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Luminescent properties of Gd_2SiO_5 powder doped with Eu^{3+} under VUV–UV excitation

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Abstract

The luminescent properties of Gd_2SiO_5 powder crystals doped with Eu^{3+} were investigated using synchrotron radiation and a VUV laser (157.6 nm) as excitation sources. The excitation spectra in the range of 160–330 nm monitoring the red emission from Eu^{3+} ions reveal bands corresponding to intraconfigurational 4f–4f transitions of Gd^{3+} and charge transfer states (CTS) of $\text{Eu}^{3+}\text{--O}^{2-}$, as well as interband transitions of the Gd_2SiO_5 host, indicating an efficient energy transfer process from the host or directly from Gd^{3+} to Eu^{3+} ions. The inspection of ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ emission lines from Eu^{3+} ions suggests that there are three inequivalent sites for Eu^{3+} in this host. The excitation band around 215 nm and the unique emission features associated with this excitation band were attributed to one of the inequivalent Eu^{3+} sites, which exhibits an unusually weak coupling with host lattice. The energy levels of Eu^{3+} in the Gd_2SiO_5 host were tentatively assigned according to the laser excited emission spectra.

1. Introduction

Gadolinium oxyorthosilicate, Gd_2SiO_5 (GSO), is the host material of a prominent scintillator, GSO:Ce, used for γ -ray detection [1–3]. The in-depth research [4, 5] on GSO:Ce has shown that in the process of Ce^{3+} luminescence there was efficient energy transfer from Gd^{3+} to Ce^{3+} , which occupy two different crystallographic sites of Gd^{3+} . The dynamical aspects of the excitons in pure GSO have been investigated from the viewpoint of the scintillation mechanism [6, 7]. The luminescence from Eu^{3+} impurity with only 0.15 ppm content was also

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observed upon excitation in the 6I_J levels of Gd^{3+} , and this indicates that the energy transfer from Gd^{3+} to Eu^{3+} is significantly remarkable.

On the other hand, the ' $Gd^{3+}-Eu^{3+}$ ' system in fluorides was recently found to be an efficient quantum cutter which can yield a quantum efficiency of visible emission close to 200% upon vacuum ultraviolet (VUV) excitation [8–10]. These newly developed quantum cutting materials can be used in plasma display panels (PDP) and mercury-free fluorescent tubes where VUV radiations generated by noble gas discharges need to be efficiently converted into visible light [11]. However, up to now, quantum cutting of the ' $Gd^{3+}-Eu^{3+}$ ' system was only realized in fluorides. This is partly due to the fact that in fluorides, charge transfer states (CTS) of $Eu^{3+}-F^-$ lie in as high as possible positions so as not to interfere with the energy transfer processes from Gd^{3+} ions to Eu^{3+} ions, while, on the other hand, the energy transfers involving cross relaxation between Gd^{3+} and Eu^{3+} 4f energy levels are crucial for the quantum cutting. But in practice, oxide materials dominate the commercial market of VUV excited phosphors [12], owing to their low cost, high VUV absorption efficiency and high chemical stability. For the same reason, combining with the efficient $Gd^{3+} \rightarrow Eu^{3+}$ energy transfer, GSO with its wide band gap (~ 6.1 eV) [7] is also a good candidate for VUV excited phosphor use, maybe even leading to a usable quantum cutter.

To the best of our knowledge, the study on the luminescent properties of Gd_2SiO_5 doped with Eu^{3+} is very limited, especially in the VUV range. In the present work, the luminescent properties of $Gd_2SiO_5:Eu^{3+}$ crystalline powder were investigated. The synchrotron radiation and F_2 laser were excitation sources in the VUV range. The results will be discussed in the light of energy transfer, and assignments of the Eu^{3+} energy levels in the GSO host were also carried out.

