

## Luminescence and Energy Migration in the Garnet $Gd_3Li_3Te_2O_{12}$ Doped with Several Rare Earths and Uranium

W. M. A. SMIT AND G. BLASSE

*Solid State Department, Physical Laboratory, University of Utrecht,  
P.O. Box 80.000, 3508 TA Utrecht, The Netherlands*

Received July 8, 1985; in revised form September 30, 1985

Energy transfer phenomena have been observed by activating the garnet host-lattice  $Gd_3Li_3Te_2O_{12}$  with  $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Tm^{3+}$ , and  $U^{6+}$ .  $Eu^{3+}$  acts as an effective trap for  $Gd^{3+}$  excitons. Even at very low europium concentrations emission from  $Eu^{3+}$  ions can be observed showing both energy migration among the  $Gd^{3+}$  ions and efficient transfer to  $Eu^{3+}$ . Also  $Dy^{3+}$  is an effective activator for  $Gd^{3+}$  excitons, transfer being possible both from the  $Gd^{3+}$   $^6I$  and  $^6P$  levels.  $Tm^{3+}$  is not very effective in picking up energy from the  $Gd^{3+}$  sublattice. The weak transfer occurs mainly from the  $Gd^{3+}$   $^6I$  levels which are in close resonance with the  $Tm^{3+}$  ( $^3P$ ) levels.  $U^{6+}$ , occupying  $Te^{6+}$  sites in the host-lattice, is a very effective trap for  $Gd^{3+}$  excitons. Even very low ( $\leq 10$  ppm) uranium concentrations are sufficient to pick up almost all excitation energy from the  $Gd^{3+}$  sublattice. The spectral data indicate a high energy transfer probability from  $Gd^{3+}$  to  $U^{6+}$  ions, based to a large extent on an exchange interaction. © 1986 Academic Press, Inc.

### 1. Introduction

Several years ago the luminescence properties of the garnet  $Y_3Li_3Te_2O_{12}$  doped with  $U^{6+}$  and  $W^{6+}$  at the octahedral positions and with various rare earth ions at the dodecahedral positions were reported (1). Since then energy migration phenomena in  $Gd^{3+}$  compounds (2) became of growing interest in our laboratory. In the course of these studies we investigated energy migration in the isostructural garnet  $Gd_3Li_3Te_2O_{12}$  doped with  $U^{6+}$  and several rare earth ions. The host-lattice crystallizes in the garnet structure with cation distribution  $\{Gd_3\}[Te_2](Li_3)O_{12}$  (3, 4).

Recently, luminescence and energy transfer phenomena in rare earth-activated  $Gd_3Li_3Te_2O_{12}$  were reported by Königeter and Kemmler-Sack (4). In this paper we

report on the luminescence spectra of the undoped host-lattice and on samples doped with  $Eu^{3+}$ ,  $Dy^{3+}$ ,  $Tm^{3+}$ , and  $U^{6+}$ . The results will be discussed in relation to energy transfer phenomena.

### 2. Experimental

The garnets were prepared by mixing stoichiometric amounts of the starting compounds, viz.  $RE_2O_3$  (Highways, purity 99.999%),  $UO_2(NO_3)_2 \cdot 6H_2O$  (Merck, p.a., purity >99%),  $TeO_2$  (Merck, purity 99.999%),  $Li_2CO_3$  (Merck, p.a., purity >99%). In view of the volatility of  $TeO_2$  this compound was always taken with an excess of 5%. After grinding, the mixtures were fired at 800°C under an oxygen atmosphere during 8 hr and after renewed grind-

