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RADIATION-INDUCED PROCESSES IN A^2B^6 AND OXIDE COMPOUNDS UNDER PROTON AND GAMMA-IRRADIATION

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Changes in scintillation and optical properties of semiconductor scintillators (SCS) based on ZnSe(O,Te), ZnSe(Cd), ZnCdS(Te), ZnSSe(Te) and $CdWO_4$ (CWO) crystals were studied under influence of ionizing radiations: gamma (~1.3 MeV, up to 500 Mrad), protons (~18 MeV, fluence up to 10^{16} per·cm^{-2}), electrons (0.54 to 2.26 MeV, up to 50 Mrad), and neutrons (source - thermal reactor channel, fluence up to 10^{18} per·cm^{-2}). SCS and CWO crystals have high radiation stability (RS) towards irradiation by gamma-rays and neutrons. Under proton irradiation, CWO scintillators have much higher RS as compared with SCS. For SCS under gamma-irradiation with D_γ>(2…5)·10^9 rad and P_γ=7.7·10^2 R·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).

INTRODUCTION

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 [1, 2]. As distinct from crystals CsI(Tl), which are the most widely used for these purposes, scintillators based on SCS crystals are not hygroscopic, their light output is 1.1 to 1.5 times higher, and afterglow level after 10 ms – by 2 to 3 orders of magnitude lower with respect to CsI(Tl) [1, 3]. Decay time (3-10 μs) and density (5.42 g·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 CWO, $Bi_4Ge_3O_{12}$, 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(O,Te)-based semiconductor scintillators (SCS) remain essentially unchanged under much higher dose loads [4]. In the present work, new data are presented on the effects of high doses of ionizing radiation (gamma, electrons, protons, neutrons) upon luminescent and optical characteristics of scintillators based on zinc selenide and CWO crystals.

EXPERIMENTAL

Gamma-irradiation of the samples was carried out using a channel type ^{60}Co installation at exposure dose rate P_γ up to 3·10^3 R·s^{-1} (the average energy of gamma-quanta E_γ≈1.25 MeV, the absorbed dose Dγ≤8.5·10^8 rad). Electron irradiation (β) (E_β=0.54…2.26 MeV, P_β=3·10^9 s^{-1}·cm^{-2}, equivalent dose $D_{\beta e}$ ≤ 5·10^7 rad) was carried out by a (^{90}Sr+^{90}Y)-source, and the proton irradiation (p) – using a U-150 type cyclotron (E_p=18 MeV; beam current density 1.9·10^8 A·cm^{-2}; fluence F_p≤1.7·10^{15} cm^{-2}). Neutron (n) irradiation of the samples was effectuated in the thermal channel of a WWR-SM type nuclear reactor at P_{tn}=1.2·10^{11} neutron·cm^{-2} up to the fluence values of F_{tn}=1.3·10^{16} neutron·cm^{-2} (cadmium ratio >6). 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≤35 mA, Cu–anticathode). Absorption spectra were measured at 293 K in the visible and IR ranges using spectrophotometers EPS-3T Hitachi and UR-20, respectively.

RESULTS AND DISCUSSION

Among the scintillation materials studied by us the highest RS under gamma- irradiation is observed with ZnSe(O,Te) and CWO crystals (Table 1). For other scintillators, such as $Bi_4Ge_3O_{12}$ and Gd_2SiO_5, gamma-luminescence intensity (I_γ) is decreased not less than by 75 % under D_γ = 5·10^7…1·10^8 rad; for CsI(Tl) crystals, light output is decreased by 20…30 % under D_γ= 2·10^3 rad, and by more than 60% under D_γ= 10^4 rad.

Table 1

Gamma-luminescence intensity I_γ for ZnSe(O,Te), ZnSe(Cd), ZnCdS(Te), ZnSSe(Te) and CWO as function of dose D_γ

Crystal	I_γ, a.u., after D_γ, rad					
	1·10^6	4·10^6	1·10^7	4·10^7	1·10^8	4·10^8
ZnSe(O,Te)	99	98	96.5	94	90	80
ZnSe(Cd)	99	98	96	93	89	78
ZnCdS(Te)	96	92	85	80	73	62
ZnSSe(Te)	97	94	88	82	76	71
CWO	97	95	93	87	80	62.5

At first all SCS 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. % = 4.17·10^{21} cm^{-3} of Se and

45.3 wt. % = $4.17 \cdot 10^{21}$ cm^{-3} of Zn. Table 2 shows the experimental data on composition of AN, AT, BN, BT, CN, CT series of ZnSe(O,Te) crystals.