2. Experimental details

The $Gd_2SiO_5:Eu^{3+}$ powder crystal samples, with nominal Eu^{3+} concentrations of 0.3, 0.5 and 1.0 at.% relative to Gd^{3+} , were prepared by the sol–gel method. The purity of the raw materials Gd_2O_3 and Eu_2O_3 was both above 99.99%. The ethyllipo orthosilicate used was analytically pure. With diluted HNO_3 as solutizer, the admixture of Gd_2O_3 and Eu_2O_3 in the appropriate ratio was dissolved in ethyllipo orthosilicate and became a sol. The sol turned into gel after being given a 70 °C water bath. The dried gel was ground into fine powder and burned in a high temperature tube furnace under 1400 °C for 10 h. The prepared samples were identified as single pure phase by means of XRD. The powder samples were squashed into tablets with 10 mm diameter to be used in spectral measurements.

The luminescence spectra under synchrotron radiation were measured at the SUPERLUMI station of HASYLAB (Hamburger Synchrotronstrahlungslabor) at DESY (Deutsches Elektronen-Synchrotron). The samples were mounted on the cold finger of a liquid He flow-type cryostat. The excitation spectra were corrected for the incident flux of the excitation beam using the sodium salicylate as a standard. The emission spectra were recorded using an Acton SpectroPro308i spectroscope coupled with a liquid nitrogen cooled CCD detector (Princeton Instruments Inc.). The emission spectra were not corrected for the sensitivity of the detection system. The laser excited emission spectra of $Gd_2SiO_5:Eu^{3+}$ were measured at the Debye Institute of Utrecht University where an F_2 excimer laser was used as excitation source [13] (157.6 nm).

3. Results and discussion

Monitoring 615 nm emission (${}^5D_0 \rightarrow {}^7F_2$) from Eu^{3+} ions, the excitation spectra of $Gd_2SiO_5:Eu^{3+}$ (0.3%) were measured at low temperature (10 K) and room temperature (296 K),

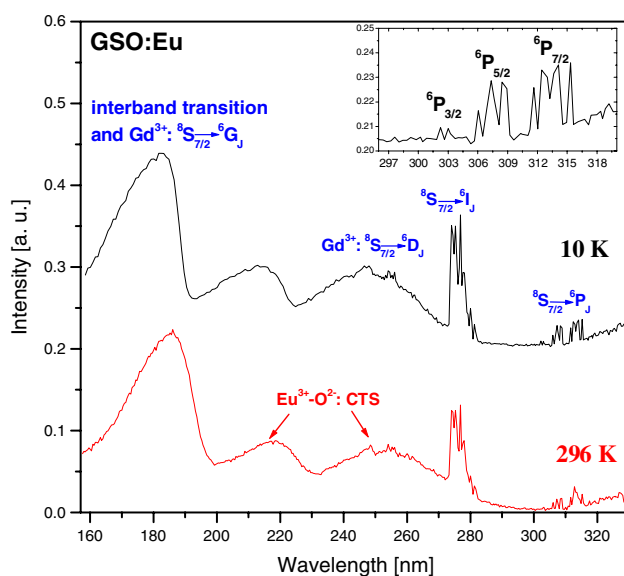


Figure 1. Excitation spectra of Gd₂SiO₅:Eu³⁺ (0.3%) monitoring 615 nm emission (⁵D₀ → ⁷F₂) from Eu³⁺. The inset shows the excitation spectra expanded in the energy region of the Gd³⁺:⁸S_{7/2} → ⁶P_J transitions.

respectively. As shown in figure 1, the excitation spectra in the range of 160–330 nm comprise several broad bands and some line structures. The two most notable groups of line structures clustering in the ranges of 301–316 and 272–283 nm are corresponding to the 4f–4f transitions of Gd³⁺ from the ⁸S_{7/2} ground state to the ⁶P_J and ⁶I_J excited states, respectively. The weakly observable line structures in the range of 247–257 nm corresponding to the higher energy transitions of ⁸S_{7/2} → ⁶D_J are overlapped with a broad band spread from 230 to 270 nm, which is characteristic of the charge transfer states (CTS) of Eu³⁺–O^{2–}. Another broad band in the range of 200–230 nm could be also due to CTS transitions, because the Eu³⁺ ions which substitute for Gd³⁺ in GSO have two crystallographic inequivalent sites with quite different environments as regards oxygen coordination. The excitation band at 160–200 nm originates from the interband transitions of the GSO host. The ⁸S_{7/2} → ⁶G_J transitions of Gd³⁺ around 200 nm, upon which the visible quantum cutting was realized in the Gd³⁺–Eu³⁺ system, were hidden by this stronger host absorption. All those strong excitations corresponding to the host and Gd³⁺ ions in the excitation spectra suggest an efficient energy transfer from the host or directly from Gd³⁺ to Eu³⁺ ions.

