sigma_d^-} + \frac{\sigma_m^+}{\sum \nu_{pj} \sigma_{pj}^+} \right) G \cdot t \right] \right\} \\ &= n_{m\infty} \left\{ 1 - \exp \left( - \frac{t}{t_{Gm}} \right) \right\} \end{aligned} \quad (10)$$

where

$$\begin{aligned} n_{m\infty} &= r_e \nu_m, \\ t_{Gm} &= \frac{1}{(\sigma_m^- / \sum \nu_d \sigma_d^- + \sigma_m^+ / \sum \nu_{pj} \sigma_{pj}^+) G} \end{aligned} \quad (11)$$

The  $t_{Gm}$  parameter differs for various traps, but their difference is determined by various localization cross sections. And since their difference is within the same order, the rates

of light sum accumulation on different traps will not differ very much. Of course, less deep traps saturate faster because  $\sigma_m^- > \sigma_k^-$  if  $m < k$ . It is also confirmed experimentally (see Figures 3 and 4).

Respectively, according to the balance equation, the kinetics of accumulation of the recharged luminescence centers will be

$$p_1(t) + p_2(t) = \sum_m n_{m\infty} \left\{ 1 - \exp\left(-\frac{t}{t_{Gm}}\right) \right\} \quad (12)$$

Considering (9), eventually, we have

$$\begin{aligned} p_1(t) &= r_h v_{p1} \frac{\sum_m n_{m\infty} \{1 - \exp(-t/t_{Gm})\}}{\sum_m n_{m\infty}}, \\ p_2(t) &= r_h v_{p2} \frac{\sum_m n_{m\infty} \{1 - \exp(-t/t_{Gm})\}}{\sum_m n_{m\infty}} \end{aligned} \quad (13)$$

Thus, a theoretical consideration of the light sum accumulation in the crystal phosphors showed that, first, the maximum value of the accumulated light sum does not depend on the intensity of the exciting radiation, and the total concentrations of the deep traps and recombination centers are decisive. Secondly, the accumulated light sum value is determined by the radiation dose (a product of the intensity of the exciting radiation by the exposure  $D_X = I_X \cdot \tau_X$ ). Thirdly, the kinetics of accumulation of the light sum on each type of deep trap are described by its simple exponential dependence, which allows determining the parameters of this exponent by several experimental points.

An important difference of the X-ray excitation is the spatial microinhomogeneity of the generation of the electronic excitations upon absorption of an X-ray quantum. Thousands of generated  $e-h$  pairs are in a small area with a diameter of less than 0.5 microns. The Coulomb interaction between electrons and holes prevents the rapid expansion of this region. As a result, if there are a sufficient number of recombination centers in the material, as in our ZnSe samples, most of the free charge carriers will recombine in this local region, creating scintillations. It is confirmed experimentally by the dose dependencies of the luminescence at low temperatures [20]. It also means that not all generated free charge carriers are involved in the conductivity and localization on deep traps [23, 24].

**3.1. The Experimental Dose Dependencies of TSC and TSL in ZnSe.** The dose dependencies for the light sum accumulation in the ZnSe single crystals on different traps were determined by the intensities of the main TSL and TSC peaks. Each TSL and TSC curve was decomposed into components so that the sum of the components did not differ from the experimental TSL and TSC curves by more than 5%. We discovered that curve shapes (their half widths and peak temperature positions) are similar for different doses of X-ray radiation. Of course, at the same time, we neglected the peaks with very low intensities.

For all dose dependencies of the TSL and TSC peaks obtained at two X-ray excitation intensities ( $I_{X1} = 0.13$  and

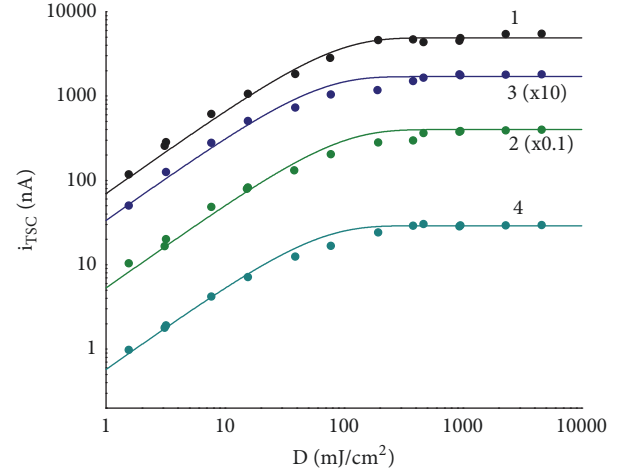


FIGURE 5: Dose dependencies of TSC peaks of ZnSe (#2)  $T_m = 143$  K (1), 170 K (2), 183 K (3), and 224 K (4) with  $U_0 = 15$  V (dots) and theoretical curves of the light sum accumulation (solid lines) by (10).

