

# Energy Levels and Luminescence of Dysprosium(III) in a Fluoride Glass With and Without Manganese(II)\*\*

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**Abstract:** Luminescence, excitation, and emission spectra are studied of vitreous {36 PbF<sub>2</sub> : 24 ZnF<sub>2</sub> : 35 GaF<sub>3</sub> : 2 AlF<sub>3</sub> : 3 YF<sub>3</sub> : 2 DyF<sub>3</sub>; mole ratios of the anhydrous fluorides} and in the analogous glass (with and without DyF<sub>3</sub>) having ZnF<sub>2</sub> replaced by MnF<sub>2</sub>. Intense narrow-band emission at  $\lambda = 483$  and 580 nm is due to the 4f<sup>9</sup> level <sup>4</sup>F<sub>9/2</sub> (lifetime 0.4 ms, shortened by a factor 30 in presence of MnF<sub>2</sub>, due to Dy<sup>III</sup> → Mn<sup>II</sup> energy transfer above 21 000 cm<sup>-1</sup>). Weak emission at 454 nm has a long-time component due to thermalization to (Dy<sup>III</sup>)<sup>4</sup>I<sub>15/2</sub> and possibly short-lived <sup>4</sup>F<sub>7/2</sub> to <sup>6</sup>H<sub>13/2</sub>. The transition to the ground state may contribute to a broadened, weak emission at 391 nm (0.01 ms). When Mn<sup>II</sup> and Dy<sup>III</sup> are simultaneously present, the broad band around 592 nm emitted by the lowest quartet state of Mn<sup>II</sup> has the lifetime shortened from 0.7 to 0.2 ms, even the former value being low because of the large manganese concentration. Energy transfer from Mn<sup>II</sup> has previously been observed in the case of near-infrared line emission of neodymium(III) and thulium(III) in such fluoride glasses.

Many solid-state lasers used today are crystalline materials, such as the garnet-type Y<sub>3-x</sub>Nd<sub>x</sub>Al<sub>5</sub>O<sub>12</sub> though silicate glasses containing neodymium(III) are also applied both for laboratory use and terawatt lasers, inducing thermonuclear fusion in deuterium-tritium mixtures. As far as emission from higher to lower *J*-levels of a partly filled 4f shell goes, a major criterion is the smallest possible rate *W*<sub>nr</sub> of non-radiative de-excitation known<sup>[1-3]</sup> to be proportional to exp(- $\alpha\Delta E$ ) where the reciprocal energy  $\alpha$  essentially is a constant characterizing the colourless host material, and  $\Delta E$  is the energy gap between the emitting *J*-level and the closest lower *J*-level. The optimized laser materials have the highest possible  $\alpha$  (as found in vitreous and crystalline fluorides<sup>[4-8]</sup>) and have emitting *J*-levels with  $\Delta E$  at least 2000 cm<sup>-1</sup> (this minimum value is at least twice as large in oxide systems). The positions and

assignments of nearly all *J*-levels are well established<sup>[2,9,10]</sup> up to at least 30 000 cm<sup>-1</sup> and the variations with neighbour atoms are of order 1 percent, excepting some larger shifts in Pr<sup>III</sup> and Nd<sup>III</sup>.

Nearly all accessible energy gaps above 2000 cm<sup>-1</sup> have been found to induce luminescence of fluoride glasses in the cases of 4f<sup>2</sup> praseodymium(III)<sup>[11]</sup>, 4f<sup>3</sup> neodymium(III)<sup>[12]</sup>, 4f<sup>6</sup> europium(III)<sup>[13]</sup>, 4f<sup>10</sup> holmium(III)<sup>[4-6]</sup>, 4f<sup>11</sup> erbium(III)<sup>[14,15]</sup>, and 4f<sup>12</sup> thulium(III)<sup>[16]</sup>. There is little doubt that the *J*-levels of 4f<sup>5</sup> samarium(III) are so crowded<sup>[2,9]</sup> that only the «classical» level <sup>4</sup>G<sub>3/2</sub> at 17 900 cm<sup>-1</sup> is likely to luminesce, even in fluoride glasses. Among the remaining alternatives, the most interesting is 4f<sup>9</sup> dysprosium(III) having a well-known fluorescent level <sup>4</sup>F<sub>9/2</sub> at 21 100 cm<sup>-1</sup> with an energy gap 7400 cm<sup>-1</sup> to the closest lower-lying level <sup>6</sup>F<sub>1/2</sub> calculated to be at 13 700 cm<sup>-1</sup> above the ground state <sup>6</sup>H<sub>15/2</sub> (the Judd-Ofelt selection rules are against this change of *J* by 7 units, and it has not

