Optical transmission and luminescence of gadolinium orthosilicate single crystals with cerium anf yttrium impurities

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Received September 2, 2009

The spectra of optical transmission, photoluminescence, photoluminescence excitation, as well as the temperature dependence of the photoluminescence intensity for GSO, G(Y)SO, G(Y)SO:Ce single crystals with different yttrium content, are obtained. The yttrium additive (15 mol per cent) is found to increase the photoluminescence intensity by about 10 % and crystal transparency in the UV and visible spectral regions.

Получены спектры оптического пропускания, фотолюминесценции, возбуждения фотолюминесценции, а также температурная зависимость интенсивности фотолюминесценции монокристаллов GSO, G(Y)SO, G(Y)SO:Ce с различным содержанием иттрия. Установлено, что добавка иттрия в количестве 15 мол.% увеличивает интенсивность фотолюминесценции приблизительно на 10 % и прозрачность кристаллов в УФ и видимой области спектра.

1. Introduction

Gd_2SiO_5:Ce (GSO:Ce) stands in a specific position among the lanthanide orthosilicates. It is used as a fast scintillator to detect γ quanta in nuclear research as well as in the positron emission tomography. A poor mechanical strength is a considerable drawback of those crystals that often results in the failure thereof during the growing. A typical failure type of GSO:Ce is the delamination (up to the complete cleavage) along the perfect cleavage plane (100). To eliminate that drawback, insertion of yttrium in an amount of 10 to 20 mol. % into GSO:Ce was proposed [1].

The optical characteristics of those crystals were not studied in detail. In [2], the transmission spectra of GSO and G(Y)SO were studied, however, the authors have restricted themselves by a narrow wavelength range of 380 to 460 nm; no singularities have been found in the UV spectral region. In this work, the optical transmission and luminescence are investigated within a broad range (210 to 700 nm) for G(Y)SO, G(Y)SO:Ce (0.6 mol. % Ce) single crystals at different yttrium concentrations (10, 15, 20 mol. %). The work is to elucidate the Ce and Y impurity effects on the crystal transparence as well as the Y effect on the luminescence and spectral composition of G(Y)SO:Ce crystals.

The crystals were grown by Czochralski technique in an inert medium [3]. The grown crystals had the space symmetry group $P2_1/_c$ (the GSO structure). The plate-shaped samples of 10×10×1 mm^3 size with polished surfaces were used in the studies. The X-ray structure of the G(Y)SO crystal samples was examined using a Xcalibur-3

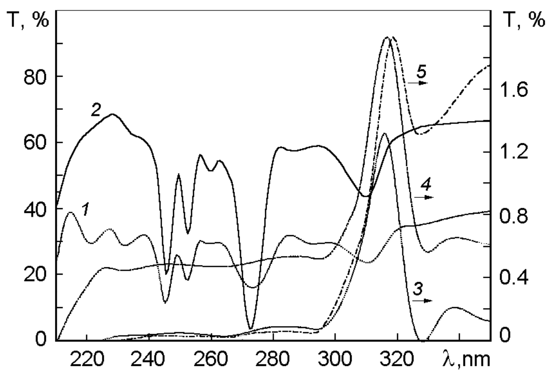

Fig. 1. Transmission spectra in UV region for G(Y)SO ang G(Y)SO:Ce samples with different Y concentrations. *1*, GSO (Y- and Ce-free); *2*, G(Y)SO (10 mol. % Y); *3*, G(Y)SO:Ce (10 mol. % Y, 0.6 mol. % Ce); *4*, G(Y)SO:Ce (15 mol. % Y, 0.6 mol. % Ce); *5*, G(Y)SO:Ce (20 mol. % Y, 0.6 mol. % Ce).

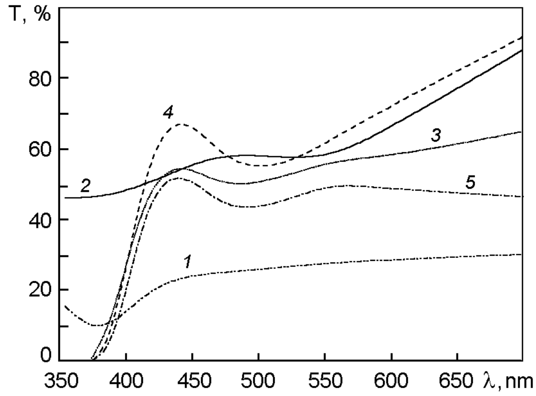

Fig. 2. Transmission spectra in visible region for G(Y)SO ang G(Y)SO:Ce samples with different Y concentrations. Curves are numbered as in Fig. 1.

single crystal diffractometer (Oxford Diffraction; MoKα emission, λ = 0.71073 Å, graphite monochromator, a Sapphire-3 CCD detector, ω/θ scanning in the 2θ≤90° range, the absorption being taken into account using equivalent reflections). The structure was calculated using SHELX-97 and WinGX software. The unit cell parameters were refined using the Rietveld method to diffraction patterns from powdered the same crystal samples using a Siemens D500 powder diffractometer in the Bragg-Brentano geometry, the angular range being 5°≤2θ≤140°. The corresponding results obtained by single crystal method were used as the initial data for the Rietveld refinement.

The transmission, luminescence excitation and emission spectra were measured using standard methods. For low-temperature measurements, a vacuum chamber with fluorite windows was used. The measuremnt apparatus comprised a light source (including a DDC-300 lamp and an incandescence one), two DMR-4 monochromators, a vacuun chamber and PMTs (FEU-100). The apparatus is shown schematically in [4].

