

A STUDY OF THE ENERGY TRANSFER PROCESSES IN SENSITIZED GADOLINIUM PHOSPHORS

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Summary

By suitable sensitization and activation it is possible to design compositions on the basis of gadolinium compounds which show extremely efficient luminescence. For the general composition $GdX_3:S,A$ the relevant energy transfer processes are sensitization ($S \rightarrow Gd$), energy migration $\{(Gd \rightarrow Gd)_{nx}\}$ and trapping ($Gd \rightarrow A$). Several examples will be presented in which $S \rightarrow Gd$ is an efficient process, whereas in other cases it is not. The energy migration process will be discussed in terms of crystal structure, the gadolinium concentration and the interaction mechanism. Finally the trapping process will be discussed. Efficient trapping is possible if the Gd^{3+} emission lines overlap with a broad allowed absorption band of the activator.

1. Introduction

Figure 1 summarizes, in a schematic way, the processes which will be discussed in this paper. A gadolinium compound contains small amounts of a sensitizer S and an activator A. The sensitizer is used to optically pump the system via an allowed absorption band Exc_S . The Gd^{3+} ($4f^7$) ion does not show such bands in the UV region. The rate of the $S \rightarrow Gd^{3+}$ transfer process should exceed the radiative rate of S, Em_S , otherwise the sensitization is ineffective.

Sensitization can be followed by energy migration among the Gd^{3+} ions (see Fig. 1). For this to occur, the rate of $Gd^{3+} \rightarrow Gd^{3+}$ transfer should be much larger than the Gd^{3+} radiative rate Em_{Gd} . Trapping of the migrating energy may occur at A, followed by emission from A, Em_A . Trapping may also occur at killer centres, where the excitation energy is lost non-radiatively.

This series of processes may yield very efficient luminescent materials. Examples are $GdMgB_5O_{10}-Ce,Tb$ [1, 2], GdF_3-Ce,Tb [3] and GdB_3O_6-Bi,Tb [4]. Therefore, we investigated these transfer processes in detail. Results are

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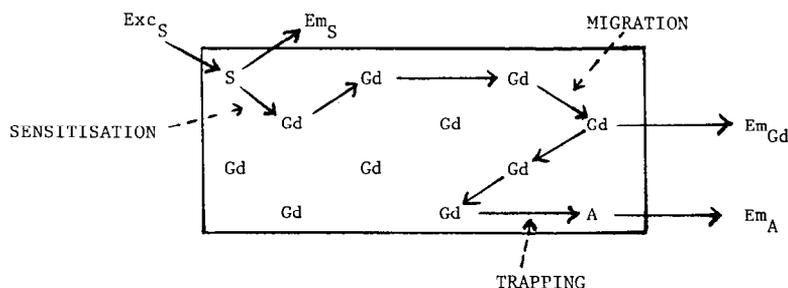


Fig. 1. Schematic representation of the energy transfer processes in a Gd^{3+} compound (see also text).

presented in this paper. For efficient lamp phosphors it is necessary that the energy $h\nu_S$ of absorption transition matches the 254 nm mercury discharge line of a fluorescent lamp.

2. Experimental details

For experimental details the reader is referred to some of our papers published elsewhere [2–5].

3. The sensitization process

Efficient sensitization requires that (i) the absorption transition on S has a high oscillator strength, *i.e.* is more or less allowed; (ii) the $S \rightarrow Gd^{3+}$ transfer efficiency has a high rate, much higher than the radiative rate of the S ion; (iii) back transfer $Gd^{3+} \rightarrow S$ is impossible.

This has been realized for a couple of S ions, but does not hold generally. Suitable choices for S are the following ions: Ce^{3+} ($4f^1$) and Bi^{3+} ($6s^2$). If their emission energy coincides with the 6P levels of the Gd^{3+} ion, efficient transfer to Gd^{3+} occurs after excitation into the Ce^{3+} ion via the allowed $4f \rightarrow 5d$ transition, or into the Bi^{3+} ion via the allowed ${}^1S_0 \rightarrow {}^3P_1$ transition. In this way the Ce^{3+} ion sensitizes the Gd^{3+} sublattice in GdF_3 [3], $NaGdF_4$ [6], $GdMgB_5O_{10}$ [1, 2] and the Bi^{3+} ion the Gd^{3+} sublattice in GdB_3O_6 [4]. Figure 2 gives an illustrative example.

