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On radiation-induced optical and luminescence phenomena in thermally pretreated GSO:Ce crystals

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Effects of thermal annealing in different gaseous media (vacuum, oxygen-containing and reductive atmospheres) upon main optical, luminescence, spectral kinetic, and scintillation characteristics of GSO:Ce crystals — both subjected and not subjected to γ-irradiation (10^4–10^6 rad) — have been studied. The heat treatment in oxygen-containing media worsens the transparence and light yield, which is explained by partial transformation of cerium ions into a state of a higher oxidation degree ($Ce^{3+} \to Ce^{4+}$), with Ce^{4+} not involved in scintillation processes and playing the role of absorption centers for the intrinsic radiation. On the contrary, the heat treatment of GSO:Ce crystals in vacuum may result in a certain improvement of their scintillation characteristics, probably related to the inverse transformation of the cerium charge state ($Ce^{4+} \to Ce^{3+}$). GSO:Ce crystals that had been thermally pre-treated in vacuum show substantial degradation of their optical and luminescent characteristics under irradiation. This can be related to oxygen vacancies V_O that emerge during vacuum annealing and form F-centers under γ-irradiation.

Исследовано влияние термического отжига в различных газовых средах (вакуум, кислородсодержащая и восстановительная среды) на основные оптико-люминесцентные, спектрально-кинетические и сцинтилляционные характеристики кристаллов GSO:Ce как необлученных, так и подвергнутых γ-облучению дозами 10^4–10^6 рад. Ухудшение уровня прозрачности и величины светового выхода при термообработке в кислородсодержащей среде объясняется частичным переходом ионов церия в состояние с более высокой степенью окисления ($Ce^{3+} \to Ce^{4+}$), при которых ионы Ce^{4+} уже не участвуют в сцинтилляционных процессах, но играют роль центров поглощения собственного излучения в кристалле и, наоборот, незначительное улучшение этих характеристик в случае термической обработки в вакууме может быть связано с обратной трансформацией зарядового состояния ($Ce^{4+} \to Ce^{3+}$). Наибольшую радиационно-индуцированную деградацию оптических и люминесцентных характеристик показывают кристаллы, предварительно прошедшие термический отжиг в вакууме, в результате чего происходит образование кислородных вакансий V_O, которые при γ-облучения образуют F-центры.

Scintillators based on cerium-activated gadolinium oxyorthosilicate (GSO:Ce) single crystals are highly promising for applications in electromagnetic calorimeters, nuclear physics, positron tomography, etc. The wide application field of GSO:Ce scintillator crystals is due to their fast action (decay times of about 30 to 60 ns),a rather high light yield (8000 to 9000 ph/MeV), high density (6.71 g/cm^3), short radiation length (1.38 cm), non-hygroscopicity, and high transparence to intrinsic radiation. Moreover, high radiation (up to 10^9 rad) and temperature (up to 200°C) stability make these crystals an optimum choice for nuclear geophysics equipment, in particular, for gamma-neutron logging. The optimum concentration of the activator dopant in GSO:Ce crystals is generally assumed to be within 0.5–1.5 % [1], though at Ce concentrations above 0.5–0.6 %, a certain decrease in scintillation yield was noted [2].

The preparation of high quality GSO:Ce scintillators is strongly conditioned by the oxygen content in the crystal growth atmosphere. At high oxygen concentrations, the grown GSO:Ce crystals are of yellow color and show low light yield, while at low concentrations, the crystals are grayish-bluish and show low mechanical strength accompanied with low radiation stability. Further, since there is a region of melt supercooling, this causes formation of intrinsic structural defects in GSO:Ce crystals, namely, microinclusions, centers of absorption and scattering of the intrinsic radiation that are related to aggregation of cationic vacancies V_{Gd}, V_{Ce}, and color centers based on Ce^{4+} ions [3, 4]. These drawbacks can be partially removed by a post-growth thermal treatment, and a very important point is the choice of conditions and especially the atmosphere where the thermal treatment will be carried out.