$I_{X2} = 0.64$  mW/cm<sup>2</sup>) we have almost similar peak intensities at the same radiation doses. That is, if  $I_{X1} \cdot \tau_{1X} = I_{X2} \cdot \tau_{2X}$ , then the corresponding TSL and TSC curves coincide with each other within the limits of error.

The characteristic dose dependencies of the TSC peaks of ZnSe single crystal at two X-ray excitation intensities are shown in Figure 5 by the example of the second sample (dots are the experimental values; lines are the theoretical dependencies (10)), the dependencies (2) and (3) are multiplied by certain coefficients for greater visibility. As expected, the  $t_{Gm}$  parameter value for different TSC peaks does not differ much from each other. Most importantly, the maximum accumulated concentration of electrons in deep traps does not depend on the intensity of the exciting X-ray radiation, that is,  $n_{m\infty} \neq f(G)$ .

Thus, the proposed multicenter model of crystal phosphor more sufficiently describes the light sum accumulation on deep traps than the classical kinetic theories. The second important point is that the kinetics of electron accumulation on traps is well described by the exponential dependence (10). The same dependence is observed for TSL. Figures 6 and 7 show the dose dependencies of TSL-630 and TSL-970.

All dose TSL and TSC curves are well approximated by the exponential dependence. Moreover,  $t_{Gm} = \tau_{exp} \cdot I_X$  for each peak (that is, for each type of trap) there are almost the same values for the two excitation intensities and which differ fivefold. It means that the rate and kinetics of the light sum accumulation for each peak are the same at any excitation intensity.

When comparing the light sum accumulation for each peak in different recording channels, it should be noted that there is a more rapid saturation of TSC peaks rather than the TSL peaks ( $t_{Gm}^{TSC}$  less related  $t_{Gm}^{TSL}$  by several times). It agrees well with the core differences between TSL and TSC. The TSC curves show the variation of the concentration of the free electrons delocalized from the traps  $N^-(T)$ , while the TSL curves are the product of the concentration of free electrons

