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RADIATION EFFECTS IN SEMICONDUCTOR SCINTILLATORS BASED ON ZINC SELENIDE

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Effects have been studied of gamma-radiation (E_γ=1.25 MeV) in doses of $D_\gamma \le 5\cdot10^9$ rad upon light output and spectral-kinetic luminescence characteristics of new semiconductor scintillators (SCS) based on isovalently doped (with tellurium and oxygen) zinc selenide crystals. SCS crystals have been shown to be of extremely high radiation stability, and changes in their optical and luminescent properties became noticeable only under doses D_γ>(7-9)$\cdot10^7$ rad. Under gamma-irradiation with D_γ>(2-5)$\cdot10^9$ rad and P_γ=7.7$\cdot10^2$ R$\cdot$s^{-1}, in the surface layer (estimated in tens of nanometers) radiolysis of the crystalline structure occurs, and the loss of mass is observed for the samples (at T=320 K). Mechanisms are considered that describes variation of SCS properties under powerful radiation fluxes.

1. INTRODUCTION

Interest in studying A^2B^6 compound based crystals has increased lately because of their promising application as scintillation detectors with some characteristics being superior to the existing ones [1]. Development of new types of semiconductor scintillators on the basis of isovalently doped zinc selenide crystals has allowed to efficiently broaden the rather short list of scintillators used in low-energy (E<100 keV) X-ray technical introscopy and medical tomography. As distinct from crystals CsI(Tl), which are the most widely used for these purposes, scintillators based on ZnSe(Te,O) crystals are not hygroscopic, their light output is 1.1 to 1.5 times higher, and afterglow level after 10 ms is by 2 to 3 orders of magnitude lower with respect to CsI(Tl) [1,3-5]. Decay time (3-10 μs) and density (5.42 g$\cdot$cm^{-3}) of these new scintillators are quite acceptable for their use in detectors for X-ray introscopy; their radiation stability is not worse, and light output is 2.5-4 times higher than with crystals $CdWO_4$, $Bi_4Ge_3O_{12}$, Gd_2SiO_5 used for similar purposes. The radiation stability of the commonly used CsI(Tl) crystals is rather low – already under gamma-radiation doses of 10^3 to 10^4 rad their scintillation properties are significantly deteriorated. At the same time, according to our preliminary data, output characteristics of ZnSe(Te,O)-based semiconductor scintillators (SCS) remain essentially unchanged under much higher dose loads [1, 4]. In the present work, new data are presented on the effects of high doses of ionizing radiation (gamma, neutrons) upon luminescent and optical characteristics of scintillators based on zinc selenide.

2. SAMPLES AND EXPERIMENTAL PROCEDURE

Isovalently doped zinc selenide crystals were grown in graphite crucibles by Bridgman-Stockbarger method in vertical compression furnaces under argon pressure 5$\cdot$10^6 Pa. Growth rate was 2 to 5 mm/hour, and the temperature in the crystallization zone was ~1850 K. As initial raw material, we used polycrystalline zinc selenide of 5N offered by ELMA Inc. Concentration of activator dopants was 0.01 to 0.5 wt. %. The main impurity in the grown crystals was carbon (from the growth crucibles), concentration of which was 0.1 to 0.3 wt. %. Three series of ZnSe(Te) crystals have been studied: i) A series - the appropriate mixture of ZnSe and ZnTe powders (with 0.5 mass % Te) was treated in reducing atmosphere before growing crystals, the samples are labeled AN; ii) B series – crystals of ZnSe with ~0.1 wt. % Te were subjected to treatment in oxygen containing atmosphere by the method described in [5], labeled BN; iii) C series - crystals of ZnSe with <0.03 wt. % Te were treated in oxygen (like B), labeled CN [5]. At the final stage of formation of scintillation properties, one half from each series of crystals was annealed in Zn vapor (24 hours, 1290 K). The samples are labeled AT, BT and CT. Further only this type of samples will be referred to as "SCS", to distinguish them from the as-grown (not annealed in Zn vapor) ZnSe(Te,O) crystals. All samples used in our experiments were of dimensions 10×10×5 mm^3.