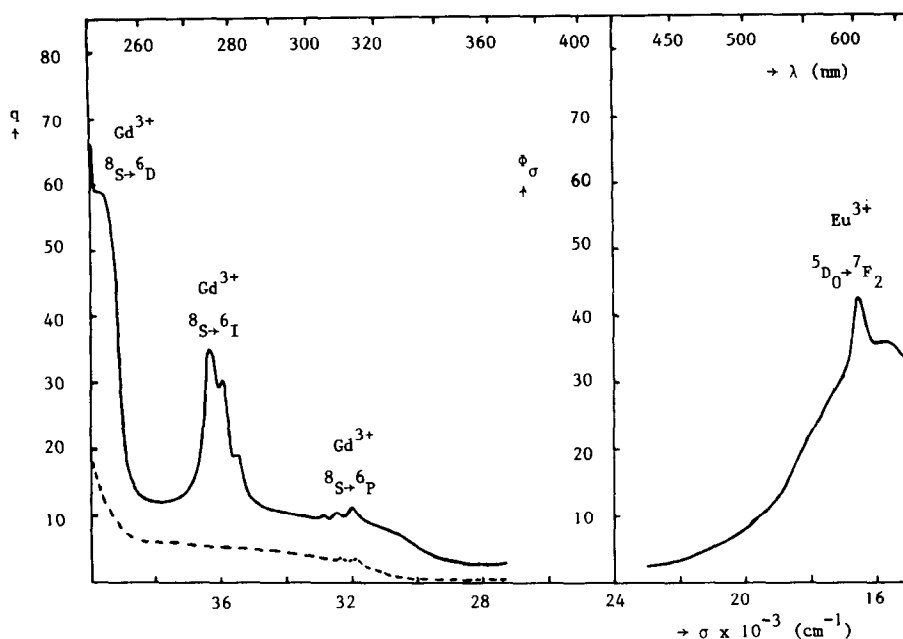


FIG. 1. Luminescence spectra of the host-lattice,  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Full lines, 77 K; broken line, room temperature. For the excitation spectrum broad band emission around 580 nm was monitored. The emission spectrum is almost independent of excitation wavelength in the region 250–320 nm.

ing fired for another period of 8 hr. All samples were checked by X-ray powder diffraction using  $\text{CaK}\alpha$  radiation. Diffuse reflectance spectra were measured with a Perkin-Elmer EPS-3T UV-VIS spectrophotometer.

The luminescence spectra were recorded on a Perkin-Elmer MPF-2A spectrofluorometer equipped with a Hamamatsu R446 photomultiplier.

According to international recommendations (6) the emission spectra are presented as  $\Phi$  (photon flux per constant wavenumber interval) vs wavenumber. Similarly, the excitation spectra are plotted as  $q$  (relative quantum output) vs wavenumber. All spectral data given refer to 77 K unless stated otherwise.

The average particle size of the polycrystalline samples was determined with electron microscopy and turned out to fall in the range of 1–3  $\mu\text{m}$ .

### 3. Results and Discussion

#### 3.1. Gd-Garnet Host-Lattice

Upon excitation into the  $\text{Gd}^{3+}$  absorption lines as well as in the optical absorption edge at about 250 nm the undoped host-lattice shows a weak, broad emission band at about 630 nm at room temperature (RT) and below (see Fig. 1). Weak  $\text{Eu}^{3+}$  emissions are observed superimposed on this band, pointing to the presence of a very small amount of  $\text{Eu}^{3+}$  impurity. In view of the high quality of the starting  $\text{Gd}_2\text{O}_3$ , viz. 99.999%, this shows that energy migration occurs in the  $\text{Gd}^{3+}$  sublattice followed by transfer to  $\text{Eu}^{3+}$  centers. The excitation spectrum of the broad emission band, also shown in Fig. 1, reveals that excitation energy is transferred from  $\text{Gd}^{3+}$  to the broad-band emitting centers. The nature of these centers is not known. The diffuse reflectance spectrum shows an absorption maxi-

