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# Energy transfer in neutron irradiated Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals

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#### Abstract

Optical absorption and luminescence of synthetic initial and neutron irradiated  $Gd_2SiO_5$ -Ce (0.5 mol.%) crystals was studied. Optical absorption spectra (1-6 eV) were measured using UV-Visible Helios Alpha spectrophotometer at T=300 K. Time-resolved luminescence spectra (1.5 – 6 eV), luminescence excitation spectra (4-20 eV) and decay kinetics were recorded at SUPERLUMI station (DESY, Hamburg). Reactor neutron's irradiation (fluence of 4·10<sup>18</sup> cm<sup>-2</sup>) leads to the effective production of defects. There were not registered any new luminescence bands in the irradiated samples, but radiation defects take significant part in the processes of energy transfer to luminescence enters.

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### 1. Introduction

The addition of co-activator ions into crystalline lattice of scintillator leads in a lot of cases to significant change of the energy transfer processes and to the improvement of scintillation properties of materials. Grown or produced defects of crystalline lattice could play the same role. Taking into account excellent radiation stability of oxide crystals, we could produce optically significant defects in these materials using solely corpuscular's irradiation (neutrons, electrons or ions). The photon's irradiation results in the changing of the charge states of the existent lattice or impurity defects.

Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystal scintillator having a monoclinic symmetry with its space group of P21/a was first reported by Takagi and Fukazawa [1]. As well as other oxyorthosilicate crystals Gd<sub>2</sub>SiO<sub>5</sub>-Ce has excellent radiation hardness. In particular, significant radiation damage at an irradiation by  $\gamma$ rays of <sup>60</sup>Co up to 10<sup>9</sup> rad was not observed for Gd<sub>2</sub>SiO<sub>5</sub>-Ce [2]. The effect of degradation in optical transmittance was greatly raised after protons irradiation (10<sup>8</sup> rad) [3]. After neutrons irradiation in a range of relatively small dozes, the effect of degradation of optical transmittance was insignificant (fluence of 10<sup>14</sup> cm<sup>-2</sup> of thermal neutrons and fluence of 10<sup>13</sup> cm<sup>-2</sup> for fast neutrons) [3]. In present work we compare optical and photoluminescence (PL) characteristics of initial Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals and the same crystals irradiated by fast reactor neutrons (fluence of 4·10<sup>18</sup> cm<sup>-2</sup>).

### 2. Experimental technique and methods

We studied Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals with 0.5 mol% Ce doping grown by Hitachi Chemical Co. using Czochralski method.

The irradiation of samples by fast neutrons was carried out in the hot camera of research reactor IVV-2M (Zarechnyi, Russia). The crystals were irradiated in the internal cavity of fuel assembly established in a cell of reactor's active zone. Estimated density of the fast neutron-flux stream (> 0.2 MeV) in this cell at the rated power of a reactor (15 MW) was 1.5<sup>10<sup>14</sup></sup> cm<sup>-2</sup>·s<sup>-1</sup>. The fluency of fast neutrons was controlled by threshold activation indicators made from nickel by means of  $\gamma$ -spectrometric determination of <sup>58</sup>Co activity. The temperature of irradiated crystals did not exceed 325 K due to the forced cooling of samples by the specially designed heatcarrier (water in the first contour of a reactor). Optical absorption spectra (1-6 eV) were measured using UV-Visible Helios Alpha spectrophotometer at T=300 K. The PL measurements were carried out at the SUPERLUMI station (VUV region) [4] at HASYLAB (DESY). The 0.3 m ARC SpectraPro-308i monochromator equipped either with the R6358P (Hamamatsu) photomultiplier was used to analyse luminescence. The photoluminescence excitation spectra were corrected for the equal number of the exciting photons using sodium salicylate, whereas the PL spectra are presented without any corrections. Simultaneously with the timeintegrated luminescence spectra, the spectra in the two time windows delayed relative to the exciting SR-pulse were registered: the fast component: the delay time  $\delta t_1 = 2.8$  ns, the length of time windows  $\Delta t_1 = 14.4$  ns; the slow component:  $\delta t_2 = 120$  ns,  $\Delta t_2 = 60$  ns. The convolution method was used for analysis of fast components of the PL decay kinetics. The time resolution of the detection system was ~250 ps (FWHM).

#### 3. Experimental results

In the result of neutron irradiation a simple and complex defects are produced in the crystalline lattice of oxide materials. We observed significant growth of sample's optical density after neutron irradiation of  $Gd_2SiO_5$ -Ce crystals at energies E > 3.5 eV (Fig. 1). The high level of crystal's optical density in energy range more than 4.5 eV induced by an neutron irradiation do not allow to use an optical absorption methods in research of the generated defects properties.

Therefore the main results of the present work are received with time-resolved luminescent spectroscopy method.