Gamma-irradiation of the samples was carried out in evacuated tubes using a channel type ^{60}Co installation at exposure dose rates P_γ up to 10^3 R$\cdot$s^{-1} (the average energy of gamma-quanta $E_\gamma \approx 1.25$ MeV, the absorbed dose $D\gamma \le 5\cdot10^9$ rad). Under irradiation of all these types, the temperature of the samples did not exceed 360 K. X-ray luminescence (XL) of semiconductor scintillator samples was measured under excitation using an IRIS-3 X-ray source (U_a=35 kV, $i_a \le 35$ mA, Cu anticathode). Concentration of activator Te in the crystals was determined by X-ray luminescence analysis, concentration of oxygen – by the neutron activation method using nuclear reaction $^{16}O(n,p)^{16}N$.

3. RESULTS AND DISCUSSION

At first all samples were weighed and studied by the method of X-ray-element analysis. The determined values were the absolute content of Te and O in wt. %, the content of Zn and Se in arbitrary units, as well as Se/Zn ratio. At the ideal stoichiometric composition of ZnSe (atom ratio Se/Zn=1) the crystals contain 54,7 wt. %=$4.17 \cdot 10^{21}$ cm^{-3} of Se and 45,3 wt. %=$4.17 \cdot 10^{21}$ cm^{-3} of Zn. Table 1 shows the experimental data on composition of AN, AT, BN, BT, CN, CT series of ZnSe(Te,O) crystals.

Table 1

Composition, stoichiometry and luminescent characteristics of ZnSe(Te,O) crystals at 300 K. Light output of XL I_{XL} (measured by Si-PD) is normalized to CsJTl I_{XL}=1, and all the intensities of GL (PM) I_{GL} are normalized to that of the reference sample CN3

Sample	[Te], wt. %	[O], wt.%	Se/Zn ratio	I_{XL}, a.u.	XL, λ_{max}, nm	GL, λ_{max},, nm	I_{GL}, at 10^6 rad, a.u.	λ_{max}, at 10^9rad, nm	I_{GL}, at 10^9 rad, a.u.
AN8	0.26	0.014	0.852	0.1	640	640	0.3	490	0.8
AN9	0.57	0.011	0.854	0.34	640	690	0.4	720	1
BN6	0.18	0.021	0.851	0.26	630	650	1.3	680	2.8
CN3	<0.01	0.029	0.861	0.16	610	620	1	-	-
CN5	<0.01	0.027	0.849	0.27	610	620	1	660	2
AT5	0.28	0.012	0.836	0.64	635	640	2.6	660	2.6
AT7	0.49	0.014	0.838	0.69	635	640	4.5	670	1.8
BT12	0.19	0.020	0.843	0.47	625	630	2.6	670	1.1
CT5	0.008	0.026	0.841	0.43	600	610	1.8	690	1.4
CT8	0.009	0.028	0.845	0.41	600	610	1.6	690	1.3

Samples from AN and AT series has about 0.25-0.5 wt. % Te. The actual content of Te in BN and BT samples was ~0.18 wt. %, and that in CN and CT samples was about 0.01 wt %. Besides, all samples turned out to be non-stoichiometric: 49 mass % Se to 51 mass % Zn, which means $3.75 \cdot 10^{21}$ cm^{-3} Se atoms to 4.68×10^{21} cm^{-3} Zn atoms. Thus, the surplus of Zn atoms (or the number of V_{Se}) was found to be ~$0.9 \cdot 10^{21}$ cm^{-3} in samples both untreated and treated in Zn vapor, slightly depending on Te content. However, measuring the Zn profile could give a higher concentration of Zn in bulk and near the surface of the treated samples (series T). The stoichiometry deviations in A^2B^6 crystals, determining the presence of pre-radiation defects are affecting significantly the radiation stability [6].