been reported in absorption, though the transition to <sup>6</sup>F<sub>3/2</sub> is clearly seen<sup>[9,17]</sup> at 13 200 cm<sup>-1</sup>). Five emission bands from the luminescent level at 21 100 cm<sup>-1</sup> were studied by Gobrecht<sup>[18]</sup> in Dy<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub> · 8 H<sub>2</sub>O and (correctly) assigned to transitions to the ground state and the four subsequent levels of <sup>6</sup>H with *J* = 13/2, 11/2, 9/2, and 7/2 in approximate Russell-Saunders coupling. The four strongest of these emission bands were also detected<sup>[19]</sup> in aqueous dysprosium(III) solutions. Judd-Ofelt parameters, branching ratios for the transitions to lower levels, and predicted laser cross-sections were discussed<sup>[20]</sup> for Dy<sup>III</sup> in borate, phosphate, and tellurite glasses. As seen in Table 1, this fluorescent level at 21 000 cm<sup>-1</sup> (to which the oscillator strength *P* in absorption<sup>[9,17]</sup> is slightly above 10<sup>-7</sup>) shows the mean lifetime close to 0.42 ms for both the emission to <sup>6</sup>H<sub>13/2</sub> at 580 nm (17 250 cm<sup>-1</sup>) and to the ground state at 483 nm (20 700 cm<sup>-1</sup>) in the manganese-free glass containing zinc fluoride. This shift from the absorption peak at 300 cm<sup>-1</sup> higher energy may be due to vibronic cooling of the excited state, and transitions to dispersed sub-levels formed from the (2*J* + 1) = 16 components of the ground state.

Besides this «classical» fluorescent level <sup>4</sup>F<sub>9/2</sub> the only energy gap predicted<sup>[9]</sup> to be above 1300 cm<sup>-1</sup> (in the region between 22 000 and 40 000 cm<sup>-1</sup>) is the distance 2400 cm<sup>-1</sup> between <sup>4</sup>F<sub>7/2</sub> and <sup>4</sup>G<sub>11/2</sub>. Actually, the excitation spectrum for 483 nm emission of the manganese-free glass shows a narrow peak at 391 nm, also observed in the absorption spectrum. The corresponding wave-number 25 600 agrees with 25 800 observed<sup>[9,17]</sup> for <sup>4</sup>F<sub>7/2</sub> of dysprosium(III) aqua ions. Excitation at 337 nm produces short-lived emission (non-exponential decay of order 0.01 ms lifetime) in the region 390 to 410 nm. Unfortunately, this evidence for luminescence of <sup>4</sup>F<sub>7/2</sub> to the ground state is marred by the presence of a broader, short-lived emission of a blank (without DyF<sub>3</sub> and MnF<sub>2</sub>) in this region, and we are continuing the investigation. The transition from <sup>4</sup>F<sub>7/2</sub> to the first excited state <sup>6</sup>H<sub>13/2</sub> is predicted at 22 000 cm<sup>-1</sup> (450 nm). Again, excitation at 337 nm produces a weak, very short-lived initial emission at 451 nm followed (Table 1) by weak emission decaying nearly as slowly as the intense 483 nm line.

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Table 1. Wave-lengths of emission bands and the exciting radiation used, and folded life-times at 300 K in microseconds. The emitting states <sup>4</sup>F<sub>7/2</sub> and <sup>4</sup>F<sub>9/2</sub> are here named Dy 7/2 and 9/2, and the lowest quartet state of manganese(II) named Mn.

Glass	$\lambda_{\text{ex}}$ [nm]	$\lambda_{\text{em}}$ [nm]	Folded Lifetimes [ $\mu\text{s}$ ]			Emitting State
			$\tau_1$	$\tau_2$	$\tau_3$	
{2 DyF <sub>3</sub> : 24 ZnF <sub>2</sub> }	337	391	7	—	—	Dy 7/2 (?)
	337	451	280	470	—	Dy (text)
	337	483, 580	350	510	—	Dy 9/2
	402	483	410	460	—	Dy 9/2
	475	483, 580	410	460	—	Dy 9/2
{24 MnF <sub>2</sub> }	337	600	600	670	900	Mn
	402	600	640	880	980	Mn
{2 DyF <sub>3</sub> : 24 MnF <sub>2</sub> }	337	483	10	—	—	Dy 9/2
	337	610	210	260	—	Mn
	402	610	190	240	—	Mn

There is little doubt that this phenomenon, as well as an emission line at 454 nm (found by steady-state 350 nm excitation of the DyF<sub>3</sub> : ZnF<sub>2</sub> glass) 60 times as weak as the 483 nm line, is due to thermal population<sup>[2,3,14,15]</sup> of <sup>4</sup>I<sub>15/2</sub><sup>[9]</sup> 1000 cm<sup>-1</sup> above <sup>4</sup>F<sub>9/2</sub>. The Boltzmann factor at  $kT = 210$  cm<sup>-1</sup> is 0.008, which may be multiplied by the ratio (16/10) of (2J+1) or a ratio close to 2 of the observed  $P$  values.