The case of $GdB_3O_6-Sb^{3+}$ is an example where sensitization is not successful at all [4]. The Sb^{3+} ion in the excited state undergoes a strong relaxation which shifts its emission into the visible. In the absence of resonance with Gd^{3+} , sensitization becomes impossible. For example, Bi^{3+} in $GdMgB_5O_{10}$ shows no sensitizing action at room temperature because the $Bi^{3+} \rightarrow Gd^{3+}$ transfer rate equals the $Gd^{3+} \rightarrow Bi^{3+}$ back transfer rate [2]. This is due to the position of the energy levels involved: not only does the Bi^{3+} emission overlap with the $Gd^{3+} {}^8S \rightarrow {}^6P$ absorption lines, but also the $Gd^{3+} {}^6P \rightarrow {}^8S$ emission lines overlap the Bi^{3+} absorption band (Fig. 3). Owing to a thermal shift in the Bi^{3+}

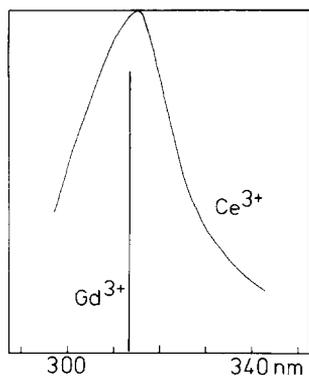


Fig. 2. Spectral overlap of the Ce^{3+} emission band and the Gd^{3+} absorption line ($^8\text{S} \rightarrow ^6\text{P}$) in lanthanide trifluorides.

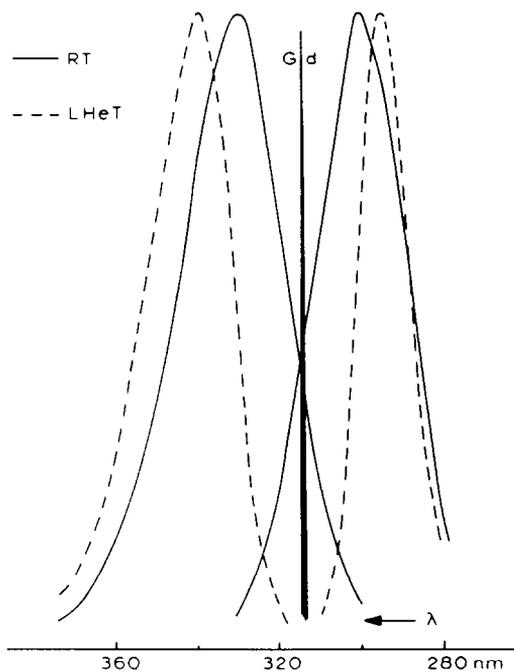


Fig. 3. Spectral data for $\text{GdMgB}_5\text{O}_{10}\text{-Bi}^{3+}$. The vertical line represents the Gd^{3+} $^8\text{S} \rightarrow ^6\text{P}$ transition. On the right-hand side the Bi^{3+} excitation spectra are given, on the left-hand side the Bi^{3+} emission spectra (full curves, room temperature; broken curves, 4.2 K).

energy level involved, the back transfer has vanished at 4.2 K. This back transfer process is more general than thought at first view. It occurs also in the case of $\text{LiGdF}_4\text{-Ce}$ [7].

The Pr^{3+} ion is another candidate as a sensitizer, but has its own difficulties owing to its specific energy level structure. The $4f^2$ configuration has all its

energy levels but one at about $23\,000\text{ cm}^{-1}$ or lower. Then there is a large gap and $^1\text{S}_0$ follows at $47\,000\text{ cm}^{-1}$. The $4f5d$ configuration of this ion shows its lowest crystal-field component at about $40\,000\text{ cm}^{-1}$, dependent on the crystal structure. This level can be used for sensitization but then the $\text{Pr}^{3+}(4f5d) \rightarrow \text{Gd}$ transfer rate has to compete also with the relaxation rate of the transition $4f5d \rightarrow ^3\text{P}_2(4f^2)$ on the Pr^{3+} ion. This relaxation rate can be suppressed if the Stokes shift of the emission of the $4f5d$ state is small, *i.e.* if its relaxation after excitation is small.