The inset in figure 1 shows the excitation spectra expanded in the energy region of the Gd³⁺:⁸S_{7/2} → ⁶P_J transitions. According to the crystal field splitting theory, the ⁶P_{7/2}, ⁶P_{5/2}, and ⁶P_{3/2} states should be split into four, three, and two Stark levels respectively in the noncubic crystal field *P*2₁/*c* of GSO [14]. Mori *et al* [7] reported double the number of lines corresponding to the ⁸S_{7/2} → ⁶P_J transitions in the absorption spectra of a pure GSO sample, indicating the two different crystallographic sites for Gd³⁺ in GSO that were confirmed by an x-ray structural analysis. But in our excitation spectra, only the expected numbers of lines corresponding to ⁶P_J (*J* = 7/2, 5/2, 3/2) were observed, in spite of the irregular shape of some lines. Although this result is partly caused by the moderate resolution (~0.3 nm) used in the excitation spectra measurements, we cannot exclude the possibility that the Gd³⁺ ions in only one site dominate in the energy transfer between Gd³⁺ and Eu³⁺ ions.

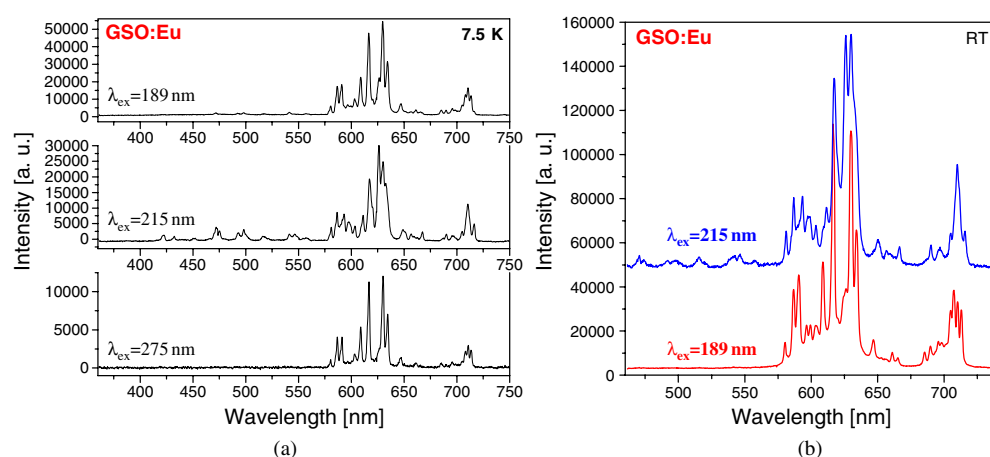


Figure 2. Emission spectra of Gd₂SiO₅:Eu³⁺ (0.3%) excited by different wavelengths of the synchrotron radiation measured at 7.5 K (a) and RT (b).

The temperature has no effect on the positions of the line structures in the excitation spectra corresponding to the Gd³⁺ 4f–4f transitions, while the excitation band at 160–200 nm shifts to longer wavelength at 296 K, relative to that at 10 K. This temperature dependence confirms that this excitation band originates from the interband transitions of the GSO host. It should be noted that the excitation band at 200–230 nm also has nearly 10 nm blue shift at 296 K relative to that at 10 K, while the other CTS band at 230–270 nm adheres to the same position at both temperatures. The different temperature effect on the two CTS bands hints at different ion–lattice couplings associated with the two inequivalent Eu³⁺ sites.