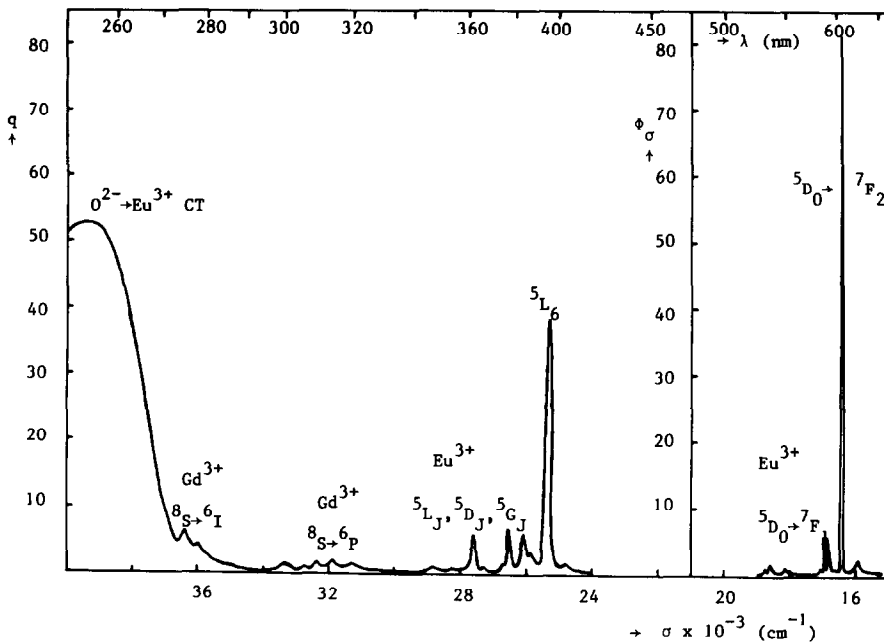


FIG. 2. Luminescence spectra of  $\text{Eu}^{3+}$ -activated  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Emission spectrum,  $\lambda_{\text{exc.}} = 395 \text{ nm}$ ; excitation spectrum,  $\lambda_{\text{em.}} = 611 \text{ nm}$ .

mum at about 242 nm (RT), in accordance with the results of Köngeter and Kemmler-Sack (4) (here after referred to as KKS) and Blasse and Brill (7). The tailing of this band to longer wavelengths is probably related to the broad-band emitting centers, in agreement with the excitation spectrum of Fig. 1. The host-lattice luminescence becomes weaker at higher temperatures but is still observable at RT. Similar observations were made by Lammers *et al.* for  $\text{Gd}_2\text{BaZnO}_5$  (8) which contains also metal ions with  $d^{10}$  configuration. Since the emission spectrum of Fig. 1 does not depend on excitation wavelength, the transfer processes must be as follows. Excitation into the host-lattice is followed by energy transfer to  $\text{Gd}^{3+}$ . Energy migration among the  $\text{Gd}^{3+}$  ions feeds the broad-band emitting centers and the  $\text{Eu}^{3+}$  centers. From Fig. 1 it is clear that the former are more successful in trapping the energy. Since the broad-band emitting centers show absorption of reasonable oscillator strength in the region where  $\text{Gd}^{3+}$

emits, whereas  $\text{Eu}^{3+}$  does not (see below), the transfer to these centers is more probable than to  $\text{Eu}^{3+}$ . Also the reflection spectra suggest that their concentration is higher.

### 3.2. Gd-Garnet with 3 mole% $\text{Eu}^{3+}$

As reported in Ref. (4) the excitation spectrum of the  ${}^5D_0 \rightarrow {}^7F_2$  emission of  $\text{Eu}^{3+}$  at 611 nm contains  $\text{Gd}^{3+}$  lines (see Fig. 2). This indicates that the energy migrating among the  $\text{Gd}^{3+}$  sites is partly transferred to  $\text{Eu}^{3+}$  ions. The strongest feature in the excitation spectrum is the  $\text{O}^{2-} \rightarrow \text{Eu}^{3+}$  CT band at about 255 nm which is also found in the reflection spectrum ( $\sim 260 \text{ nm}$ , RT). The value given by KKS from their reflection spectrum, viz.  $\sim 37,500 \text{ cm}^{-1}$  (267 nm) is in reasonable agreement with our value. However, the value reported by KKS from their excitation spectrum, viz.  $36,500 \text{ cm}^{-1}$  (274 nm) is different from our value. This is on the one hand due to the fact that KKS made no corrections for the intensity distribution

of the xenon lamp while on the other hand a temperature influence plays a role. The KKS excitation spectra were taken at RT, ours at 77 K. In our corrected RT excitation spectrum the CT band is found at 260 nm, in complete agreement with our reflection spectrum. This shift of the O<sup>2-</sup> → Eu<sup>3+</sup> CT-band to lower energy at higher temperatures is well known (8). At the same time the relative intensity of the Gd<sup>3+</sup> excitation lines at RT (4) is larger than at 77 K (see Fig. 2), indicating that energy migration among the Gd<sup>3+</sup> ions followed by transfer to Eu<sup>3+</sup> ions is more effective at RT than at 77 K.

Similar positions for the Eu<sup>3+</sup> CT-band have been reported by Natansohn (9) for Eu<sup>3+</sup>-activated RE<sub>2</sub>TeO<sub>6</sub> (RE = Lu, Y, Gd, La), viz. 240, 255, 260, and 272 nm, respectively. Moreover, in the excitation spectrum of the Gd<sub>2</sub>TeO<sub>6</sub>-Eu<sup>3+</sup> sample Gd<sup>3+</sup> lines showed up, revealing the same energy transfer process being operative as observed for Gd<sub>3</sub>Li<sub>3</sub>Te<sub>2</sub>O<sub>12</sub>-Eu<sup>3+</sup>.