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 $\sim 0.9 \cdot 10^{21}$ 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 [5].

It is well seen from the Table 2 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.

Table 2

Composition, stoichiometry and luminescent characteristics of ZnSe(O,Te) crystals at 300 K. Light output of XL I_{XL} (measured by Si-PD) is normalized to CsI(Tl) 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 10^9 rad, 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

After neutron irradiation of ZnSe-based SCS, ZnCdS(Te) and ZnSSe(Te) crystals, XL spectra remained practically unchanged (Figs. 1, 2), and integral XL intensity of neutron-irradiated samples increased by 20 to 50 % as compared with non-irradiated samples. This kind of irradiation of SCS crystals leads to an increase in optical absorption in the visible spectral range. In this range absorption is of selective character, with maximum at 510 to 530 nm. One should note that absorption band in the same spectral region is also observed in SCS samples that were not subjected to neutron irradiation, but were only annealed in Zn vapor.

Neutron irradiation leads also to increased absorption in the IR region (Fig. 3, curve 2), which is especially strong at λ>6 μm. Resistivity of neutron-irradiated SCS samples falls by an order of magnitude. Both for neutron-irradiated and non-irradiated samples, it was possible to describe absorption in the IR region by a λ^p law ($p \approx 2$).

Proton irradiation of SCS samples led to sharp degradation of their optical and scintillation properties, and at $F_p \geq 10^{15}$ cm^{-2} XL intensity decreased by almost 90 %. A long-wave maximum shift is observed in the XL spectrum of proton-irradiated SCS samples (Fig. 1, curves 3, 4). Their non-selective absorption increases in the visible spectral range by 17 to 20 %, but decreases in the IR range. At the same time, selective absorption bands appear in the 3 to 7 μm region (Fig. 3, curve 3).The resistivity of proton-irradiated SCS samples increased by more than 1.5 to 2 orders of magnitude.

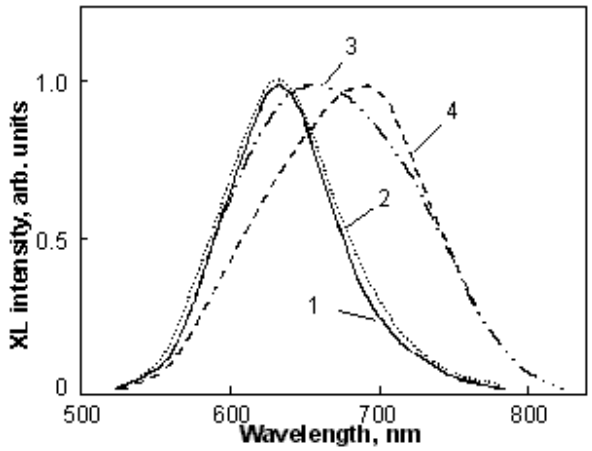

Fig. 1. XL spectra of ZnSe(O,Te) samples:
1- non-irradiated; 2- after neutron irradiation (F_{nt}=1.3·10^{16} neutrons·cm^{-2}); 3, 4 - after proton irradiation (F_p=1.2·10^{14} protons·cm^{-2} and 1.7·10^{15} protons·cm^{-2}, respectively)

ZnSe(O,Te) and CWO crystals have also high RS towards irradiation by neutrons (Fig.4). The shape of luminescence spectrum being preserved, I_γ of ZnSe(O,Te) crystals pre-irradiated by reactor neutrons increases by 10… 300 %, depending upon F_{ntf} and the type of crystal. For CWO crystals, I_γ is monotonously decreasing, reaching 80 % of the initial value at F_{ntf}= 10^{14} cm^{-1} and 0.5…5 % at F_{ntf}= 10^{18}…10^{19} cm^{-2}. For ZnSe(O,Te), I_γ is monotonously decreased with higher F_{ntf}; at F_{ntf}= 1.3·10^{16} cm^{-2} it is 78 % of the initial value for non-irradiated crystals. The decrease of the integral output I_γ is accompanied, with ZnSe(O,Te) crystals pre-irradiated by neutrons, by a short-wave shift in the luminescence spectrum (from $h\nu_{max}$ = 1.55…1.78 eV for non-irradiated crystals to $h\nu_{max}$ = 1.91…1.97).