Figure 2 presents emission spectra of Gd₂SiO₅:Eu³⁺ (0.3%) excited by different wavelengths from the synchrotron radiation measured at 7.5 K and room temperature (RT). Focusing on the relative intensities of the emission lines from Eu³⁺ 4f–4f transitions, the emission spectra achieved by 189 and 275 nm excitation exhibit more similarities between them than with that excited by 215 nm (see figure 2(a)). The most unique features in the 215 nm excited emission spectra are several groups of structures spanned from 410 to 570 nm, which are results of higher energy $^5D_{1,2,3} \rightarrow ^7F_J$ transitions of Eu³⁺ other than the $^5D_0 \rightarrow ^7F_J$ transitions. On the enlarged scale, the emissions in this region are also recognizable in the 189 nm excited emission spectra, but they are completely absent in the 275 nm excited emission spectra. For the $^5D_0 \rightarrow ^7F_J$ transition lines in the longer wavelength region (>570 nm), 215 nm excited emission spectra at both temperatures also demonstrate some peculiarities concerning the relative intensities of the individual lines. For example, the 597 and 626 nm lines are much stronger and 611 nm lines are much weaker in the 215 nm excited emission spectra than their counterparts in the 189 and 275 nm excited emission spectra.

The emission spectra at RT behave similarly as those at the low temperature, so only 189 and 215 nm excited emission spectra (see figure 2(b)) are given here for comparison. The emission spectra (not shown here) excited by other wavelengths corresponding to the peaks in the excitation spectra, such as 258 nm, were also measured at both temperatures. Neglecting the minor differences, these spectra all look similar to those excited by 189 and 275 nm. The energy gaps between the 5D_0 , 5D_1 , and 5D_2 levels of Eu³⁺ ions are around 2000 cm⁻¹, and the gap between the 5D_2 and 5D_3 is about 3000 cm⁻¹. If the energy of the host lattice phonons is large enough (~ 1000 cm⁻¹), these gaps between 5D_J levels can be easily bridged by multiphonon

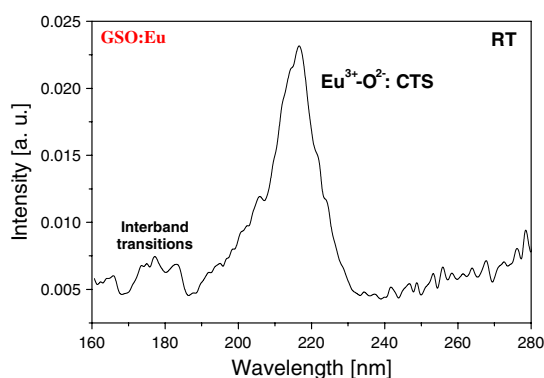


Figure 3. Excitation spectra of Gd₂SiO₅:Eu³⁺ (0.3%) monitoring 545 nm emission (⁵D₁ → ⁷F_J) from Eu³⁺, measured at RT.

processes, which lead to nonradiative relaxation from the ⁵D_J ($J = 1, 2, 3$) to the ⁵D₀ levels. Like other oxyorthosilicates, the GSO host has a vibrational band around 900 cm⁻¹ due to the asymmetric stretching of Si–O bonds, characteristic of silicate groups [15, 16]. Therefore, nonradiative relaxations from the ⁵D_{1,2,3} to ⁵D₀ are expected, and the emissions from the ⁵D_{1,2,3} levels should be quenched. But this is not the case for 215 nm excitation. It seems that the Eu³⁺ site associated with 215 nm excitation has an unusual low ion–lattice coupling.

In GSO host, the two inequivalent Gd³⁺ sites are coordinated by seven and nine oxygen ions, respectively [14, 17]. In a site with coordination number (CN) 7, the Gd³⁺ ion is bonded to three isolated oxygen ions, and to three tetrahedral (SiO₄)⁴⁻ ions through two oxygen atoms in one case and through one oxygen atom in two cases. In a site with CN = 9, the Gd³⁺ ion is bonded to one isolated oxygen ion, and to six (SiO₄)⁴⁻ ions through two oxygen atoms in two cases and through one oxygen atom in four cases. The average Gd–O bond distance is 2.39 and 2.49 Å for CN = 7 and 9, respectively. When Eu³⁺ ions are doped into the GSO host, Eu³⁺ ions will substitute the Gd³⁺ ions in the two sites with equal probabilities. Because for the site with CN = 7, there are more isolated oxygen ions and fewer bonded oxygen ions from the (SiO₄)⁴⁻ group in its coordination environment than that for the site with CN = 9, it is reasonable to relate CN = 7 to a low ion–lattice coupling site. Thus the 215 nm excitation band is suggested to result from the CTS transitions associated with Eu³⁺ ions occupying sites with CN = 7.