### 3.3. Gd-Garnet with 3 mole% Dy<sup>3+</sup>

In agreement with Köngeter and Kemmler-Sack (4) energy transfer is observed from Gd<sup>3+</sup> (<sup>6</sup>I, <sup>6</sup>P) to Dy<sup>3+</sup> (levels S to Z (10)) as shown by the excitation spectrum of Fig. 3a. The relative contribution of the Gd<sup>3+</sup> <sup>6</sup>I and <sup>6</sup>P levels to the Dy<sup>3+</sup> emission changes somewhat with temperature. At increasing temperature the relative intensity of the Gd<sup>3+</sup> (<sup>6</sup>P) lines becomes higher than that of the Gd<sup>3+</sup> (<sup>6</sup>I) lines (see Fig. 3a), which is due to the fact that the host-lattice absorption band at 242 nm broadens and shifts to lower energy at increasing temperature, leading to a strong host-lattice absorption at the position of the Gd<sup>3+</sup> (<sup>6</sup>I) lines. The Dy<sup>3+</sup> emission spectrum, shown in Fig. 3b, is independent of the excitation wavelength and contains the usual lines at 488 nm (<sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>15/2</sub>) and 580 nm (<sup>4</sup>F<sub>9/2</sub> → <sup>6</sup>H<sub>13/2</sub>).

Note the high intensity of the yellow emission lines. This has also been observed

for the garnet NaCa<sub>2</sub>Mg<sub>2</sub>V<sub>3</sub>O<sub>12</sub>-Dy<sup>3+</sup> and is due to the hypersensitive nature of this transition in which  $\Delta J = 2$ . The same is true for the <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> emission of Eu<sup>3+</sup> as has been discussed elsewhere (11, 12).

Recently the system (Y<sub>1-x</sub>Gd<sub>x</sub>)<sub>3</sub>Li<sub>3</sub>Te<sub>2</sub>O<sub>12</sub>-Dy<sup>3+</sup> has been investigated. Interpretation of the observed Dy<sup>3+</sup> emission upon excitation in the Gd<sup>3+</sup> <sup>6</sup>P levels revealed that energy migration in the Gd<sup>3+</sup> sublattice takes place for x < 0.5 (13). This shows in an independent way that migration through the Gd<sup>3+</sup> sublattice occurs.

### 3.4. Gd-Garnet with 3 mole% Tm<sup>3+</sup>

The emission spectrum of the garnet sample doped with Tm<sup>3+</sup> is shown in Fig. 4. Excitation took place in the strong Tm<sup>3+</sup> <sup>3</sup>H<sub>6</sub> → <sup>1</sup>D<sub>2</sub> absorption line at 358 nm, leading to an intense <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>4</sub> emission. The excitation spectrum of this emission is dominated by the Tm<sup>3+</sup> <sup>3</sup>H<sub>6</sub> → <sup>1</sup>D<sub>2</sub> transition. With much lower intensity (see Fig. 4) the Gd<sup>3+</sup> transitions <sup>8</sup>S → <sup>6</sup>I and <sup>8</sup>S → <sup>6</sup>D at 277 at 254 nm, respectively, are also observed, whereas the <sup>8</sup>S → <sup>6</sup>P transitions around 310 nm are hardly discernable. This shows that only transfer from the Gd<sup>3+</sup> <sup>6</sup>I level to Tm<sup>3+</sup> is effective, due to the fact that the Gd<sup>3+</sup> (<sup>6</sup>I) levels are close to the Tm<sup>3+</sup> <sup>3</sup>P<sub>0</sub> and <sup>3</sup>P<sub>1</sub> levels. The Gd<sup>3+</sup> (<sup>6</sup>P) levels are too far out of resonance with the Tm<sup>3+</sup> levels to result in an appreciable transfer. Therefore, the excitation spectrum suggests the following relaxation processes upon Gd<sup>3+</sup> excitation: (i) migration of Gd<sup>3+</sup> (<sup>6</sup>P) excitons in the Gd<sup>3+</sup> sublattice, followed mainly by transfer to other centers, since transfer to Tm<sup>3+</sup> is very improbable; (ii) migration of Gd<sup>3+</sup> (<sup>6</sup>I) excitons, followed partly by transfer to Tm<sup>3+</sup> (<sup>3</sup>P<sub>1,0</sub>), partly by relaxation to the <sup>6</sup>P levels; (iii) migration of Gd<sup>3+</sup> (<sup>6</sup>D) excitons, followed by relaxation to the <sup>6</sup>I levels.