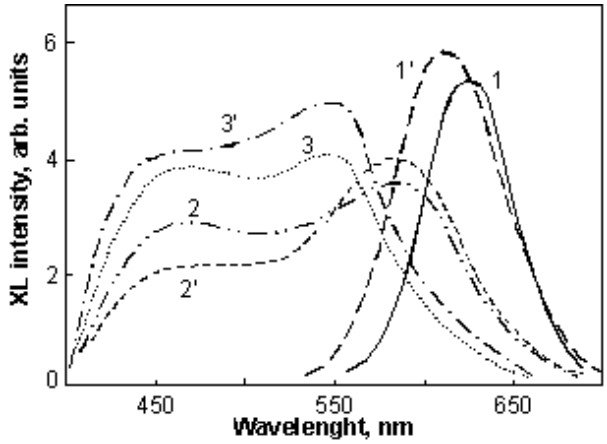

Fig. 2. XL spectra of ZnSe(Cd) (1,1'), ZnCdS(Te) (2,2') and ZnSSe(Te) (3,3') and after (1',2',3') neutron irradiation (F_{nt}=1.3·10^{16} neutrons·cm^{-2})

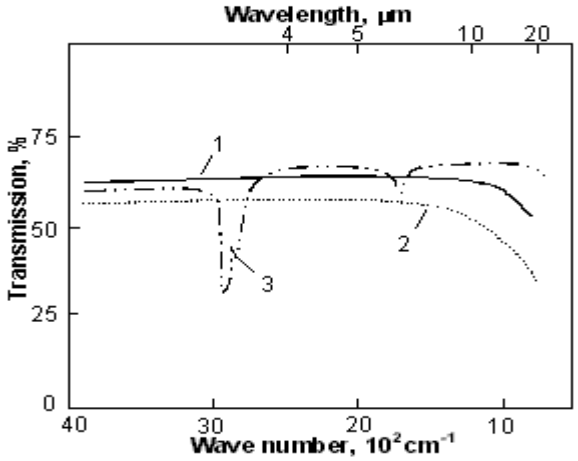

Fig. 3. IR absorption spectra: 1 - non-irradiated SCS samples; 2 - after neutron irradiation ($F_{nt}=1.2\cdot10^{14}$ neutrons·cm^{-2}); 3 - after proton irradiation ($F_p=1.7\cdot10^{15}$ protons·cm^{-2})

Under proton irradiation, CWO scintillators have much higher RS as compared with ZnSe(O,Te). Thus, under $F_p = 8.7\cdot10^{14}\ldots1.7\cdot10^{15}$ cm^{-2} I_γ for CWO is 30-40 % of the initial value for crystals which were not pre-irradiated, for ZnSe(O,Te) – 0.9…1.2 %. Besides this, for zinc selenides long-wave shifts in the luminescence spectrum were observed.

Scintillator ZnSe(O,Te) has the highest RS towards electron irradiation (^{90}Sr + ^{90}Y source, A = 2000 mCu). Under $D_{ee} = 5\cdot10^7$ rad no changes in I_γ or spectral composition of intrinsic radiation were noted within measurement errors.

Transparence R of ZnSe(O,Te) is most strongly and non-trivially changed under neutron and proton irradiation. In the case of neutron irradiation of ZnSe(O,Te), simultaneous decrease of R at $\lambda > 4$ mcm (due to free carrier density increase) and increase of I_γ are the evidence of higher density of radiation recombination centers of $Zn_iV_{Zn}Te_{Se}$ type; concentration of Zn_i can increase both due to the defect formation processes $Zn_{Zn}\rightarrow Zn_i+V_{Zn}$ (*) and dissociation of complexes $l\cdot(Zn_o)\rightarrow m\cdot(Zn_0)+n\cdot(Zn_i+e^-)$, l = m+n. For ZnSe(O,Te) crystals, processes of (*) type are the most important, as well as neutron-stimulated annealing of other defects. This leads to the increase of R and short-wave reconstruction of the luminescence spectrum.