Let us illustrate this by some results. In $(\text{Y,Gd})_3\text{Al}_5\text{O}_{12}-\text{Pr}^{3+}$ the Pr^{3+} ion sensitizes the Gd^{3+} ions, but even at 4.2 K back transfer occurs, because the $\text{Pr}^{3+} 4f5d$ level is at too low energy [8]. In the oxyapatite $\text{Gd}_{0.33}\square_{0.67}(\text{SiO}_4)_6\text{O}_2-\text{Pr}^{3+}$ this level is at higher energy, in fact at an energy high enough to allow transfer to the Gd^{3+} ions. This time the relaxation rate is so large (Stokes shift, about 7000 cm^{-1}), that the $\text{Pr}^{3+}-\text{Gd}^{3+}$ transfer cannot compete. De Hair [9] has given a successful example of Pr^{3+} sensitization, *viz.* in $\text{BaY}_4\text{Si}_5\text{O}_{17}$, a compound with a complicated crystal structure. The Stokes shift is only 3000 cm^{-1} , so that the transfer rate becomes larger than the relaxation rate.

The mechanism by which the $\text{S} \rightarrow \text{Gd}^{3+}$ transfer occurs has not been completely elucidated. The calculations made to date suggest that there is at least a contribution from exchange interaction. The back transfer occurs by dipole-dipole interaction [2, 7].

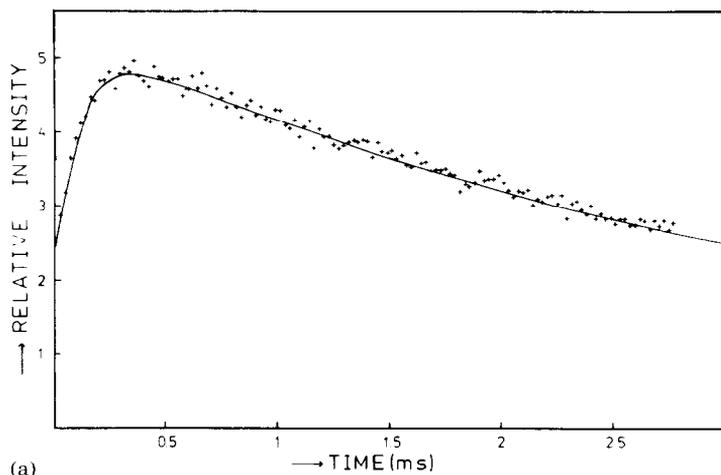
We conclude that the $\text{S} \rightarrow \text{Gd}$ transfer rate is predictable, if the spectral characteristics of the S ion are predictable.