### 3.5. Gd-Garnet with U<sup>6+</sup>

The U<sup>6+</sup>-doped garnet samples show the usual emission pattern of the octahedral

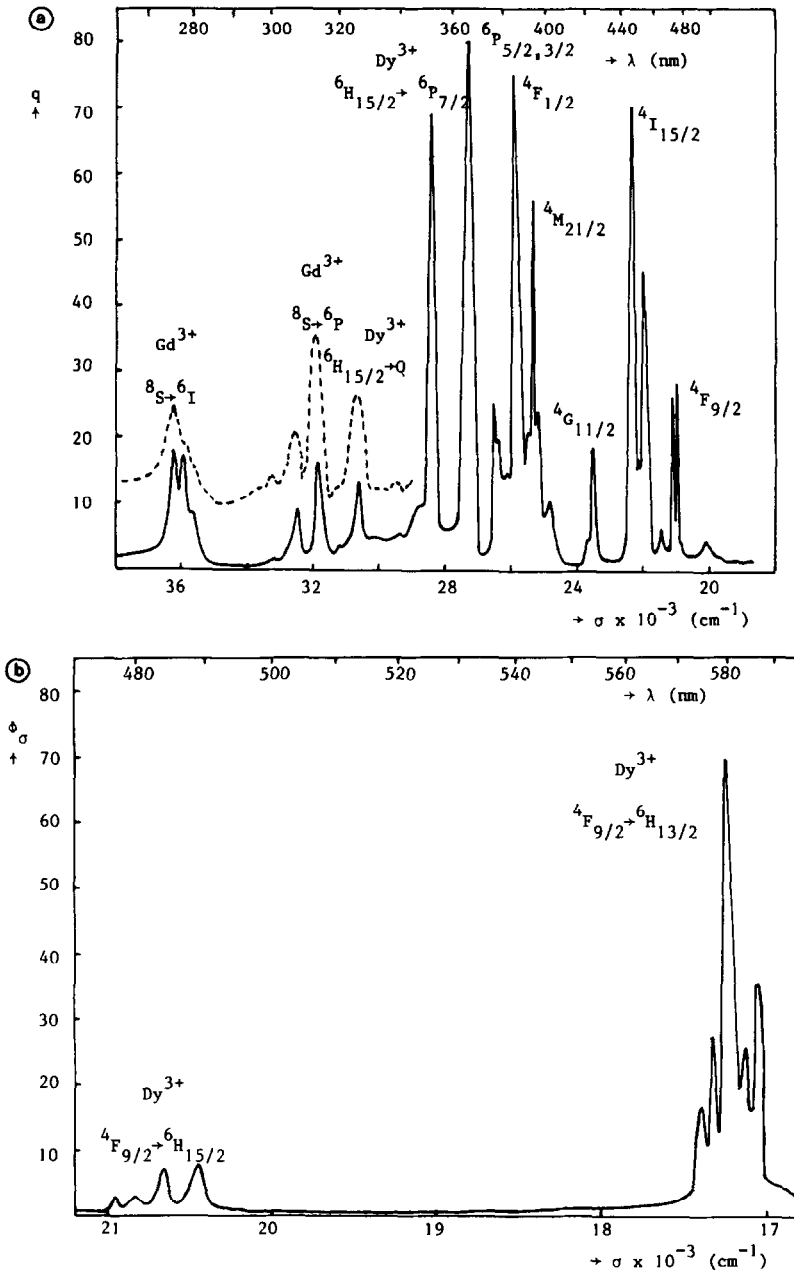


FIG. 3. (a) Excitation spectrum of  $\text{Dy}^{3+}$ -activated  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Emission wavelength, 580 nm. Full line, 77 K; broken line, room temperature. (b) Emission spectrum of  $\text{Dy}^{3+}$ -activated  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Excitation in any of the  $\text{Gd}^{3+}$  and  $\text{Dy}^{3+}$  excitation lines shown in (a).

