Luminescence of Cation Excitons in Gd_2SiO_5 Crystals

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Materials based on complex rare-earth oxides are of high thermal, chemical and radiation resistance as well as of high light yield of scintillation. In case of doping with Ce^{3+} luminescence ions these materials also possess fast response (see, e.g., [1]). Ce^{3+}-doped gadolinium orthosilicates (Gd_2SiO_5) and their more complex analogues are promising scintillators as well [1-3]. In the present study, the novel results on a complex study of Gd_2SiO_5 single crystals of high optical quality and purity level are presented. Some characteristics of Gd_2SiO_5 and $Gd_2SiO_5:Ce^{3+}$ have been already studied in [2–3]. Special attention has been focused on the role of cation electronic excitations in the processes of low-temperature luminescence under the excitation of Gd_2SiO_5 by UV and VUV radiation or 5-10 keV electrons (see also [4]). Gd_2SiO_5 and $Gd_2SiO_5:Ce^{3+}$(0.5 mol%) crystals were grown by the Czochralski technique in the Institute for Scintillation Materials (Kharkov). Polished sample plates of $\sim 6 \times 6 \times 0.4$ mm^3 have been investigated at 8 K using synchrotron radiation of 4–20 eV at the SUPERLUMI station of HASYLAB. The excitation spectra for several emissions selected through a secondary monochromator were normalized using a reference signal from a sodium salicylate.

Weak narrow lines in the absorption spectrum of Gd_2SiO_5 correspond to $4f^7 \rightarrow 4f^7$ forbidden electron transitions in Gd^{3+} ions: $^8S_{7/2} \rightarrow {}^6P_J$ (in the region of 4 eV), $^8S_{7/2} \rightarrow {}^6I_J$ (~4,5 eV) and $^8S_{7/2} \rightarrow {}^6D_J$ (~5 eV). Significantly stronger broadband absorption at ~3.6 and 4.3 eV in $Gd_2SiO_5:Ce^{3+}$ are related to the allowed $4f^1 \rightarrow 5d^1$ transitions in Ce^{3+} ions [4]. The cathodoluminescence spectrum of Gd_2SiO_5 contains a narrow and intense emission at ~3.95 eV and the emission lines at ~4.4 and ~4.85 eV with significantly lower intensity, which correspond to the luminescence of Gd^{3+} cations ($^6P_J \rightarrow {}^8S_{7/2}$, $^6I_J{}^8 \rightarrow {}^8S_{7/2}$ and $^6D_J \rightarrow {}^8S_{7/2}$ electron transitions, respectively) as well as a broadband emission with the maximum at ~2 eV (its short-wavelength component is peaked at ~2.6 eV) [4]. Even highly pure Gd_2SiO_5 samples contain some amount of Ce^{3+} impurity ions (≤ 0.01 mol%). The introduction of 0.5 mol% of Ce^{3+} ions into Gd_2SiO_5 causes about a three-fold decrease of Gd^{3+}-emission (3.95 eV) as well as a decrease of the intensity of the ~2 eV emission tentatively ascribed to the luminescence of self-trapped excitons at oxygen ions. The emission of Gd^{3+} cation excitons at 3.95 eV is clearly detected only in the phosphorescence spectrum of a pure Gd_2SiO_5.

Fig. 1 shows the excitation spectra for 3.95 eV (emission of Gd^{3+}), 2.6 and 2.1 eV emissions measured in the region of 4-20 eV at 8 K. Gd^{3+}-emission is efficiently excited in the regions of 4.1, 4.45, 6.5-8.0 and 16-20 eV, while the efficiency of 2.6-eV emission of Ce^{3+} ions is especially high at 5.5-9.0 eV. Photons of 16-20 eV form hot (non-relaxed) carriers (conduction electrons or holes) the energy of which is sufficient for the creation of secondary electronic excitations (i.e. the multiplication process). In our case, hot carriers with the energy of 6.8-8.0 eV are needed for the excitation of oxygen ions adjacent to Gd^{3+}. At 8 K, the efficiency of Gd^{3+}-emission is really high in the region of exciting photons of 6.8-8.0 eV, when the energy transfer from oxygen excited states to Gd^{3+} ions takes place. A sharp quenching of the 3.95-eV emission occurs with temperature rise to 40 K (see inset in Fig. 1). An activation energy of this thermal quenching is about 0.15-0.20 eV and slightly depends on the exciting photon energy (7.2, 8.5 or 16.5 eV).