It is well seen from the Table that the light output of T-series samples (treated in Zn vapor) is higher than in N-series (untreated), as it should be expected [1]. The treatment in Zn vapor was found to decrease the number of single Zn vacancies, unless they were trapped at Te sites to form stable luminescent centers responsible for high light output of XL at 635-640 nm. Luminescent centers containing oxygen impurity in B and C series of samples are responsible for another band peaked at 600-610 nm.

Spectral composition of gamma-luminescence (GL) induced by steady ^{60}Co-gamma-irradiation of ZnSe(Te,O) at the dose rate of $7.7 \cdot 10$ $R \cdot s^{-1}$ at 77 and 300 K was studied using the set-up including a light guide and monochromator SPM2 with photomultiplier (PM). The accumulated gamma-dose after the first scanning of GL spectrum at 77 K was $3 \cdot 10^5$ rad, and 10^6 rad after the second scanning at 300 K (shown in figures 1-4,a). Spectra of GL were taken at 77 and 300 K after prolonged irradiation of the samples to high gamma-doses of $<10^9$ rad and washing out the radiolysis products (shown in figures 1-4, b). For a better comparison all GL measurements were carried out at the same conditions (slit width and amplification degree) and normalized to the intensity of GL at 300 K I_{GL}=1. It should be noted that the monochromator was 5 m apart from the samples under the gamma-source, so the actual intensity of GL was much higher. No correction was done for spectral sensitivity of PM, since the aim of this study was to compare impurity and dose effects on intensity and wavelength of GL. Both the figures and Table 1 demonstrate clearly these effects.

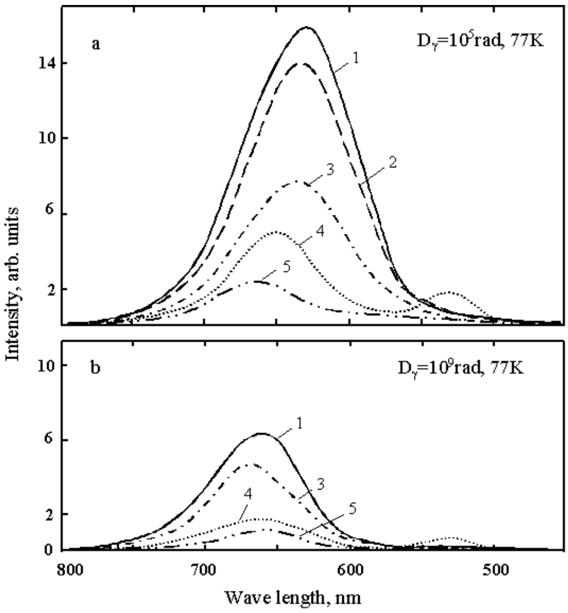

Fig. 1. Gamma-luminescence of ZnSe(Te,O) crystals (as-grown; 1 – CN5, 2 – CN3, 3 – BN6, 4 – AN9, 5 – AN8) at 77 K and different doses (a – 10^5 rad, b – 10^9 rad). Reference sample CN 3 was not irradiated to 10^9 rad. Characteristics of the labeled samples are shown in Table 1

Comparison of XL and GL spectra at 300 K (see Table 1 and Figs. 2 and 4) shows that the wavelength of the GL band maximum λ_{max} is shifted to the "red" side. This is because XL is excited in the thin subsurface ZnSe(Te,O)-ZnO layer, and GL – in the whole bulk mostly untreated and having just the intrinsic defects.