$\text{UO}_6^{6-}$  group at about 550 nm ( $I$ ) (see Fig. 5). At 77 K the vibronic structure is partly resolved. The quantum efficiency is rather

high (>70%) at low temperatures, but decreases to about 30% at RT. This quenching temperature is much lower than in the iso-

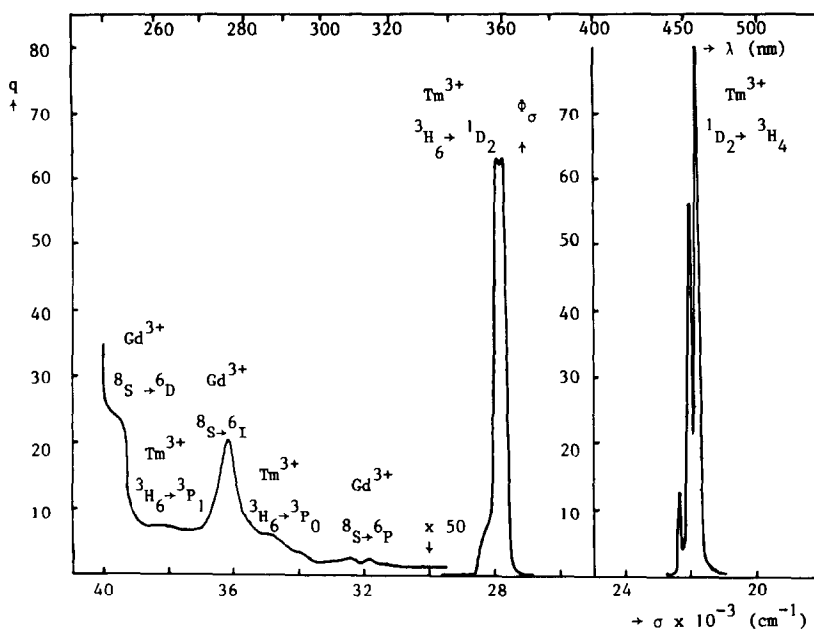


FIG. 4. Luminescence spectra of  $\text{Tm}^{3+}$ -activated  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Emission spectrum,  $\lambda_{\text{exc.}} = 358$  nm; excitation spectrum,  $\lambda_{\text{em.}} = 457$  nm. Note the weakness of the short wavelength part of the excitation spectrum relative to the  $\text{Tm}^{3+} 3H_6 \rightarrow 1D_2$  excitation line.

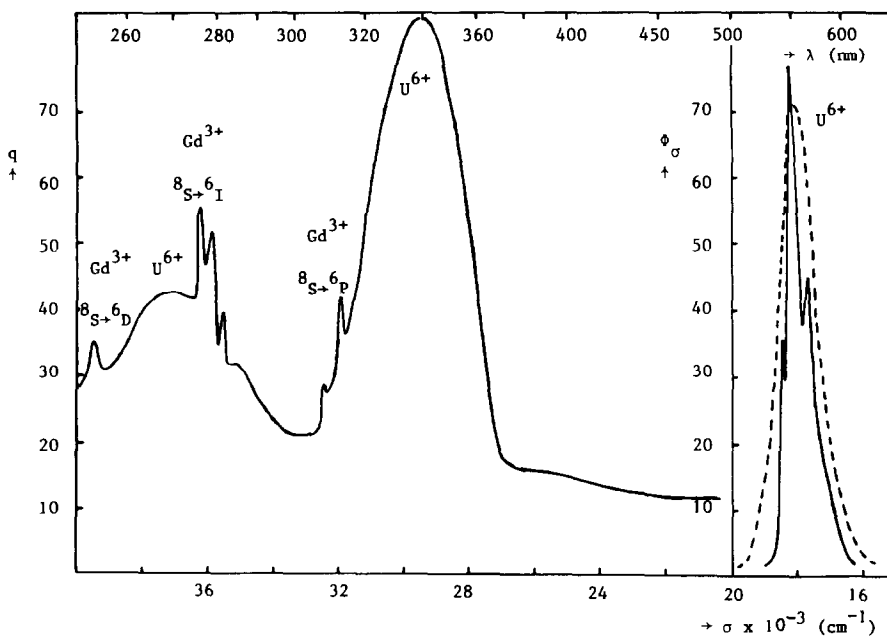


FIG. 5. Luminescence spectra of  $\text{U}^{6+}$ -activated  $\text{Gd}_3\text{Li}_3\text{Te}_2\text{O}_{12}$ . Full lines, 77 K; broken line, room temperature. Emission spectrum, excitation in any of the  $\text{Gd}^{3+}$  and  $\text{U}^{6+}$  excitation lines. Excitation spectrum,  $\lambda_{\text{em.}} = 550$  nm.

morphous  $Y_3Li_3Te_2O_{12}$  (I), where quenching occurs only above RT.