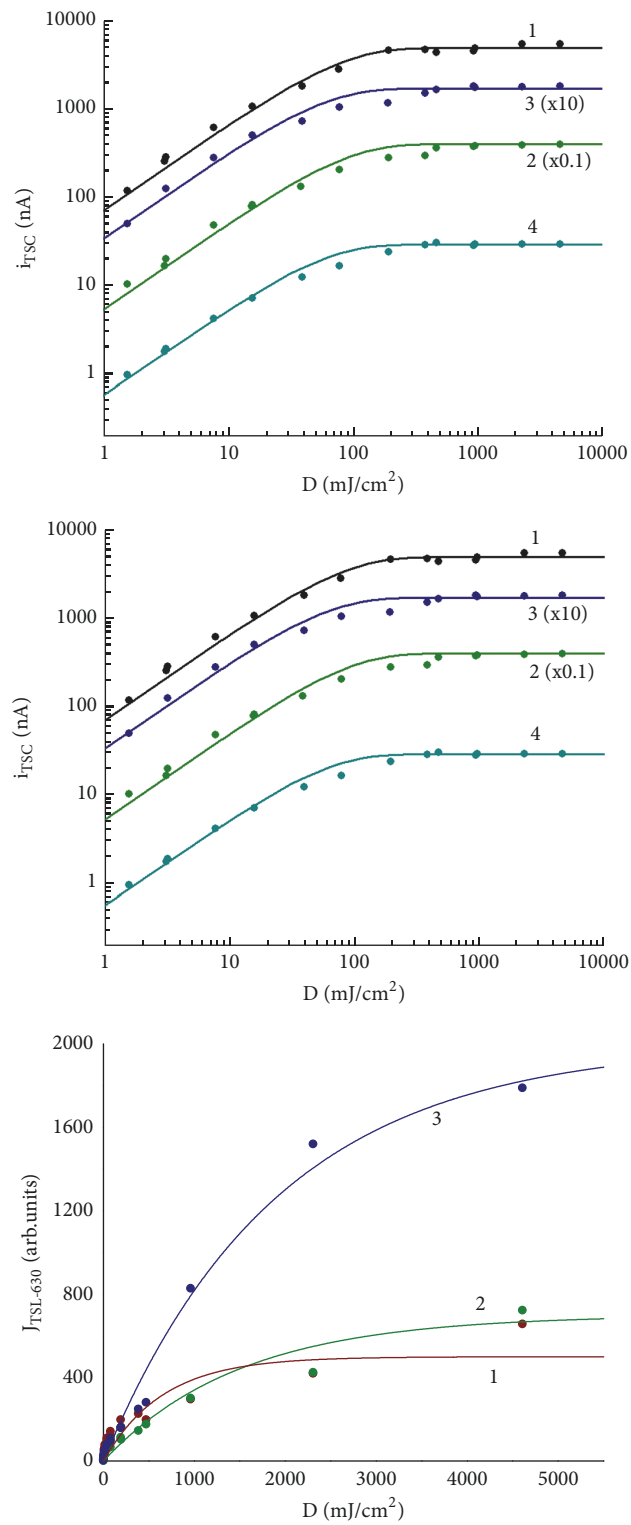


FIGURE 6: Dose dependencies of the TSL-630 peaks at  $T_m = 129$  K (1), 184 K (2), and 211 K (3) of the sample #1 under two intensities of X-ray excitation and the theoretical curves of the light sum accumulation (solid lines).

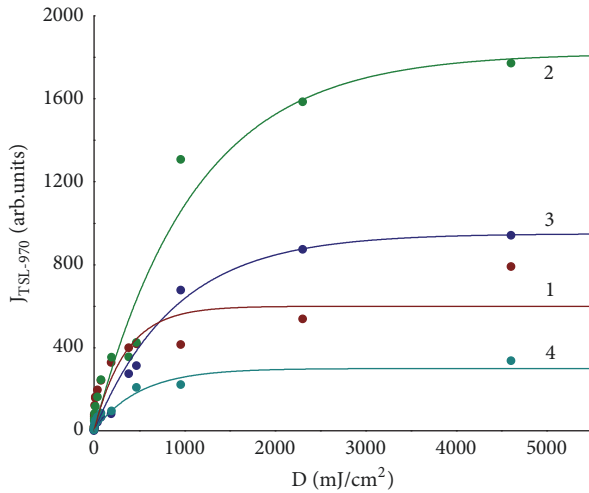


FIGURE 7: Dose dependencies of the TSL-970 peaks at  $T_m = 129$  K (1), 184 K (2), and 211 K (3) of the sample #1 under two intensities of X-ray excitation (dots) and the theoretical curves of the light sum accumulation (solid lines) by (10).

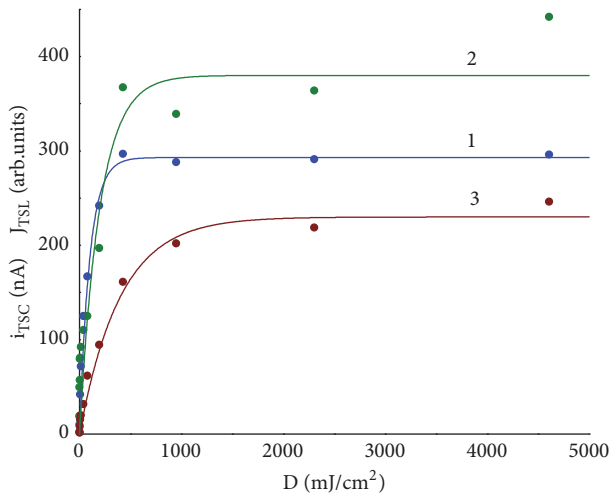


FIGURE 8: Dose dependencies of TSC (1), TSL-630 (2), and TSL-970 (3) peak  $T_m = 224$  K of the ZnSe #2 sample at two X-ray excitation intensities (dots) and theoretical light sum accumulation curves (solid lines) by (10).

