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# Thermally stimulated luminescence of undoped and $Ce^{3+}$-doped $Gd_2SiO_5$ and $(Lu,Gd)_2SiO_5$ single crystals

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ABSTRACT

Thermally stimulated luminescence (TSL) characteristics (TSL glow curves and TSL spectra) are investigated in the 4–520 K temperature range for the single crystals of gadolinium and lutetium–gadolinium oxyorthosilicates X-ray irradiated at 4 K, 8 K, or 80 K. The nominally undoped $Gd_2SiO_5$ and $(Lu,Gd)_2SiO_5$ crystals, containing traces of $Ce^{3+}$, $Tb^{3+}$, and $Eu^{3+}$ ions, and $Ce^{3+}$-doped $Gd_2SiO_5$ and $(Lu,Gd)_2SiO_5$ crystals are studied. For the first time, the TSL glow curves of these materials are measured separately for the electron (intrinsic, $Ce^{3+}$- or $Tb^{3+}$-related) and hole ($Eu^{3+}$-related) recombination luminescence, and the TSL glow curve peaks, arising from thermal decay of various electron and hole centers, are identified. The origin of the traps related to the TSL peaks is discussed, and thermal stability parameters of the electron and hole traps are calculated.



## 1. Introduction

Since the first publication [1], the $Gd_2SiO_5$:Ce (GSO:Ce) single crystal has been extensively studied as a promising scintillation material for applications in high energy physics, nuclear physics, tomographic medical X-ray imaging, gamma-ray detectors for positron emission tomography and nuclear well logging, nuclear geophysics equipment (e.g., for gamma-neutron logging), for detection of thermal neutrons, etc. (see, e.g., Refs. [1–18]). Indeed, this material has a high density (6.71 g/cm$^3$), high effective atomic number ($Z$=59), fast decay time (20–60 ns), large light yield (in some samples, up to 11,500 photons/MeV [11] or 12,500 photons/MeV [19]) which is about 20–25% of that of NaI:Tl [1,5,20,21] and considerably larger compared to $Bi_4Ge_3O_{12}$ (BGO) (8000–9000 photons/MeV (see, e.g., Refs. [15,16]). It has energy resolution of 7.8% (662 keV, 1 cm$^3$ crystal) better than in BGO, short radiation length (1.38 cm), excellent radiation stability (up to $10^9$ rad), high thermal stability (up to 200 °C), and the emission in the blue spectral region (see, e.g., Refs. [1,5,7,10,11,19,22]). Besides, GSO:Ce is relatively cheaper to produce as compared with $Lu_2SiO_5$:Ce (LSO:Ce), the best $Ce^{3+}$-doped oxyorthosilicate-based scintillation material and has no natural radioactivity. A much larger Ce concentration ($C_{Ce}$) can be achieved in GSO:Ce (up to 5 mol%) [5,7] as compared with LSO. Both the light output and the scintillation decay time of GSO depend on $C_{Ce}$, reaching the best values at $C_{Ce}$=0.5–0.6 mol% (see, e.g., Refs. [1,3,5–7,11–13,17,20–27]). Besides GSO, mixed $Lu_{2x}Gd_{2-2x}SiO_5$ crystals (with $x$ varying from 0 to 1), which have even more attractive scintillation characteristics, were also prepared and studied (see, e.g., Refs. [16,28–35] and references therein). These crystals were denoted also as $(Lu,Gd)_2SiO_5$:Ce [30] (LGSO:Ce) crystals.

Thermally stimulated luminescence (TSL) of GSO:Ce crystals had been studied only in a few papers. The TSL glow curves were mainly measured with a heating rate of $\beta$=5 K/min for the integrated emission of the crystals X-ray irradiated at room temperature (RT). In Refs. [36,37], a complex TSL peak, consisting of strongly overlapping unresolved components located at about 400 K, 425 K, 490 K, and 550 K, was reported. In Ref. [38], the main peak was observed at 391 K, and much weaker peaks at 420 K, 490 K and 550 K. The first peak was shown to be characterized by the first-order kinetics. The corresponding trap depth $E_t$ was 1.16 eV and the frequency factor $f_0$, $3.17 \times 10^{14}$ s$^{-1}$. Like in the other Ce-doped oxyorthosilicates, this peak was ascribed to an electron trapped at an oxygen vacancy. In Ref. [39], a similar TSL glow curve was observed but the dominating peak was located at 373 K. In Ref. [40], the presence at the TSL glow curve of the main 463 K peak and weaker 543 K and 633 K peaks was reported. It was also shown that in GSO:Ce nanophosphors, the main peak is strongly reduced and shifted to lower temperatures (down to 365 K [39] or 433 K [40]).