The first excitation band of the uranate emission is at 340 nm in the  $Gd^{3+}$  garnet, but at 325 nm in the  $Y^{3+}$  garnet. It has been shown that the quenching temperature depends on the position of the excitation band (14), in agreement with the present observation. The excitation spectrum of the 550-nm emission shows, apart from the  $UO_6^{6-}$  bands at about 270 and 340 nm, the  $Gd^{3+}$  ( $^6I$ ,  $^6P$ ) lines, revealing energy transfer from  $Gd^{3+}$  to  $U^{6+}$  centers. Samples with  $10^{-5}$ – $1$  mole%  $U^{6+}$  show essentially similar spectra, although the  $Gd^{3+}$  lines in the excitation spectrum become relatively weak for the higher  $U^{6+}$  concentrations.

The diffuse reflectance spectra are in agreement with the excitation spectra, showing  $U^{6+}$  absorption bands at approximately 400 (weak), 340, and 270 nm. These observations add  $U^{6+}$  to the large family of ions which are able to trap the excitation energy from the  $Gd^{3+}$  sublattice: lanthanide ions ( $Eu^{3+}$ ,  $Tb^{3+}$ ,  $Dy^{3+}$ , and so on), transition metal ions ( $Mn^{2+}$ ,  $Cr^{3+}$ ) and now an actinide ion,  $U^{6+}$ .

The spectral data enable us to estimate the spectral overlap between the  $Gd^{3+}$  emission line and the uranate excitation band at 340 nm. Its value is about  $0.03$   $eV^{-1}$ . With an oscillator strength of  $10^{-2}$  for the uranate band, the absorption cross section has the value  $5 \times 10^{-18}$   $eV$   $cm^2$  (15) leading to a critical distance  $R_c$  for energy transfer from  $Gd^{3+}$  to  $U^{6+}$  of about 12 Å. The shortest  $Gd^{3+}$ – $U^{6+}$  distance in the  $Gd_3Li_3Te_2O_{12}$  lattice is about 3.5 Å (5). By taking  $\tau_r(Gd^{3+}) = 3$  msec, the probability for nearest-neighbor transfer,  $P_{Gd \rightarrow U}^{nn}$  ( $dd$ ) can be calculated to be about  $5 \times 10^5$   $sec^{-1}$ . For  $Gd^{3+} \rightarrow Tb^{3+}$  and  $Gd^{3+} \rightarrow Mn^{2+}$  values have been found which are one order of magnitude larger (2a). Since we have observed that samples containing very low uranium concentrations ( $<10$  ppm) are still able to trap the greater amount of the  $Gd^{3+}$

excitation energy, we can estimate a lower limit for the exciton hopping probability within the  $Gd^{3+}$  sublattice. From the cell constant  $a = 12.39$  Å (5) and the  $U^{6+}$  concentration ( $\leq 10^{-5}$ ) the average available volume per  $U^{6+}$  ion can be calculated to be  $\geq 1.2 \times 10^7$  Å<sup>3</sup>, corresponding to a sphere with radius  $r \geq 140$  Å. The value of this radius may be considered as an estimate of the minimum diffusion length  $\bar{x}$  for  $Gd \rightarrow Gd$  energy migration. It is important to note that in view of the average particle diameter of 1–3  $\mu m$  (see Section 2) much longer diffusion lengths are readily possible and, therefore, surface effects may be expected to be of minor importance. Considering only nearest-neighbor transfer the jump distance,  $d$ , in the  $Gd_3Li_3Te_2O_{12}$  lattice is 3.79 Å (5). For the minimum number of jumps,  $n_{min}$ , we now find  $n_{min} = (\bar{x}/d)^2 \approx 1400$ . Since  $n_{min} \approx t/\tau_h$  where  $\tau_h$  is the characteristic hopping time, and  $t$  must be  $\leq \tau_r(Gd^{3+})$  (16), we obtain  $\tau_h^{-1} = P_{Gd \rightarrow Gd}^{nn} \geq 5 \times 10^5$   $sec^{-1}$ .

The intensity ratio of the emission from  $U^{6+}$  trap centra and  $Gd^{3+}$  intrinsic centra at excitation in the  $Gd^{3+}$ ( $^6I$ ) levels at 276 nm can be given as (17, 18)

$$\frac{I_{em,U^{6+}}}{I_{em,Gd^{3+}}} (\text{exc. } 276 \text{ nm}) = \frac{x_U P_{Gd \rightarrow U} P_{Gd}^{rad}}{P_{Gd}^{rad} P_{Gd \rightarrow U} e^{-\Delta/kT} + P_{Gd}^{rad} P_U^{rad}}$$