on the concentration of the recharged luminescence centers  $N^-(T) \cdot p(T)$ . As is known, the intensity of luminescence recombination is understood as the total number of free carriers' recombination events at the recharged recombination centers. It means that the dose dependencies of the TSC and TSL will differ, since  $p(T)$  also changes during the excitation and the light sum accumulation and, accordingly, when recombining delocalized electrons. But it should be noted that the change in the concentration of the recharged luminescence centers occurs only by the magnitude of the delocalized electrons. That is, a relative change in the number of the recharged luminescence centers is not very significant when one type of an electron trap gets emptied. That is why the temperature positions of the corresponding TSL and TSC peaks differ slightly. For example, Figure 8 presents the dose

dependencies of the peak at  $T_m = 224$  K of the second sample observed in both TSC and TSL-630, as well as TSL-970.

When comparing TSL-630 and TSL-970 it is necessary to take into account the fact that the intensity of the luminescence, which is being recorded, is due to the intracenter quantum output of the luminescence center and its temperature dependence; the geometric coefficient (determined by that part of the luminescent quanta that enters the recording system) by the spectral sensitivity of the recording system in the region of the luminescence spectrum. In fact, we consider a relative intensity, which is proportional to the product of the concentrations of free electrons and recharges of the recombination centers. The study of TSL and TSC of other zinc selenide single crystals did not reveal experimental facts that would contradict with these experimental results and theoretical conclusions.

Based on the results obtained, one can explain the behavior of the dose dependencies of the TSL and TSC for all traps. Thus, the total concentration of traps in the second sample is greater than in the first ZnSe sample. The light sum accumulation rate is determined by the ratio of recombination centers in the concentration of traps (and not just the traps concentration). The smaller the size of the localization region of the carriers at the absorption of an X-ray quantum is, the greater the concentration of traps is. Accordingly, in the first sample, a smaller part (than in the second one) of charge carriers goes to localization when one X-ray quantum is absorbed. It causes a slower initial rate of the light sum accumulation in the sample.

#### 4. Conclusions

In ZnSe single crystals, the TSL curves, when detected on two luminescence bands (630 and 970 nm), and TSC curves have a similar character. It indicates that the peaks in the TSL and TSC are due to delocalization of the carriers from a trap to a zone of their subsequent recombination on both types of the recharged luminescence centers (630 and 970 nm). While the differences in the parameters of the light sum accumulation during the TSL registration on two luminescence bands are due to the difference in the parameters of the luminescence centers and their concentrations.

A theoretical model of crystal phosphors with several types of traps has been proposed for which was found next: (1) the accumulation of the light sum on each trap is described by a simple exponential dependence with its characteristic accumulation time and (2) the maximum accumulated light sum at the X-ray excitation does not depend on the intensity of exciting radiation. These conclusions are experimentally confirmed by the research of light sum accumulation in ZnSe single crystals at X-ray excitation.

It means that the classical model of crystal phosphor with one type of traps, which provides for a maximum accumulated light sum the dependence  $n_{\infty} \sim \sqrt{I_{ex}}$  is too simplistic. It is necessary to use a model of crystal phosphors with several types of traps, for which the dynamics of the accumulation of the light sum on each trap is described by a simple exponential dependence with its characteristic accumulation time and which gives the independence of



the value of the maximum accumulated light sum from the excitation intensity.

### Data Availability

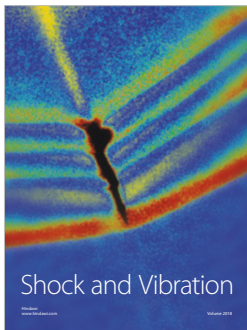
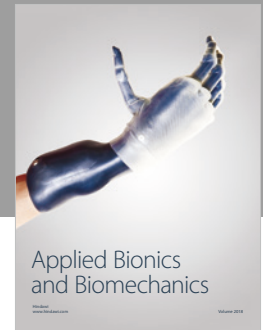
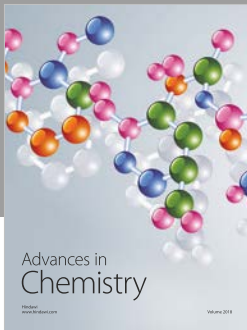
All authors declare that they agree to share the data underlying the findings of their manuscripts. Accordingly, they were provided “data availability” to publish the data used in their manuscripts.

### Conflicts of Interest

The authors declare that they have no conflicts of interest.

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