Fig.1. Optical density spectra for initial (1) and neutron irradiated (2)  $Gd_2SiO_5$ -Ce crystals at T = 300 K.

PL spectra and luminescence excitation spectra for the  $Gd_2SiO_5$ -Ce crystals (initial and irradiated by neutrons), as well as decay kinetics are presented on Fig. 2-5.

One could see, that the intensity of cerium impurity luminescence, determing scintillation properties of crystals, significantly decreased after neutron irradiation of crystals (Fig.2, curve 2). Before irradiation in photoluminescence spectrum of Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals dominates the well-known luminescence of impurity Ce<sup>3+</sup> ions (curve 1 on fig. 2). After the neutron irradiation intensity of this impurity luminescence concedes to intensity of a luminescence with a maximum nearby 3.9 eV, corresponding to well-known radiating transitions <sup>6</sup>P<sub>J</sub>  $\rightarrow$  <sup>8</sup>S<sub>7/2</sub> in Gd<sup>3+</sup> ions. In a spectrum 2 on fig. 2 these transitions are not resolved because the luminescence in the field of 1.5-3.5 eV has weak intensity, therefore the resolution of a registration system at measurements was low (not less than 20 nm). At the same time on fig. 2 appearance of a new luminescence bans with a maximum nearby 2.1 eV is well noticeable.



Fig.2. Photoluminescence spectra of  $Gd_2SiO_5$ -Ce crystals at T = 10 K for initial (1) and neutron irradiated (2) crystals. Energy of excitation is 7.0 eV. By thin lines decomposition of low-energy band of a curve 2 on Gaussian components is shown.

The change of PL profile of neutron irradiated crystals is accompanied by occurrence of new intensive band of excitation with maximum near 5.8 eV in the crystal's field of transparency (below of the fundamental absorption edge), Fig.3, curve 2,3. This band apparently dominates in excitation spectrum of 2.1 eV luminescence which has appeared in the crystal due to a neutron irradiation.



Fig. 3. Luminescence excitation spectra of Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals for emission band  $E_{emiss} = 3.0 \text{ eV}$  at T = 10 K for initial crystals (1) and for emission bands  $E_{emiss} = 3.0 \text{ eV}$  (2) and 2.1 eV (3) for neutron irradiated crystals.

PL decay kinetics of 3.0 eV luminescence greatly varies for initial and neutron irradiated crystals (Fig.4 and Fig.5). For example, there is known rise stage of PL kinetics 3.0 eV in Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals [5, 6]. This rise stage disappears after irradiation. Especially it is noticeable at excitation at 7.3 eV (Fig. 4, curve 1). Secondly, the decay kinetics of the luminescence is extremely slow. It should be noted that slow decay kinetic are character to both luminescence bands at 3.0 eV and 2.0 eV.

Thus, as a result of influence by a reactor neutrons flux with fluence of  $4 \cdot 10^{18}$  cm<sup>-2</sup> in Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals the luminescence yield of impurity Ce<sup>3+</sup> ions has substantially decreased and simultaneously arise new 2.1 eV band in photoluminescence spectra and 5.8 eV band in excitation spectra of crystals. The 2.1 eV luminescence band is characterized with very slow decay kinetic which quantitative estimation is complicated on the used experimental facility.

#### 4. Discussion

Fast neutrons in crystal volume lose the energy mainly during elastic scattering processes on the nucleus of lattice atoms, generally displacing from regular position light nucleus, and uppermost oxygens. The maximum of energy loss at such interaction taking into account weight of oxygen nucleus can reach 12,5 % energy of a incident neutron, i.e. to reach value of tens keV that it is quite enough for Frenkel pair formation.



Fig. 4. Decay kinetics of 3.0 eV luminescence of  $Gd_2SiO_5$ -Ce crystals at T = 10 K under excitation at 7.3 eV for initial (1) and neutron irradiated (2) crystals.



Fig. 5. Decay kinetics of 3.0 eV (1,2) and 2.0 eV (3) luminescence of  $Gd_2SiO_5$ -Ce at T = 10 K under excitation at 6.04 eV for initial (1) and neutron irradiated (2,3) crystals.

The neutrons which have energy loss in elastic interaction acts, and also the penetrating into crystal thermal neutrons from a irradiation zone, mainly participate in a neutron capture reactions with nucleus of lattice atoms. Among the last known it is abnormal high absorption cross-section of thermal neutrons  $^{155}$ Gd (61000 barn) and  $^{157}$ Gd (250000 barn) isotopes, that forms 14,7% and 15,68% Gd natural isotopic composition. After capture of a thermal neutron these isotopes are transformed to stable <sup>156</sup>Gd and <sup>158</sup>Gd isotopes, raising that their percentage comparing to natural isotopic composition. Thus, the majority of thermal neutrons are captured in Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystal by nucleus of Gd isotopes, slightly changing isotope composition, but does not lead to occurrence of nucleus of other elements. Emitted in  $(n, \gamma)$  reactions with participation of Gd isotopes gamma quanta have energy no more than 0.1 MeV and, in our opinion, cannot substantially affect crystal structure imperfection.