The excitation spectra monitoring 545 nm emissions (⁵D₁ → ⁷F_J) from Eu³⁺ ions verify that the emissions from the ⁵D₁ level are observable only upon excitation with wavelength shorter than 230 nm (see figure 3). The spectra are dominated by a broad band peaking at 217 nm which has been already attributed to CTS transitions of Eu³⁺ ions at sites with CN = 7. The pronounced band at 160–200 nm corresponding to the host interband transition in figure 1 is suppressed substantially in intensity and reduced in width in figure 3, and is only marginally visible. The irregular shapes of the two bands are mainly caused by a low signal to noise ratio, which is consequence of the weak intensity of ⁵D₁ emissions.

From the absence of Gd³⁺ transition lines in figure 3, it can be concluded that the energy transfer from Gd³⁺ to Eu³⁺ ions is only effective for one type of Eu³⁺ sites, namely the site with CN = 9. Even for the energy transfer from the GSO host to Eu³⁺ ions, it is also much less efficient for the sites with CN = 7 than for the sites with CN = 9. From this point on, we can associate the emission lines in the 275 nm excited emission spectra exclusively with Eu³⁺ ions on the CN = 9 sites. Despite the changes of the relative intensities, most of these lines

also appear in the 215 nm excited emission spectra (see figure 2), so it can be supposed that the excitation energy can be transferred from the Eu^{3+} ions on the CN = 7 sites to the Eu^{3+} ions on the CN = 9 sites, in addition to the energy transfer from the host and Gd^{3+} ions to the Eu^{3+} ions on the sites with CN = 9. The study of the samples with different Eu^{3+} concentrations (0.5 and 1.0 at.%) shows a trend of concentration quenching of Eu^{3+} luminescence, as expected for a system where the energy transfers between different ions play such active roles in the process of luminescence.

Combining with the results displayed in figure 2, the better resolved emission spectra (figure 4) achieved by VUV laser excitation (157.6 nm) provides a chance to assign the values of the Stark energy levels of Eu^{3+} ions in the GSO host. Even though the 157.6 nm excitation does not coincide with the strongest intrinsic absorption band, the high excitation density of the laser provides the appearance of emissions with sufficient intensity. Although having different efficiencies, the excitation energies absorbed by the interband transition were transferred from the host to Eu^{3+} ions at both sites, so there are emission lines from Eu^{3+} ions at both sites in figure 4 like that observed in the 189 nm excited emission spectra in figure 2.

The ${}^7\text{F}_0$ and ${}^5\text{D}_0$ levels of Eu^{3+} are non-degenerate and the emission spectra associated with transitions between them should contain as many lines as there are inequivalent sites in the structure. However, the inset in figure 4(a) shows that there are three peaks, 577.3 nm ($17\,322\text{ cm}^{-1}$), 578.2 nm ($17\,295\text{ cm}^{-1}$), and 579.0 nm ($17\,271\text{ cm}^{-1}$), in the wavelength range corresponding to the ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ transitions, not as expected for the two inequivalent Eu^{3+} sites. The middle peak ($17\,295\text{ cm}^{-1}$) is rather weak, comparing to the other two, indicating that a third site is only present in very small amounts. Camargo *et al* [16] reported the existence of Gd_2O_3 inclusion in $\text{Gd}_2\text{SiO}_5:\text{Er}^{3+}$, contributing extra sites for Er^{3+} ions. This may also be the case for the $\text{Gd}_2\text{SiO}_5:\text{Eu}^{3+}$, because Gd_2O_5 was used as one of the precursors in the preparation of our samples. The stronger $17\,322\text{ cm}^{-1}$ peak and the weaker $17\,271\text{ cm}^{-1}$ peak can be assigned to the CN = 9 sites and the CN = 7 sites, respectively, because the energy transfers from the host to Eu^{3+} ions are more efficient for the Eu^{3+} ions at the CN = 9 sites.