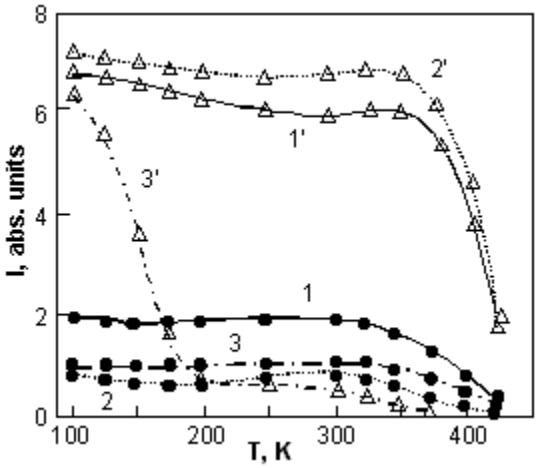

Fig. 4. Temperature dependence of I_γ for CWO (1,2,3) and ZnSe(O,Te): (1',2',3') crystals irradiated by neutrons (2, 2') and protons (3,3'); 1, 1' - initial sample

During proton irradiation of ZnSe(O,Te) crystals, the main role is played by the processes of formation of powerful plasma tracks, leading to an increase of high-energy "tail" of the distribution function in the zone, which promote highly efficient defect formation and/or radiation-stimulated aggregation under the scheme $k(Zn_i+e^-) \rightarrow k\cdot(Zn_0)$, with the corresponding decrease of IR-absorption on free carriers and long-wave reconstruction of the luminescence spectra (V_{Zn}, $V_{Zn}Te_{Se}$ centers).

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РАДИАЦИОННО-ИЗЛУЧАТЕЛЬНЫЕ ПРОЦЕССЫ В A^2B^6 И ОКСИДНЫХ СОЕДИНЕНИЯХ ПОД ПРОТОННЫМ И ГАММА-ОБЛУЧЕНИЕМ

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Изучено изменение сцинтилляционных и оптических свойств полупроводниковых сцинтилляторов (ППС) ZnSe(O,Te), ZnSe(Cd), ZnCdS(Te), ZnSSe(Te) и $CdWO_4$ (CWO) кристаллов при воздействии различных видов ионизирующих излучений (гамма, протонов, нейтронов). При облучении кристаллов ППС нейтронами их световыход возрастает на 20…150 % и наблюдаются заметные изменения их оптических характеристик в видимом и инфракрасном диапазонах. Протонное облучение приводит к существенной деградации оптических и сцинтилляционных параметров кристаллов ППС, при этом в инфракрасной области наблюдаются селективные полосы поглощения (при 4…7 мкм). Кристаллы CWO обладают более высокой радиационной стойкостью к протонному облучению, чем ППС. При высоких дозах облучения ППС (D>2…5·10^9 рад) в поверхностном слое кристаллов наблюдаются процессы радиолиза и потеря массы облученных образцов.

РАДИАЦІЙНО-ВИПРОМІНЮВАЛЬНІ ПРОЦЕСИ В A^2B^6 ТА ОКСИДНИХ СПОЛУЧЕННЯХ ПІД ПРОТОННИМ ТА ГАМА-ОПРОМІНЕННЯМ

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Вивчено зміну сцинтиляційних і оптичних властивостей напівпровідникових сцинтиляторів (НПС) ZnSe(O,Te), ZnSe(Cd), ZnCdS(Te), ZnSSe(Te) та $CdWO_4$ (CWO) кристалів при впливі різних видів іонізуючих випромінювань (гамма, протонів, нейтронів). При опроміненні кристалів НПС нейтронами їх світловий вихід зростає на 20...150 % і спостерігаються помітні зміни їхніх оптичних характеристик у видимому та інфрачервоному діапазонах. Протонне опромінення приводить до суттєвої деградації оптичних та сцинтиляційних параметрів кристалів НПС при тому в інфрачервоній області спостерігаються селективні смуги поглинання (при 4...7 мкм). Кристали CWO мають більш високу радіаційну стійкість до протонного опромінення, ніж НПС. При високих дозах опромінення НПС (D>2...5·10^9 рад) у поверхневому шарі кристалів спостерігаються процеси радіолізу і втрата маси опромінених зразків.