which reduces for  $\Delta \gg kT$  to

$$\frac{I_{em,U^{6+}}}{I_{em,Gd^{3+}}} (\text{exc. } 276 \text{ nm}) = \frac{x_U P_{Gd \rightarrow U}}{P_{Gd}^{rad}}$$

where  $x_U$  denotes the relative uranium concentration and  $\Delta$  the energy difference between the lowest absorption level of  $Gd^{3+}$  and the emitting level of  $U^{6+}$ . In the present case this energy difference is about 13,000  $cm^{-1}$ , certainly allowing the use of the reduced expression for the intensity ratio. The observed value for this intensity ratio at 77 K for a sample with  $x_U = 1.7 \times 10^{-4}$  is  $3.6 \times 10^3$ . This value is corrected for direct

$\text{U}^{6+}$  excitation at 276 nm (see Fig. 5). With the estimated value for  $P_{\text{Gd} \rightarrow \text{U}}^{\text{nn}}(dd)$ , viz.  $5 \times 10^5 \text{ sec}^{-1}$  and with  $\tau_r(\text{Gd}^{3+}) = 3 \text{ msec}$ , the calculated intensity ratio becomes 0.25. In order to reproduce the experimental ratio, we need a value for  $P_{\text{Gd} \rightarrow \text{U}}$  of about  $7 \times 10^9 \text{ sec}^{-1}$ , strongly suggesting that an exchange-type interaction contributes to the transfer probability. The rather short nn  $\text{Gd}^{3+}-\text{U}^{6+}$  distance of about  $3.5 \text{ \AA}$  certainly favors the possibility of such a contribution. Similar suggestions have been made for  $\text{Gd}^{3+}-\text{Mn}^{2+}$  transfer (8).

### Acknowledgments

Mrs. A. W. E. de Boer, P. J. de Boer, S. Harder, C. A. J. J. van Rossum, H. Kooyman, and M. C. Schoondermark are gratefully acknowledged for sample preparation and measurement of the luminescence spectra.

### References

1. R. H. ALBERDA AND G. BLASSE, *J. Lumin.* **12/13**, 687 (1976).
2. (a) M. LESKELÄ, M. SAAKES, AND G. BLASSE, *Mater. Res. Bull.* **19**, 151 (1984); (b) HAO ZHIRAN AND G. BLASSE, *J. Lumin.* **31/32**, 817 (1984); (c) HAO ZHIRAN AND G. BLASSE, *Mater. Chem. Phys.* **12**, 257 (1985).
3. D. KROL AND G. BLASSE, *J. Inorg. Nucl. Chem.* **37**, 1328 (1975).
4. B. KÖNGETER AND S. KEMMLER-SACK, *Z. Naturforsch. A* **39**, 490 (1984).
5. H. M. KASPER, *Inorg. Chem.* **8**, 1000 (1969).
6. J. H. CHAPMAN, TH. FÖRSTER, G. KORTÜM, E. LIPPERT, W. H. MELHUISH, G. NEBBIA, AND C. A. PARKER, *Appl. Spectrosc.* **17**, 171 (1963).
7. G. BLASSE AND A. BRIL, *J. Solid State Chem.* **2**, 291 (1970).
8. M. J. J. LAMMERS, H. DONKER, AND G. BLASSE, *Mater. Chem. Phys.* **13**, 527 (1985).
9. S. NATANSOHN, *J. Electrochem. Soc.* **116**, 1250 (1969).
10. G. F. IMBUSCH, in "Luminescence Spectroscopy" (M. D. Lumb, Ed.), Academic Press, New York/London (1978).
11. J. L. SOMMERDIJK, A. BRIL, AND F. M. J. H. HOEX-STRIK, *Philips Res. Rep.* **32**, 149 (1977).
12. G. BLASSE AND A. BRIL, *J. Chem. Phys.* **47**, 5442 (1967).
13. A. J. DE VRIES, H. S. KILIAAN, AND G. BLASSE, *J. Solid State Chem.* (1986).
14. G. BLASSE, *J. Electrochem. Soc.* **124**, 1280 (1977).
15. G. BLASSE, *Philips Res. Rep.* **24**, 131 (1969).
16. G. E. VENIKOUAS AND R. C. POWELL, *J. Lumin.* **16**, 29 (1978).
17. R. L. GREENE, D. D. SELL, R. S. FEIGELSON, G. F. IMBUSCH, AND H. J. GUGGENHEIM, *Phys. Rev.* **171**, 600 (1968).
18. D. M. KROL AND A. ROOS, *Phys. Rev. B* **23**, 2135 (1981).