Table 1 gives the tentative assignments of some experimental values to selected multiplets of Eu^{3+} in the GSO crystal. The Stark levels corresponding to Eu^{3+} ions at site 2 (CN = 7) are derived by subtracting the emission lines in 275 nm excited emission spectra from that of the laser excited emission spectra. The energy value of ${}^7\text{F}_0$ level of Eu^{3+} ions at site 1 (CN = 9) is set to zero and referenced to the energy levels of Eu^{3+} ions at both sites. Because only some unambiguously determined peaks are used in the assignments, the number of assigned Stark levels is much lower than that expected for crystal field splitting levels in GSO.

So far as quantum cutting is concerned, there are two facts from our spectral results making $\text{Gd}_2\text{SiO}_5:\text{Eu}^{3+}$ seemingly not a promising quantum cutter. One is that the positions of both CTS bands are located below the ${}^6\text{G}_J$ multiplets of Gd^{3+} , obstructing the cross relaxation between Gd^{3+} and Eu^{3+} . The other is that the ${}^8\text{S}_{7/2} \rightarrow {}^6\text{G}_J$ transitions of Gd^{3+} are overlapped and overshadowed by the interband transitions of the GSO host, so the excitation energy in this range is absorbed mainly by the host, and not by ${}^6\text{G}_J$ levels, from which the quantum cutting processes start. However, taking into consideration the strong absorption in the VUV range and the efficient energy transfer from the GSO host to the doping Eu^{3+} ions, $\text{Gd}_2\text{SiO}_5:\text{Eu}^{3+}$ is still a very promising VUV phosphor. On the other hand, Eu^{3+} with its unsplit ${}^7\text{F}_0$ ground level and relatively simple energy level scheme is a very convenient probe of the activator sites, acquiring structural information along with knowledge of the crystal field in these sites. So $\text{Gd}_2\text{SiO}_5:\text{Eu}^{3+}$ is certainly an interesting sample for further studies involving luminescence kinetics to elucidate the differences and nature associated with the two inequivalent sites.