By gamma-ray spectrometer analysis completed immediately after the irradiation we found out that in the process of an irradiation in Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals unstable isotopes also arise. Namely, through reactions <sup>152</sup>Gd (n,  $\gamma$ ) <sup>153</sup>Gd<sup>\*</sup> (the capture cross-section of thermal neutrons by <sup>152</sup>Gd isotope is 735 barn, half-life of <sup>153</sup>Gd<sup>\*</sup> isotope is 241.55 days), <sup>140</sup>Ce (n,  $\gamma$ ) <sup>141</sup>Ce<sup>\*</sup> (0.57 barn, 32.5 days), <sup>160</sup>Gd (n,  $\gamma$ ) <sup>160</sup>Tb<sup>\*</sup> (0.77 barn, 72.3 days) the total specific induced activity of crystals was 1.55•10<sup>11</sup> Bk/kg. The major portion (to 99 %) of this activity is caused <sup>153</sup>Gd<sup>\*</sup> which radioactive decay is accompanied by emission of gamma quanta with energy nearby 100 keV. A product nucleus – a stable isotope <sup>153</sup>Gd. Product nucleus of <sup>141</sup>Ce<sup>\*</sup> decay is the stable isotope <sup>153</sup>Gd. Product nucleus of <sup>141</sup>Ce<sup>\*</sup> decay is the stable isotope <sup>141</sup>Pr. In the irradiated crystals we did not observe discrete luminescence spectrum typical for Pr<sup>3+</sup> ion. Thus, radioactive decay of the unstable products nucleus formed in Gd<sub>2</sub>SiO<sub>5</sub>-Ce through the neutron irradiation, also does not influence considerable crystal structure imperfection.

Our assumption that capture of thermal neutrons does not lead to significant degradation of a crystal which agrees with conclusions of work [3] where absence of such effects also was observed at low fluences (up to  $10^{14}$  sm<sup>-2</sup>) of thermal neutrons.

Besides processes in a crystal's nuclear subsystem an irradiation of crystals by fast reactor neutrons and simultaneous influence by intensive gamma radiation can lead to rearrangement of an electron subsystem. From the standpoint of degradation of scintillation properties the most essential result of such influence is change of valency of cerium ions from  $Ce^{3+}$  to  $Ce^{4+}$ . Charge compensation of arised state is possible, for example, through interstitial defects of  $O^{2-}$  type as a result of impact displacement of oxygen atoms. In consequence of small (in comparison with elements of a regular lattice) number of an impurity ions degree of influence of this process on the general change of structure imperfection is also represented to small.

Thus, in our opinion, the dominating factor causing arising of defects in  $Gd_2SiO_5$ -Ce crystal at an irradiation by reactor neutrons is represented by elastic scattering of the last leading to displacement from the regular positions of mainly light atomic components of a lattice.

Thus, in the result of neutron irradiation a simple and complex defects could be produced in crystalline lattice of oxide materials. The significant growth of photon absorption by  $Gd_2SiO_5$ -Ce after neutron irradiation taking place at E > 3.5 eV (Fig.1) is an evidence of the process of defect generation. In photoluminescence spectra as well as in luminescence excitation spectra addition bands were discovered which could be connected with this defects.

For the first time possible existence of defects in  $Gd_2SiO_5$ -Ce crystals was mentioned by the authors [7], who discovered two weak luminescence bands with maxima 582 nm and 651 nm. It is necessary to note that in [7] studied the fiber crystals received by LHPG method, therefore it is not excluded that investigated objects just differed the raised defect structure.

Anion vacancies refer to the most known defects in oxides. Luminescence band with the maximum near 2.0 eV is characterized by significant decay kinetic. Long time of decay kinetic are typical for radiative decay of triplet states of Fcenters in oxides.

According to our assumptions about quality of influence on Gd<sub>2</sub>SiO<sub>5</sub>-Ce crystals of a neutron irradiation it is not necessary to expect significant changes in Gd ions sublattice. Same concerns to impurity  $Ce^{3+}$  ions . Therefore we have supposed that observed reduction of intensity impurity luminescences is caused by breaking of initial process of energy transfer to impurity ions. Absorption of energy by the defects produced after neutron radiation is the powerful competing channel of the general process in the energy transfer.

## Conclusion

Optical absorption and luminescence of synthetic initial and neutron irradiated  $Gd_2SiO_5$ -Ce (0.5 mol.%) crystals was studied. We have registered new luminescence band in the irradiated samples, as well as the appearance of new intensive band in the luminescence excitation spectra. Generated radiation defects significantly change the stage of energy transfer of scintillation process.

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