2. Results and discussion

Fig. 1 presents typical optical transmission spectra of the GSO, G(Y)SO and G(Y)SO:Ce (0.6 mol. % Ce) samples with different yttrium concentrations. The insertion of yttrium (10 %) into the GSO matrix results in a general increase of the transmission (curves *1*, *2*). Moreover, some change occur in the spectrum. So the weak absorption bands at 220 and 230 nm disappear almost completely, while the absorption in the 245 and 272 nm bands inherent in gadolinium [5] increases noticeably. The causes thereof are still unclear, so a special study is necessary to elucidate them. In the same work, an increased transmission of the crystals due to Y insertion has been observed. A comparison of spectra for G(Y)SO and G(Y)SO:Ce samples with the same yttrium concentration (curves *2* and *3*, respectively) evidences that the Ce^{3+} insertion into G(Y)SO causes considerable changes. So the transmission value in the 210–295 nm range drops by about two decimal orders. Within the 290–350 nm range, a weak 310–320 nm transmission band appears instead of the 310 nm one, however, as a whole, the transmission in that range is one decimal order lower than that in cerium-free samples.

The transmission dependence on Y concentration for G(Y)SO:Ce samples is not monotonous. So the Y content increase from 10 to 15 mol. % results in the transmission increase within the whole wavelength range, but the further increase up to 20 mol. % causes the transmission dropping down to the level typical of samples containing 10 mol. % Y. The transmission maximum at 320 nm increases in this case (curves *3*, *4*, *5*).

The transmission variations in the visible region connected with the Y concentration increase are shown in Fig. 2. The presence of 10 mol % Y in the GSO matrix causes about doubled transmission in the luminescence region as compared with the nominally pure crystal. The Y content increase from 10 to 15 % results in a further transmission increase in the luminescence maximum ares by addiditonal 10 %. At the fur-

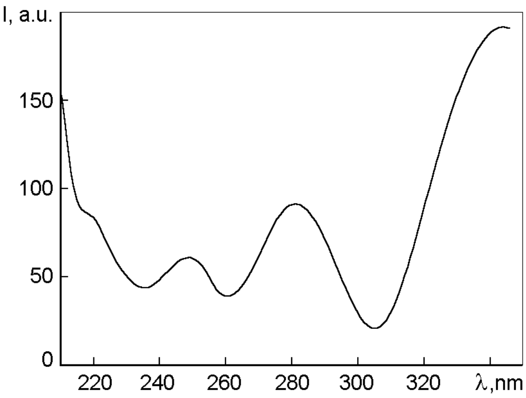

Fig. 3. Photoluminescence excitation spectrum of a G(Y)SO:Ce crystal (10 mol. % Y, 0.6 mol. % Ce).

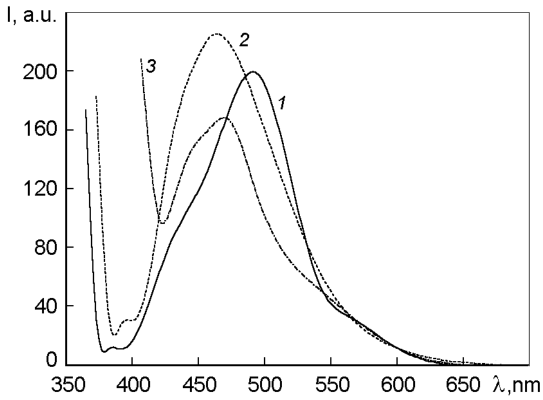

Fig. 4. Photoluminescence spectra of G(Y)SO:Ce (0.6 mol. % Ce) samples with different Y concentrations (mol.%): *1*, 10; *2*, 15; *3*, 20.

ther enrichment in Y, the crystal transparence drops.

Fig. 3 shows the photoluminescence (PL) excitation spectrum for the G(Y)SO:Ce crystal (Y, 10 mol. %; Ce, 0.6 mol. %). The PL excitation spectrum is seen to include maxima near the absorption bands typical of cerium-free samples (curves *1* and *2* in Fig. 1). The rather wide PL excitation bands are observed at 220, 250, 280, and 340 nm are observed. It is to note that the excitation efficiency values in said bands are different and correspond not always to the absorption ones. Thus, the PL intensity under 220 nm excitation is higher than that under 240–260 nm range, while in contrast, the absorption at 240–260 nm range exceeds that at 220 nm. This evidences a parallel channel of the excitation energy transformation.

The spectral position of the PL maximum and its intensity depend also on yttrium concentration (Fig. 4). At 10 mol. % yttrium (curve *1*), the PL maximum is at 495 nm. The Y concentration increase up to 15 mol. % (curve *2*), the maximum is shifted towards shorter wavelengths, while its intensity grows by 10 %. Thus, the excitation energy loss decreases and its efficiency increases. The further increase in Y concentration up to 20 % (curve *3*) does not change significantly the spectral position of the PL maximum but causes its intensity drop by 15 % as compared to that at 10 % Y. Thus, the optimum Y concentration is 15 mol. %. The PL tempertautr quenching starts at temperatures above 200°C.

References

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Оптичне пропускання та люмінесценція монокристалів оксиортосилікату гадолінію з домішками церію та ітрію

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Отримано спектри оптичного пропускання, фотолюмінесценції, збудження фотолюмінесценції, а також температурну залежність інтенсивності фотолюмінесценції монокристалів GSO, G(Y)SO, G(Y)SO:Ce з різним вмістом ітрію. Встановлено, що домішка ітрію у кількості 15 мол.% збільшує інтенсивність фотолюмінесценції приблизно на 10 % та прозорість кристалів в УФ та видимій області спектра.