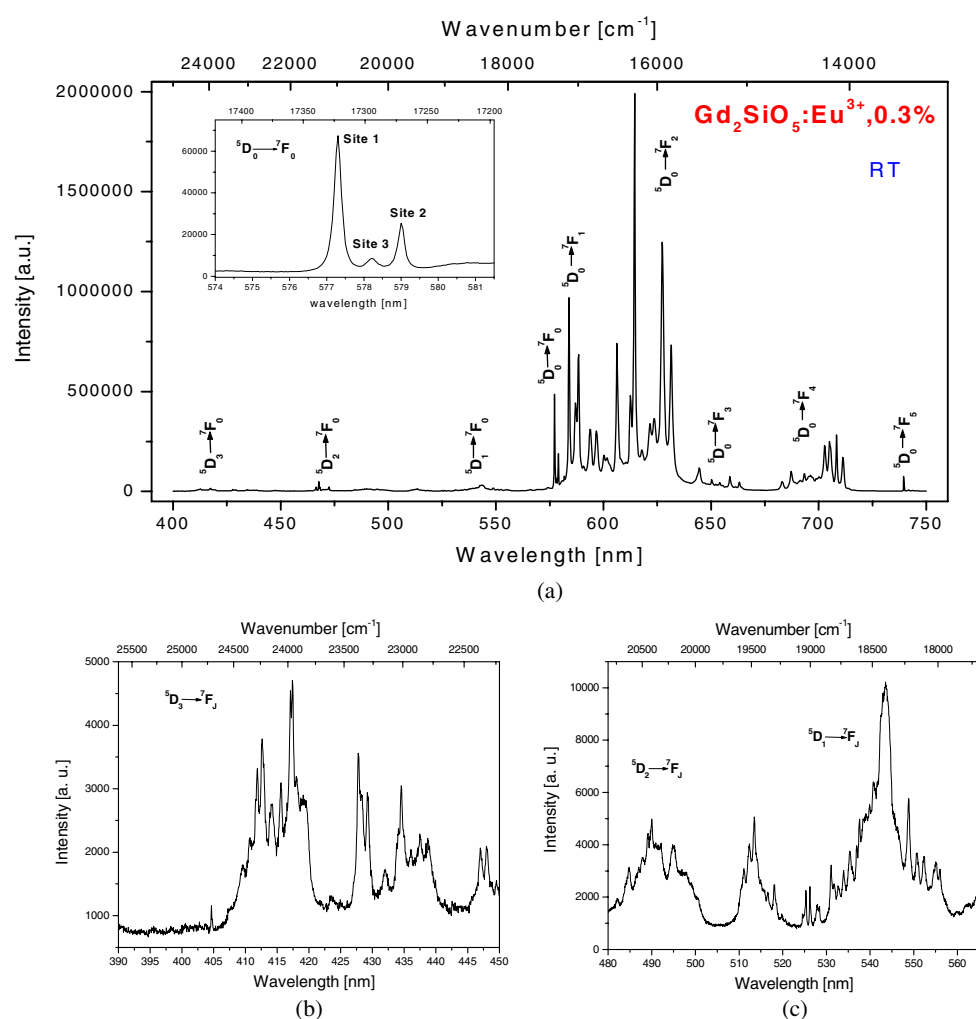


Figure 4. Emission spectra of Gd₂SiO₅:Eu³⁺ (0.3%) excited by a VUV laser (157.6 nm) measured at RT. The inset in (a) shows the emission spectrum expanded in the wavelength range corresponding to the Eu³⁺:⁵D₀ → ⁷F₀ transitions. (b) and (c) are enlarged spectra in the shorter wavelength range of spectra (a).

4. Conclusions

The investigations of the luminescent properties of Gd₂SiO₅:Eu³⁺ reveal an efficient energy transfer from the host or directly from the Gd³⁺ ions to Eu³⁺ ions, which occupy the sites with CN = 9. The 215 nm excitation band and the ⁵D_{*J*} (*J* = 1, 2, 3) emissions from Eu³⁺ ions observed in the 215 nm excited emission spectra are attributed to the Eu³⁺ ions at inequivalent sites with CN = 7. The ⁵D_{*J*} (*J* = 1, 2, 3) emissions suggest an unusually weak ion–lattice coupling associated with the CN = 7 sites. The inspection of the ⁵D₀ → ⁷F₀ emission discloses a third site, but only at the impurity level, probably caused by Gd₂O₃ inclusion in the samples. Combining the results obtained with the synchrotron radiation and the VUV laser, the tentative assignments of some experimental values to selected Eu³⁺ multiplets and different sites are given.

Table 1. Assignments of some experimental values to selected Eu^{3+} multiplets and different sites in the Gd_2SiO_5 powder crystal. The calculated positions of centres of gravity for the $\text{LaF}_3:\text{Eu}^{3+}$ crystal [18] are given for comparison.

$2S+1L_J$	Energy (cm^{-1})		Centres of gravity for $\text{LaF}_3:\text{Eu}^{3+}$
	Site 1 (CN = 9)	Site 2 (CN = 7)	
7F_0	0	51	0
7F_1	132, 199, 325, 487	288, 569	372
7F_2	826, 1049, 1138, 1236, 1383, 1487	998, 1287	1 026
7F_3	1807, 1945, 2142,	1990, 2031, 2244	1 866
7F_4	2685, 2901, 3094, 3138, 3205	2959, 3040, 3149, 3265	2 823
7F_5	3799, 3840, 3872		3 849
5D_0	17 322	17 322	17 293
5D_1		18 996, 19 055, 19 088	19 027
5D_2		21 339, 21 407, 21 430, 21 638	21 483
5D_3		24 285, 24 329, 24 400, 24 764	24 355

Acknowledgments

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