In all samples irradiated to the high gamma-dose

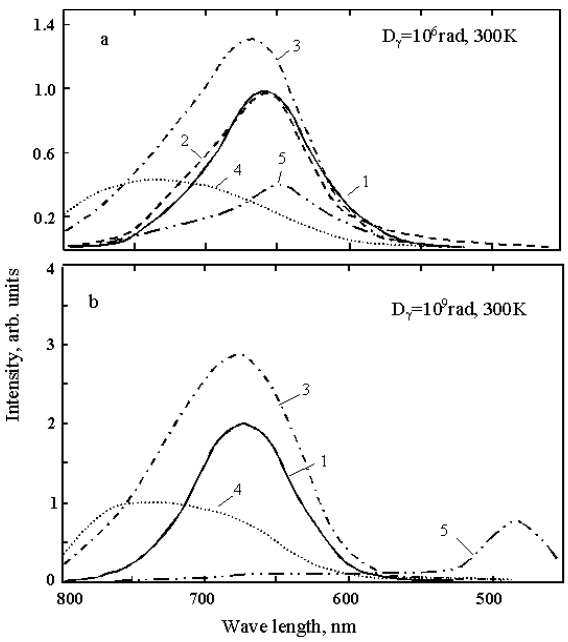

Fig. 2. GL of ZnSe(Te,O) crystals (as-grown; 1 – CN5, 2 – CN3, 3 – BN6, 4 – AN9, 5 – AN8) at 300 K (a – 10^6 rad, b – 10^9 rad). Reference CN3 was not irradiated to 10^9 rad

(2-5)·10^9 rad (Figures 1-4, b) the spectra of GL at 77 and 300 K changed both in wavelength and intensity. The intensity of GL at 77 K decreased by about 2-3 times, except the bands at 480 and 530 nm, which remained unchanged (Fig. 1, b and Fig. 3, b).

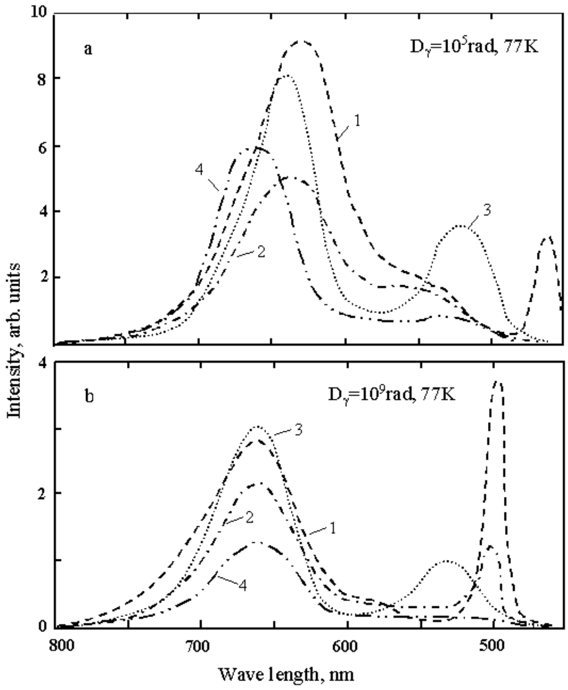

Fig. 3. GL of SCS crystals (treated in Zn vapor; 1 – CT8, 2 – BT12, 3 – AT7, 4 – AT5) at 77 K (a – 10^5 rad, b – 10^9 rad)

As expected, the intensity of GL at 300 K decreased by two times only for 2 samples - AT7 and BT12, while AT5 and CT8 remained unchanged (Fig. 4, b). It should be pointed out that in AN8 sample containing 0.26 % Te the weak band at 650 nm vanished, and a new much more intense band appeared at 470-490 nm. In the rest of the studied samples of N series the intensity of GL at 300 K even increased by 2 times (Fig. 2, b). Defect centers of different energies have been generated under irradiation at 300 K, and the as-grown centers have been destroyed. The number of the deepest centers containing Te (mostly in A series of samples) was unchanged or decreased to a lesser extent than those related to oxygen (in B and C series). The long irradiation seemed to destroy the impurity defect complexes and to create both shallow recombination centers (480 nm) and deep centers (red bands). Then the red luminescence at 670-720 nm can be attributed to recombination at the radiation-induced isolated V_{Zn} in the presence of Te in A and B series or O in B and C series of crystals [1,2,5]. Then the green-yellow bands at 500-600 nm can be ascribed to isolated O impurity defects.