If a dysprosium-free glass containing MnF<sub>2</sub> (rather than ZnF<sub>2</sub>) is excited at the manganese(II) peaks at 338 (<sup>4</sup>D) or 401 nm (<sup>4</sup>G), a broad Gaussian-curve emission band has the maximum at 593 nm and a lifetime of order 0.7 ms (Table 1) not deviating dramatically from exponential decay. If the same experiment is performed on the sample containing both DyF<sub>3</sub> and MnF<sub>2</sub>, the broad band centered at 592 nm shows a lifetime close to 0.2 ms, meaning that the lifetime of the lowest quartet state of manganese(II) has been multiplied by a factor 0.3 (measured at 610 nm to avoid Dy 580 nm emission).

It is not known (nor easy to decide) whether the decreased orange luminescence intensity of manganese(II) is due to energy transfer to Dy<sup>III</sup> levels below <sup>6</sup>F<sub>1/2</sub> at 13 700 cm<sup>-1</sup>, or that the broad-band emission of Mn<sup>II</sup> encounters competition due to a propensity of degradation to heat in the sheer presence of DyF<sub>3</sub> (it may be noted that rapid cascading<sup>[6]</sup> is likely to occur between all the <sup>6</sup>F and <sup>6</sup>H levels with the exception of <sup>6</sup>H<sub>13/2</sub> only 3500 cm<sup>-1</sup> above the ground state, of which we do not have ways of detecting luminescence). The explicit influence of DyF<sub>3</sub> is rendered less unlikely by the low energy about 16 900 cm<sup>-1</sup> of manganese(II) emission in {24 MnF<sub>2</sub>} glasses, compared to the green emission centered around 18 500 cm<sup>-1</sup> in a zirconium barium fluoride glass<sup>[8]</sup> containing only 1 mole percent MnF<sub>2</sub>. Such effects are observed in a large number of phosphate glasses<sup>[21]</sup> showing shifts toward lower energies (typically from 600 in direction of 700 nm) of the broad emission as a function of increasing manganese(II) concentration. It is likely that these shifts are due in part to anti-ferromagnetic coupling and (perhaps to a larger extent) to energy migration between Mn<sup>II</sup> sites and trapping at sites emitting at low energy.

It may be added that when the glass containing both DyF<sub>3</sub> and MnF<sub>2</sub> is excited at  $\lambda = 337$  nm, an absorption band of Mn<sup>II</sup> superposes a weak Dy<sup>III</sup> peak due to a level<sup>[9]</sup> with  $J = 5/2$ , the lifetimes of Mn<sup>II</sup> emission (Table 1) are about a third of the lifetimes in dysprosium-free MnF<sub>2</sub> glass, while the intensity of the 483 nm emission of Dy<sup>III</sup> due to the level <sup>4</sup>F<sub>9/2</sub> is decreased by a factor around 30 and its lifetime decreases to about 0.01 ms. This seems to be the first case of energy transfer from 4f<sup>n</sup> levels above 21 000 cm<sup>-1</sup> to manganese(II), or any 3d-group ion.

The excitation spectrum for emission at 620 nm (at the low end of manganese luminescence) shows additional peaks at 325,

350, and 364 nm in the presence of DyF<sub>3</sub>, but with an area some 10 times smaller than the asymmetric (sharp edge toward UV) peak at 400 nm due to Mn<sup>II</sup>. The combined  $P$  values for the three Dy<sup>III</sup> peaks can be estimated to some  $8 \cdot 10^{-6}$ <sup>[9,17]</sup> and for the Mn<sup>II</sup> peak a few times  $10^{-7}$ <sup>[22]</sup>. Hence, the expected Dy : Mn ratio of absorption intensity in the {2 DyF<sub>3</sub> : 24 MnF<sub>2</sub>} glass should be in the interval 2 to 5. This result is confirmed by the absorption spectrum (after correction for the background raising, below 400 nm) where the area of the 350 nm peak of dysprosium is comparable to the 400 nm manganese peak. Hence, the probability of energy transfer from high-lying short-lived dysprosium levels above 27 000 cm<sup>-1</sup> to manganese(II) is only  $0.03 \pm 0.01$  (to be compared with a value above 0.9 for the long-lived level at 21 000 cm<sup>-1</sup>). On the other hand, the excitation spectrum of 485 nm emission consists essentially of Dy<sup>III</sup> absorption peaks, with a marginal enhancement at 364, and 380 to 400 nm, demonstrating very low efficiency of feeding <sup>4</sup>F<sub>9/2</sub> from higher-lying Mn<sup>II</sup> states. The yield of 575 nm luminescence is 25 times weaker, when excited in the dysprosium peaks at 296, 327, 367, and 455 nm, than in the analogous {ZnF<sub>2</sub> : DyF<sub>3</sub>} glass. This ratio is close to 20 in the dysprosium peaks at 353 and 391 nm, coinciding with a certain amount of manganese absorption.