First, the thermal annealing decreases stresses in GSO:Ce crystals that emerge in the growth process. This improves mechanical properties of the crystals and diminishes the number of defects that affect negatively the scintillation parameters. Second, since maintaining the required oxygen concentrations during crystal growth is rather problematic, studies of the post-growth thermal treatment in gaseous media (neutral and with pre-specified oxidation-reduction ability) and its effects become very important. Before [5], it has been established that thermal annealing of GSO:Ce crystals in atmosphere with a specified chemical potential improves the crystal transparence and scintillation characteristics, but no studies of radiation effects upon such crystals were reported.

In this work, we studied the effects of heat treatment in various gaseous media upon main optical, luminescence, spectral kinetic, and scintillation characteristics of GSO:Ce crystals, including crystals that had been subjected to γ-irradiation at doses of 10^4 to 10^6 rad. The GSO:Ce crystals were grown by the Czochralski method from iridium crucibles in nitrogen atmosphere with addition of up to 1.5 vol.% oxygen [6]. The pulling rate of the crystal ingot was 1.4 to 3.0 $\mathrm{mm \cdot h^{-1}}$, rotation speed 30 to 40 $\mathrm{min^{-1}}$. The concentration of Ce activating dopant in the crystals was 0.6 mol. %. The annealing in vacuum was carried out in a furnace with hermetically sealed and prepumped out working space, with the chemical potential of the annealing medium being 38 to 42 $\mathrm{J \cdot mol^{-1}}$ (the annealing temperature T about 0.7 T_m). Thermal treatments in the oxygen-containing (air) and reductive (CO) media was carried out at 1700 K for 24 hours.

Optical transmission and X-ray luminescence spectra were measured using a universal spectrophotometric complex KSVU-23. The afterglow level of scintillators after a specified time was determined using a measuring-calculating system (MCS) designed for determination of kinetic parameters of scintillator luminescence [7]. The X-ray luminescence light yield values for GSO:Ce crystals were determined both in the current and spectrometric mode. The light yield determined by the current method (relative current signal) was determined by comparison of signals from the studied and reference samples. The signal from the reference sample of the same size as the studied samples was put as 100 %. To measure the spectrometric characteristics (light yield I_{pulse}, amplitude resolution R) of GSO:Ce scintillator samples, we used a standard spectrometric circuit comprising a R1306 type PMT, a linear spectrometric amplifier and a multi-channel pulse analyzer based on a personal computer.

The main parameter generally used to quantify the effects of various factors upon the crystal (including irradiation) for oxide scintillation crystals is the degradation of the transparence level, i.e., the value of induced absorption Δα [1, 8]. This value is determined as

$$\Delta\alpha = \frac{\ln(T/T_0)}{d},$$

where T is the transmission coefficient after annealing, T_0, that of the initial sample, d, the sample thickness.

Besides, the influence of a specified factor upon a scintillator can be characterized by changes in the light yield, energy resolution and kinetic characteristics (decay time and afterglow level). When studying the effects of various types of thermal annealing and subsequent irradiation upon GSO:Ce crystals, we carried out complex measurements of these parameters. The annealing in a neutral atmosphere, which is an indispensable element of the crystal growth technological process (so-called post-growth an-

Table 1. Main scintillation and optical characteristics of GSO:Ce crystals before and after thermal treatment of different kinds.

Conditions of thermal annealing	Light yield, r.u.		R, %	Induced absorption $\Delta\alpha$, cm^{-1}	Afterglow level η, %	Decay time τ, ns
	Current method	Spectro-metric method				
Initial sample	1.00	1.00	9.8	0	0.003	$\tau_1 = 48.2$ $\tau_2 = 361$
In air	0.92	0.89	10.4	0.01	0.002	$\tau_1 = 50.0$ $\tau_2 = 338$
In vacuum	1.21	1.20	8.3	−0.02	0.086	$\tau_1 = 53.3$ $\tau_2 = 385$
In a reductive medium	–	–	–	0.21	0.061	$\tau_1 = 43.2$ $\tau_2 = 334$