A generalized diagram of electron transitions in Gd^{3+} ions suggested for wide-gap fluorides ($LiGdF_4$, GdF_3, etc) [5] and later applied to $CaSO_4:Gd^{3+}$ [6] has been used for the analysis of radiative and non-radiative transitions in a cation sublattice of Gd_2SiO_5 and $Gd_2SiO_5:Ce^{3+}$. According to this diagram, unusually high energy of about 11 eV is needed for $4f^7 \rightarrow 4f^6 5d^1$ allowed transitions in the absorption of Gd^{3+} ions. Besides the reverse $4f^6 5d^1 \rightarrow 4f^7$ radiative transitions, there also take place $4f^7 \rightarrow 4f^7$ transitions in a red spectral region, as well as radiative transitions from ^6D_J, ^6I_J and especially from ^6P_J to the ground state of gadolinium ($^8S_{7/2}$). The

analysis of the data presented in Fig. 1 shows that the efficient excitation of Ce^{3+} impurity ions occurs in the region of $^8S_{7/2} \rightarrow {}^6I_J$ and $^8S_{7/2} \rightarrow {}^6D_J$ electron transitions in Gd^{3+}. The ~3.95 eV emission of Gd^{3+} is located in a deep dip of the absorption spectrum of Ce^{3+} centres [4]. In wide-gap crystals, the creation of electronic excitations on the ions surrounding the impurity ions takes place in addition to the direct excitation of the emission of impurity ions. In Gd_2SiO_5, the excitation of oxygen ions adjacent to Gd^{3+} cations can be considered as an analogue of such near-impurity-localized electronic excitations .

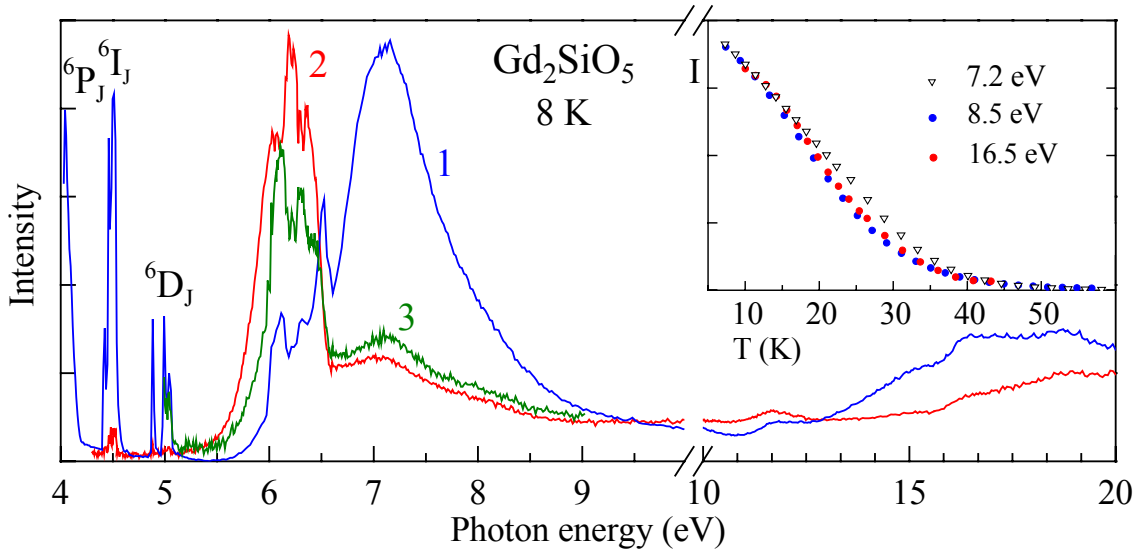

Figure 1. Excitation spectra measured for 3.95 eV (curve 1 – emission of Gd^{3+}), 2.6 (curve 2 – emission of Ce^{3+} impurity ions) and 2.1 eV emissions (curve 3 – tentatively, intrinsic emission) measured in Gd_2SiO_5 at 8 K. Temperature dependence of the 3.95-eV emission of Gd^{3+} ions under the excitation of Gd_2SiO_5 by photons of 7.2, 8.5 or 16.5 eV.

In conclusion, the efficiency of the 3.95 eV emission of Gd^{3+} at 8 K is especially high if an exciting photon of 6.8-8.0 eV causes the excitation of an oxygen ion nearby Gd^{3+}. In our opinion, a high efficiency of low-temperature hopping diffusion of cation excitons causes the efficient energy transfer from Gd^{3+} to impurity ions or structural defects. This work was supported by Estonian Science Foundation (Grant No. 7825) and the "EC Research Infrastructure Action within the FP6 Program through the Contract RII3-CT-2004-506008 (IA-SFS)".

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