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After irradiation at 77 K, the TSL of GSO:Ce was studied only in Refs. [41,42]. In Ref. [41], the peaks at 100 K, 145 K, and 350 K were observed at the TSL glow curve of X-ray irradiated crystals. The value of $E_t$=0.7 eV was obtained for the 350 K peak. After thermal annealing in vacuum, the intensities of all the peaks increased and a new peak appeared at 280 K. In Ref. [42], the most intense peak at 140 K and weaker peaks at about 180 K, 240 K, 300 K, 350 K, 390 K, 450 K, and 540 K were observed with $\beta$=0.2 K/s after γ-irradiation of GSO:Ce. The TSL glow curve of the X-ray irradiated at 10 K LGSO:Ce crystal, measured with $\beta$=0.16 K/s, was reported in Ref. [30]. Several strongly overlapping TSL peaks in the 20–150 K temperature range and the peak around 320 K were observed. The trap depth values $E_t$ varied from 0.08 eV for the TSL peak located at about 50 K to 0.29 eV for the peak around 120 K. For the 320 K peak, $E_t$=0.51 eV. For the improved LGSO:Ce crystal X-ray irradiated at 80 K, two main peaks located at 110 K and 315 K were obtained in Ref. [31] with $\beta$=5 K/min.

Thus, very different information is reported in different papers on the positions and parameters of the TSL glow curve peaks in GSO:Ce and LGSO:Ce crystals. The TSL characteristics of the undoped GSO and LGSO crystals were not studied yet. In all the above-mentioned papers, the TSL glow curves were measured only for the integrated luminescence.

Like in other oxyorthosilicate crystals, in the X-ray irradiated GSO and LGSO crystals, the holes can be trapped at oxygen $O^{2-}$ ions (see, e.g., Ref. [43]). Similar to aluminum garnets (see, e.g., Ref. [44]), in $Ce^{3+}$- and $Tb^{3+}$-containing GSO and LGSO crystals, the holes can be trapped also at the impurity $Ce^{3+}$ and $Tb^{3+}$ ions. The recombination of thermally released electrons with the $O^-$-type, $Ce^{4+}$ or $Tb^{4+}$ hole centers is accompanied with the intrinsic, $Ce^{3+}$ or $Tb^{3+}$ emission, respectively. The electrons can be trapped at intrinsic crystal lattice defects (e.g., at oxygen vacancies [45–47]) as well as at impurity (e.g., $Eu^{3+}$) ions [44]. The recombination of thermally released holes with the electron $Eu^{2+}$ centers is accompanied with the $Eu^{3+}$ emission. Owing to that, the peaks of an electron origin should dominate at the TSL glow curves measured for the intrinsic and $Tb^{3+}$-, $Ce^{3+}$-related emission, while at the TSL glow curves measured for the $Eu^{3+}$-related emission, the peaks of a hole origin should dominate. The emission bands of the intrinsic, $Ce^{3+}$-, $Tb^{3+}$-related and $Eu^{3+}$-related luminescence centers are located in the 2.5–3.2 eV and 1.7–2.1 eV energy ranges, respectively (see, e.g., Refs. [20,32,39,46,48–57]), i.e. they are well separated.

To identify the TSL peaks, arising from the thermal decay of electron and hole centers in GSO- and LGSO-based crystals, we have carried out a detailed and systematic study of the TSL characteristics for the $Ce^{3+}$-doped and the nominally undoped but $Ce^{3+}$-, $Tb^{3+}$-, and $Eu^{3+}$-contaminated GSO and LGSO single crystals X-ray irradiated at 80 K and at 4 K or 8 K. The TSL glow curves are measured in the 4–520 K temperature range separately for the intrinsic, $Ce^{3+}$- or $Tb^{3+}$-related and for the $Eu^{3+}$-related emission bands. Besides, the TSL spectra are measured for each TSL glow curve peak and compared with the spectra of the X-ray excited luminescence, photoluminescence and afterglow. The thermal stability parameters (the trap depths $E_t$ and the frequency factors $f_0$) are defined for the defects responsible for different TSL glow curve peaks. Due to a large nuclear spin of Gd, the electron paramagnetic resonance studies for these crystals are not possible. Therefore, the TSL method becomes especially important for investigation of electron and hole traps in these materials.