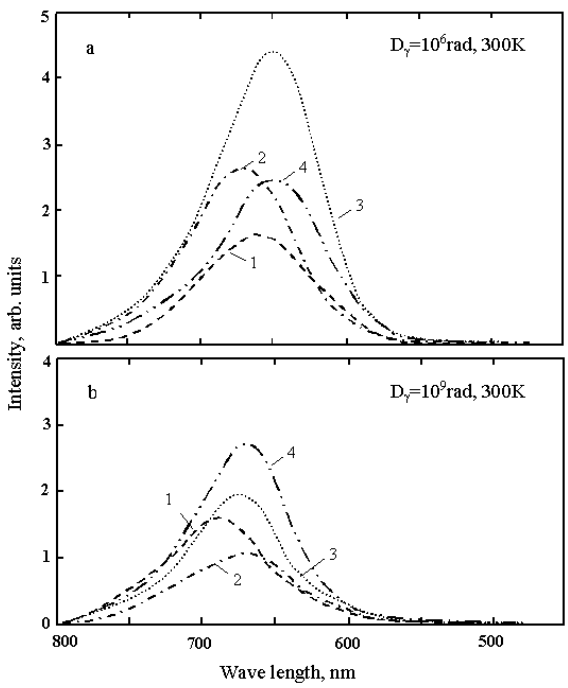

Fig. 4. GL of SCS crystals at 300 K (1 – CT8, 2 – BT12, 3 – AT7, 4, 4' – AT5; a – 10^6 rad, b – 10^9 rad)

The product of radiolysis of the surface layer after gamma-irradiation to 10^9 rad at 300 K was studied by the X-ray-analysis: the amount of the product and the depth of the removed layer were estimated quantitatively. The total activity of the layer washed out from the surface of all 8 samples (160 mm^2) was $1.6 \cdot 10^{-5}$ g for Zn isotopes and $1.35 \cdot 10^{-5}$ g for Se isotopes, which made 10^{-7} g/mm^2. The composition of the radiolytic product was found to be the same as that for the non-irradiated samples. Taking into account the density of ZnSe matrix [1], the depth of the damaged and removed layer was about 5-20 nm. It should be mentioned that the most obvious part of the radiation damage occurred at the edges and corners of a sample bar, because they change color (become reddish) and become smoothened.

Gamma-irradiation to a moderate dose $(5\text{-}8)\cdot 10^7$ rad alone caused neither a noticeable radiolysis nor optical changes. Neutron-irradiation ($F_n < 10^{15}$ cm^{-2}) results only in 10-40 % increasing of the light output [4]. A higher dose ($\sim 2\times 10^9$ rad) caused more damage of the subsurface layer. The zinc mass loss turned out to be larger than that of selenium, and the absorption edge and the luminescence band shifted toward longer wavelengths. Radiation induced adsorption of oxygen followed by formation of ZnO micro-inclusions in the sub-surface layer is suggested for explaining the observed radiolysis effects and changes in the optical spectra and luminescence kinetics. The recombination luminescence under gamma-irradiation at different temperatures will be discussed below as a competing factor for the radiolysis (the more intense GL is, the less effective the radiolysis and the higher the radiation hardness should be).

Among several experimental facts obtained here the observation of extremely high radiation stability of SCS and radiolysis products after the high gamma-dose of 10^9 rad seems to be the most interesting. Theoretical description of high radiation hardness of isovalently doped and nonstoichiometric A^2B^6 crystals at low irradiation dose rates was carried out in [6]. For high dose rates, since the radiation-induced damage occurs in a thin subsurface layer of about 5-10 nm, the following model is suggested. The gamma-irradiation produces defects in the whole bulk of samples by means of ionization. The ionization is a source of elastic shock waves, and the waves become a source of the surface damage. In this model all edges and corners of a sample bar must be damaged more effectively, what indeed occurs in the experiment. Such a factor of the surface damage under a high dose gamma-irradiation is considered below

$$E_k^{(1)} > E_k^{(2)} > E_k^{(3)} \,;\; E_l^{(1)} > E_l^{(2)} > E_l^{(3)},\;\; E_m^{(1)} > E_m^{(2)} > E_m^{(3)}.$$