nealing) does not change the scintillation or optical parameters and spectral kinetic characteristics of GSO:Ce crystal luminescence. This type of annealing is mainly aimed at removing internal mechanical stresses in the grown crystals, which facilitates their further mechanical treatment. In Table 1, main scintillation and optical characteristics are presented for GSO:Ce crystals before and after thermal annealing of various kinds. Fig. 1 shows the induced absorption spectra of GSO:Ce samples after thermal annealing in various atmospheres. A slight decrease of the transparence level in the 400–550 nm region and lowering of the light yield by about 10 % after heat treatment in an oxygen-containing medium (air), with the X-ray luminescence spectrum unchanged, can be explained by partial transition of cerium ions into a state with higher oxidation degree ($Ce^{3+} \rightarrow Ce^{4+}$). Ce^{4+} ions are not involved in scintillation processes, but play the role of absorption centers for the intrinsic radiation of the GSO:Ce scintillator.

In contrast to annealing in an oxidative medium, the heat treatment in vacuum (chemical potential 38–40 J/mol) enhances the optical characteristics. An improved transparence is observed in the 400–550 nm range, with maximum at $\lambda = 420$ nm. This is accompanied by an increase in light yield by about 20 %. This can be explained by assuming that under thermal treatment of this kind, an inverse process occurs, i.e., partial transformation of Ce^{4+} to Ce^{3+}. In this case, there is a high formation probability of oxygen vacancies (V_O) in the crystal matrix, resulting in secondary defect formation under irradiation with subsequent formation of vacancy coagulation complexes at higher radiation doses. Here, it is to note a substantial increase in the afterglow level.

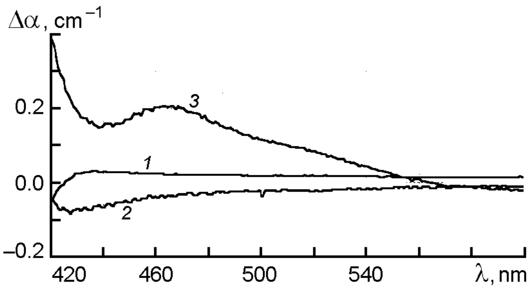

Fig. 1. The induced absorption spectra of GSO:Ce samples after thermal annealing in different atmospheres: *1* — in an oxygen-containing medium; *2* — in an vacuum; *3* — in a reductive medium (CO).

The heat treatment in a reductive medium (CO) at $T = 1700$°C results in a noticeable visual changes of the sample, namely, to formation of blue-colored regions and partial layering. This gives rise to an induced absorption band in the 400–550 nm region, the value of which at the maximum ($\lambda = 460$ nm) reaches 0.2 cm^{-1}. However, to get a full understanding of the processes occurring under such treatment, one should look for optimum conditions for their realization.

γ-Irradiation of GSO:Ce samples without annealing shows that the initial stages of irradiation ($D \approx 10^4$ rad) cause higher transmission levels. At higher doses, the transmittance is decreased, and at 10^6 rad becomes even lower than in the initial sample. The same picture is observed also for

Table 2. Main scintillation and optical characteristics of GSO:Ce crystals before and after thermal and radiation treatment of various kinds

Treatment	Light yield, r.u.		*R*, %	Induced absorption $\Delta\alpha$, cm^{-1}	Afterglow level η, %
	Current method	Spectro-metric method			
Untreated samples	1.00	1.00	7.8	0	0.003
γ-irradiation (10^4 rad)		0.99	8.3	−0.02	0.002
γ-irradiation (10^5 rad)		1.10	7.3	0.013	0.003
γ-irradiation (10^6 rad)		0.99	1.17	8.1	0.015
Annealing in air + γ-irradiation (10^6 rad)	0.93	0.98	8.3	0.02	0.002
Annealing in vacuum + γ-irradiation (10^6 rad)	0.52	Large noises	Large noises	1.18	0.124

samples that had been pre-treated in an oxygen-containing medium. In Table 2, main scintillation and optical characteristics of GSO:Ce crystals before and after heat and radiation treatment of various kinds are presented. The induced absorption spectra for this case are shown in Fig. 2.