## 2. Experimental procedure

We have studied $Ce^{3+}$-doped $Gd_2SiO_5$ (GSO) and $(LuGd)_2SiO_5$ (LGSO) crystals, and the nominally undoped GSO and LGSO crystals. The Gd concentration in the LGSO and LGSO:Ce samples was 50 at% related to the sum of lanthanides (Lu+Gd). Therefore, the formula of the LGSO crystals used in this paper can be written as $LuGdSiO_5$. All the crystals were grown under the same conditions in the Institute for Scintillation Materials, Kharkiv, Ukraine. The single crystals were grown by the Czochralski method in iridium crucibles under argon atmosphere with addition of oxygen up to 1.5 vol%. Powders of $Lu_2O_3$, $Gd_2O_3$, $SiO_2$, and $CeO_2$ with the purity not worse than 99.99% mixed in stoichiometric ratio were taken as the starting materials for crystal growth. According to Ref. [58], the melting temperatures of GSO and LGSO are 1800 °C and 1890 °C, respectively. The GSO and GSO:Ce crystals were grown along the [1 0 0] direction. The LGSO and LGSO:Ce crystals were grown along the [2 1 0] direction. According to the XRD analysis, GSO belongs to the monoclinic P21/c structure ($a$=9.127, $b$=7.051, $c$=6,743, $V$=413,831, $\beta$=107.519). The LGSO samples studied belong to the monoclinic C2/c structure ($a$=14.415, $b$=6.726, $c$=10.451, $V$=857.714, $\beta$=122.179). No admixtures of other phases were found. The typical size of the crystals was 30 mm in diameter and 50 mm in height. All the crystals were imposed to post-growth annealing at 1500 °C to prevent cracking at cutting and polishing. The Ce-doped crystals contained from 0.4 to 0.6 mol% of Ce. The nominally undoped crystal contained traces (few ppm) of $Ce^{3+}$, $Eu^{3+}$, and $Tb^{3+}$ ions.

Photoluminescence characteristics of the crystals studied were measured in the 80–400 K temperature range at the setup, consisting of a deuterium lamp (DDS-400), two monochromators (SF-4 and SPM-1) and a photomultiplier tube (FEU-39 or FEU-79) connected to an amplifier and recorder. All the spectra were corrected for the spectral distribution of the excitation light, the transmission and dispersion of the monochromators and spectral sensitivity of the detectors.

The X-ray luminescence spectra were excited at 8 K or 80 K with a X-ray tube (with a W anode operated at 30 kV, 15 mA) and measured with an Andor Shamrock B-303i spectrograph equipped with a CCD camera (Andor DU-401A-BV). These spectra were not corrected.

For the TSL studies, a crystal located in a nitrogen or helium cryostat was irradiated for 20 min by an X-ray source (with a Mo or W anode) operating at 50 kV or 30 kV and 15 mA. The TSL glow curves were measured in the 4–520 K temperature range separately for the intrinsic, $Ce^{3+}$- and/or $Tb^{3+}$-related emission and for the $Eu^{3+}$-related emission. In the 8–320 K range (in a closed cycle helium cryostat) and in the 4–300 K range (in a liquid helium cryostat), the heating rate was 0.1 K/s, the needed emission ranges were separated by a monochromator Andor Shamrock B-303i or by the optical filters (ZhS-4+FS-7, KS-14, or UFS-6 with the transmittance in the 3.0–3.5 eV, $E$ < 2.0 eV, and 3.25–3.85 eV energy ranges, respectively). The TSL intensity was detected with a CCD camera (Andor DU-401A BV) or a photon counting head Hamamatsu H8259. For the TSL glow curves measurement in the 80–520 K range (in a vacuum nitrogen cryostat), the heating rate was 0.2 K/s, the needed emission ranges ($E_{em}$=2.95–3.20 eV or $E_{em}$=1.85–2.00 eV) were separated by the monochromator SPM-1, and the TSL intensity was detected by a photomultiplier tube (FEU-39 or FEU-79) connected to an amplifier and recorder. The TSL glow curves were not corrected for the temperature dependences of the corresponding emissions intensity. The TSL spectra were measured with the use of the Andor Shamrock B-303i spectrograph equipped with a CCD camera (Andor DU-401A-BV) and were not corrected either. At the same experimental conditions, the TSL of the non-irradiated crystals was not detectable.

## 3. Experimental results and discussion

### 3.1. Nominally undoped and Ce-doped GSO crystals

In the photoluminescence spectrum of ***the nominally undoped GSO crystal*** measured at 80 K, a broad intrinsic emission band located at about 2.55 eV considerably dominates. Additionally, the