Let us select the types of atoms in the spheres in such a way that

$$E_k^{(1)} - E_l^{(1)} \geq 3E_k^{(2)};\quad E_k^{(2)} - E_l^{(2)} \geq 3E_k^{(3)}\,;\;\; E_k^{(3)} - E_l^{(3)} \geq 3E_k^{(4)}.$$

Since the ionization cross-section for a high energy Auger-electron (E) has the maximum at $E \geq 3E_i$, the primary ionization of k-shell of the central heavy atom will cause a specific picture of Auger-cascade evolution in the onion-like structure having such a hierarchy.

Indeed, the Auger-electron of the central atom, emitted with the energy

$$E_{k\text{-}l}^{(1)} = E_k^{(1)} - E_l^{(1)},$$

causes the ionization of k-shell of an atom of the second layer with the probability $w_2 = l_2\sigma_2 N_2$. Auger decay of the generated hole in the second layer produces a fast electron with the energy

$$E_{k\text{-}l}^{(2)} = E_k^{(2)} - E_l^{(2)}$$

and the probability $w_3 = l_3\sigma_3 N_3$ etc, where l_i is the thickness of the i-layer of the “onion”, N_i – concentration of i-type atoms in i-layer, σ_3 – cross-section of k-ionization in i-layer. As a result, k-holes are produced in all layers of the onion structure, each of them creating its own “Coulomb explosion” with the probability $\alpha_A^i\,\eta^i$, where η^i – probability of ion channel of relaxation of multi-charge state in i-layer after Auger-cascade, and the whole structure releases a large energy for very short time $\tau_{tot} = \sum\tau^i$ (from i to n) $E_{exp} = E_k^{(1)} - \sum E_{k\text{-}l}^{(1)}$.

The probability (or cross-section) of the considered process is

$$W_{tot} = \prod_{i=1}^{n} W_i\,,\sigma_{tot} = \sigma_k^{(1)} \prod_{i=2}^{n} W_i\,,$$

where n is the number of layers of the “onion”, $W_i(\sigma_i)$ – probability (cross-section) of ionization of k-hole in the central atom.

An energy density released in the “onion” is $\Lambda = E_k^{(1)} \left(\sum_{i=1}^{n} l_i \right)^{-3}$. If to accept $l_i = l_o$, the cross-section of the process exerting the energy E_{exp} will be

$$\sigma_{tot}(E) = \sigma_k^{(1)} (\sigma_o N_o l_o)^{n-1} = \\ = \sigma_k^{(1)} (\sigma_o N_o)^{n-1} \left[\frac{E_k^{(1)}}{\Lambda} \right]^{n-1/3} n^{1-n} \sim \Lambda^{\frac{1-n}{3}}.$$

Thus, $\sigma_{tot}(E)$ decreases with increasing the density of the exerted energy.

For the case of Auger-cascade in an isolated heavy atom the density of the exerted energy is estimated as

$$\Lambda_1 = \left[E_k^{(1)} - \sum_{i=1}^{n} E_1^{Auger} \right] \Omega^{-1} \approx 10 eV \overset{0}{A}^{-3}.$$

Here $\sum_{i=1}^{n} E_1^{Auger}$ - the sum of kinetic energies of all Auger-electrons in the atom where the Auger cascade develops: Ω - the atomic volume. Then for “onion” structure of 3 layers the exerted energy density is

$$\Lambda_2 = E_k^{(1)} \left(3\Omega^{1/3} \right)^{-3} \geq 1000 eV \overset{o}{A}^{-3} >> \Lambda_1.$$

Obviously, the destruction effect in the both cases is quite different. It is caused both by the Coulomb explosion inside the “onion” and structure damage in its environment by means of shock waves. The shock wave exerts the pressure on the front $P \sim \left(E_k^{(1)} \right)^{6/5} t^{5/6}$, where t is the time passed since the moment of exerting energy in the “onion”. This effect can be initiated both
by external influence and k-capture in the central atom.