Analogous fluoride glasses containing low concentrations of neodymium(III)<sup>[12]</sup> or thulium(III)<sup>[16]</sup> together with manganese(II) emit narrow bands (due to low-lying levels of 4f<sup>3</sup> or 4f<sup>2</sup>) in the near infrared. Thus, the glass {36 PbF<sub>2</sub> : 24 MnF<sub>2</sub> : 35 GaF<sub>3</sub> : 2 AlF<sub>3</sub> : 3 YF<sub>3</sub> : 3.8 LaF<sub>3</sub> : 0.2 NdF<sub>3</sub>} shows the narrow emission band at 865 nm due to the transition from <sup>4</sup>F<sub>3/2</sub> to the ground state <sup>4</sup>I<sub>9/2</sub> of neodymium(III) with the lifetime 0.3 ms when excited directly in the <sup>4</sup>G<sub>5/2</sub> band at 579 nm, but 0.64 ms (with rise-time 0.08 ms) when excited at 407 nm in the <sup>4</sup>G band of Mn<sup>II</sup>. The energy transfer from Mn<sup>II</sup> to Nd<sup>III</sup> is very efficient. The neodymium-free glass was reported<sup>[12]</sup> to show the broad Mn<sup>II</sup> emission maximum at 620 nm. We have now re-measured this band on a new spectrofluorimeter and find it at 593 nm. It is not too likely that this discrepancy is connected with a time-evolution of the sample, but rather that the broad band (not being corrected at differing wavelengths by comparison with standard emission of a rhodamine solution) is much more subject to wavelength uncertainty than emission lines are. The lowest manganese(II) quartet state also transfers energy very efficiently<sup>[16]</sup> to thulium(III) in {36 PbF<sub>2</sub> : 24MnF<sub>2</sub> : 35 GaF<sub>3</sub> : 2 AlF<sub>3</sub> : 3 YF<sub>3</sub> : 2 TmF<sub>3</sub>} presumably via the levels <sup>3</sup>F<sub>2</sub> at 15 200 and <sup>3</sup>F<sub>3</sub> at 14 640 cm<sup>-1</sup> then very rapidly undergoing non-radiative transitions to the luminescent <sup>3</sup>H<sub>4</sub> at 12 820 cm<sup>-1</sup> (lifetime around 0.2 ms). A comparable thulium-free glass shows a broad Mn<sup>II</sup> emission at 595 nm (16 800 cm<sup>-1</sup>) with lifetime of the order 1 ms. This emission is far

weaker in the presence of TmF<sub>3</sub>, with an initial lifetime raising from below 0.02 to above 0.05 ms, most likely corresponding to Mn-Tm couples with increasing inter-nuclear distances.

As far as conceivable laser action goes, the (at least at room temperature) three-level candidate based on the kingfisher-(Eisvogelblau)-blue emission at 483 nm is not as attractive as the four-level system applying the yellow line at 580 nm.

### Experimental

The two glasses of composition (in mole ratios of the anhydrous fluorides) 36 PbF<sub>2</sub> : 24 ZnF<sub>2</sub> : 35 GaF<sub>3</sub> : 2 AlF<sub>3</sub> : 3 YF<sub>3</sub> : 2 DyF<sub>3</sub> and 36 PbF<sub>2</sub> : 24 MnF<sub>2</sub> : 35 GaF<sub>3</sub> : 2 AlF<sub>3</sub> : 3 YF<sub>3</sub> : 2 DyF<sub>3</sub> as well as the two corresponding glasses with no dysprosium, but 5 YF<sub>3</sub>, were prepared in Le Mans.

The instrumentation for spectroscopic measurements at room temperature performed in Jerusalem was previously described<sup>[7,12,16]</sup> except that in the present study, emission spectra were recorded on a Jasco FP-770 spectrometer (usually with a total band width 1.5 nm) receiving the monochromatic radiation selected for the excitation.

In Table 1, the lifetime  $\tau_1$  is the time for decrease of the luminescence intensity to (1/e) of its original value,  $\tau_2$  half the time for decrease to (1/e<sup>2</sup>), and  $\tau_3$  a-third of the time required to arrive at (1/e<sup>3</sup>).

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