GSO:Ce crystals that had been thermally pre-treated in vacuum showed the most substantial radiation-induced degradation of their optical and luminescent characteristics (see Table 2). At γ-radiation doses of about 10^6 rad, the induced absorption values were as high as $\alpha_{440\mathrm{nm}} \sim 1.3–1.5$ cm^{-1}, the light yield decreased, the afterglow became higher by a factor of several tens, and a residual phosphorescence appeared. The intense residual phosphorescence with long relaxation times may be caused by localization of the charge carriers excited by irradiation upon intermediary energy capture centers due to admixtures or matrix ions. In this case, the probability is increased of the transfer to the radiative levels of the activator, which results in prolonged luminescence and higher decay times. Fig. 3 illustrates the kinetics of induced absorption spectra after stopping the irradiation. In stable room conditions, gradual restoration of the properties is observed, which is characteristic for the case of color center formation.

It can be concluded that in the case of thermal pre-treatment in vacuum, oxygen vacancies V_O are formed, which are bound to ionized electrons formed as a result of irradiation, i.e., *F*-centers are formed. Pre-treatment in oxygen-containing atmosphere does not cause formation of V_O and, consequently, to additional coloring of the sample.

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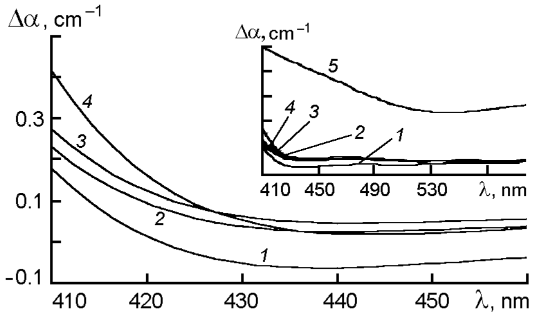

Fig. 2. The induced absorption spectra of GSO:Ce samples after thermal and γ-irradiation treatment of different kinds: *1* — 10^4 rad; *2* — 10^5 rad; *3* — 10^6 rad; *4* — 10^6 rad (after the thermally pre-treatment in an oxygen-containing medium); 5 – 10^6 rad (after the thermally pre-treatment in vacuum).

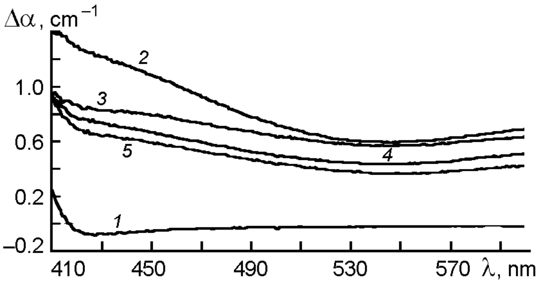

Fig. 3. The kinetics of induced absorption spectra of GSO:Ce samples after stopping the irradiation: *1* — after the thermal treatment into vacuum; *2* — in 1 h after irradiation; *3* — in 3 h; *4* — in 5 h; *5* — in 25 h.

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Радіаційно-стимульовані оптичні і люмінесцентні явища у термічно оброблених кристалах GSO:Ce

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Досліджено вплив термічного відпалу у різних газових середовищах (вакуум, окислювальне і відновлювальне середовища) на основні оптико-люмінесцентні, спектрально-кінетичні і сцинтиляційні характеристики кристалів GSO:Ce як неопромінених, так і після γ-опромінювання дозами 10^4–10^6 рад. Погіршення прозорості і світлового виходу при термообробці в окислювальному середовищі пояснюється частковим переходом іонів церію у стан з вищим ступенем окислення ($Ce^{3+} \to Ce^{4+}$), при яких іони Ce^{4+} вже не беруть участі у сцинтиляційних процесах, але грають роль центрів поглинання власного випромінювання у кристалі і, навпаки, незначне поліпшення цих характеристик у разі термічної обробки у вакуумі, може бути пов'язано із зворотньою трансформацією зарядного стану ($Ce^{4+} \to Ce^{3+}$). Найбільшу радіаційно-індуковану деградацію оптичних і люмінесцентних характеристик показують кристали GSO:Ce, що заздалегідь пройшли термічний відпал у вакуумі, внаслідок чого відбувається утворення кисневих вакансій V_O, які при γ-опромінюванні утворюють F-центри.