Thus, in ZnSe and especially ZnSe(Te,O) crystals intensive gamma-irradiation generates quite powerful shock waves. On reaching the surface of crystals, these waves can destroy it. The estimations show, that the condition, when the pressure of the shock waves P is larger than the Young modulus E, can be realized at rather large radius r, which confirms the suggested model.

4. CONCLUSION

Scintillators based on ZnSe(Te,O) crystals have high radiation stability, preserving satisfactory output characteristics up to gamma -irradiation doses of $D_\gamma = 1 \cdot 10^8$ rad. High dose ($>10^9$ R) gamma-irradiation induces elastic shock waves causing heavy lattice damage and radiolysis of ~10-20 nm subsurface layer.

Accounting for their high light output and low afterglow level, SCS are now the most suitable choice of scintillator material for modern X-ray introscopic systems and tomographs, as well as dosimeters for detection of power X-ray and gamma-radiation fluxes.

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РАДІАЦІЙНІ ЕФЕКТИ У НАПІВПРОВІДНИКОВИХ СЦИНТИЛЯТОРАХ НА ОСНОВІ СЕЛЕНІДУ ЦИНКУ

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Вивчено вплив гамма-випромінення з енергією E_γ =1.25 МеВ і дозами $D_\gamma \leq 5 \cdot 10^9$ рад а також нейтронів ($E_n > 0.55$ еВ, з них 85% с $E_n > 3$ МеВ) на світловий вихід і спектрально-кінетичні характеристики люмінесценції нових напівпровідникових сцинтиляторів (НПС) на основі ізовалентно легованих (телуром, киснем) кристалів селеніда цинку. Показано, що кристали НПС мають дуже високу радіаційну стійкість, і зміна їх оптичних і люмінесцентних властивостей стає помітним тільки при дозах $D_\gamma > (7 \ldots 9) \cdot 10^7$ рад. При дозах гамма-випромінення $D_\gamma > (2 \ldots 5) \cdot 10^9$ рад і $P_\gamma = 7.7 \cdot 10^2$ Р·с$^{-1}$ у поверхневому прошарку, оцінюваному в десятки нм, спостерігаються радіоліз кристалічної структури і втрата маси зразків (при T=320 К). Розглянуто механізми змін властивостей НПС під дією потужних потоків випромінювань.

РАДИАЦИОННЫЕ ЭФФЕКТЫ В ПОЛУПРОВОДНИКОВЫХ СЦИНТИЛЛЯТОРАХ НА ОСНОВЕ СЕЛЕНИДА ЦИНКА

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Изучено влияние гамма-излучения с энергией E_γ=1.25 МэВ и дозами $D_\gamma \leq 5 \cdot 10^9$ рад, а также нейтронов ($E_n > 0.55$ эВ, из них 85% с $E_n > 3$МэВ) с флюенсами $F_n \leq 10^{19}$см^2, на световыход и спектрально-кинетические характеристики люминесценции новых полупроводниковых сцинтилляторов (ППС) на основе изовалентно легированных (теллуром, кислородом) кристаллов селенида цинка. Показано, что кристаллы ППС обладают очень высокой радиационной стойкостью, и изменение их оптических и люминесцентных свойств становится заметным только при дозах $D_\gamma > (7 \ldots 9) \cdot 10^7$ рад. При дозах гамма-излучения $D_\gamma > (2 \ldots 5) \cdot 10^9$ рад и $P_\gamma = 7.7 \cdot 10^2$ Р·с$^{-1}$ в поверхностном слое, оцениваемом в десятки нм, наблюдаются радиолиз кристаллической структуры и потеря массы образцов (при T=320 К). Рассмотрены механизмы изменений свойств ППС под действием мощных потоков излучений.