4. The migration process

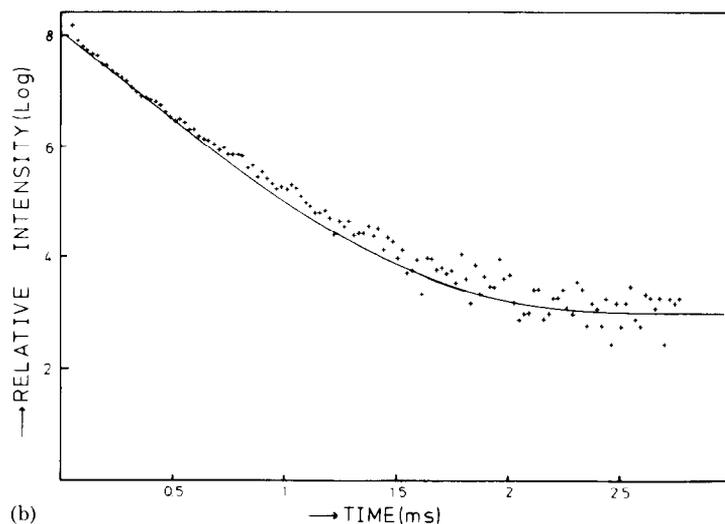
The energy migration on the Gd^{3+} sublattice can be of the fast-diffusion type. This has been shown for $\text{GdB}_3\text{O}_6-\text{Bi}^{3+}, \text{Tb}^{3+}$ by decay time measurements [5]. Figure 4(a) shows the $\text{Tb}^{3+} ^5\text{D}_4$ emission decay curve. It is interesting to note the build-up of this curve, indicating that it takes some time to reach the Tb^{3+} ion owing to the migration process. Figure 4(b) shows the Gd^{3+} decay curve. This curve is exponential with a decay time which is much shorter than the radiative decay time of the isolated Gd^{3+} ion. Its value depends, *inter alia* on the Tb^{3+} concentration. This observation indicates fast migration, *i.e.* the $\text{Gd}^{3+}-\text{Gd}^{3+}$ transfer rate exceeds the trapping rate. These measurements do not allow a conclusion on the interaction mechanism involved.

This was possible, however, by studying the transfer processes in the system $\text{LiY}_{1-x}\text{Gd}_x\text{F}_4-\text{Ce}, \text{Tb}$ [7]. In Table 1 we have summarized the transfer rates and the radiative rates involved in this system. These values are rather characteristic of systems depicted in Fig. 1. It was also possible to find the transfer rate for $\text{Gd}^{3+}-\text{Gd}^{3+}$ transfer between nearest and next-nearest Gd^{3+} neighbours, *viz.* $10^{7\pm 1}\text{ s}^{-1}$ and $10^{3\pm 1}\text{ s}^{-1}$. The corresponding distances are 3.8 \AA and 5.2 \AA respectively. From the distance dependence of the transfer rate it follows that the $\text{Gd}^{3+}-\text{Gd}^{3+}$ transfer is mediated by exchange interaction.

The critical distance R_c for $\text{Gd}^{3+}-\text{Gd}^{3+}$ energy transfer was derived by



(a)



(b)

Fig. 4. (a) $\text{Tb}^{3+} \ ^5\text{D}_4$ emission decay in $\text{GdB}_3\text{O}_6\text{-Bi, Tb}^{3+}$ at 135 K for excitation into Bi^{3+} ; (b) Gd^{3+} emission decay in $\text{GdB}_3\text{O}_6\text{-Bi, Tb}^{3+}$ at 230 K for excitation into Bi^{3+} .

TABLE 1

Energy transfer and radiative rates for $\text{LiGd}_{0.98}\text{Ce}_{0.01}\text{Tb}_{0.01}\text{F}_4$ at 300 K [7]

Process	Rate (s^{-1})
Radiative rate Ce^{3+}	2.5×10^7
Transfer rate $\text{Ce}^{3+} \rightarrow \text{Gd}^{3+}$	10^8
Radiative rate Gd^{3+}	2×10^2
Transfer rate $\text{Gd}^{3+} \rightarrow \text{Gd}^{3+}$ (nearest neighbours)	$10^{7 \pm 1}$
Back transfer rate $\text{Gd}^{3+} \rightarrow \text{Ce}^{3+}$	10^5
Trapping rate $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+}$	5×10^6

studying the influence of a dilution of the Gd^{3+} sublattice by optically inactive Y^{3+} ions on the luminescence properties. This approach is discussed in detail in ref. 10. Results are given in Fig. 5. Although the result for a single system may be inaccurate, all the results together show that (i) for fluorides and for compounds in which the Gd^{3+} ion occupies a site with inversion symmetry, the value of R_c is 5 Å. This value exceeds the usual Gd–Gd separation in Gd^{3+} compounds; (ii) for compounds (oxides) in which the Gd^{3+} ion occupies a site without inversion symmetry, R_c is 6.5 Å.

Taking all results together it can be concluded that the Gd^{3+} – Gd^{3+} transfer has a range of 5 Å if mediated by exchange interaction only. The addition of dipole–dipole interaction lengthens this range to about 6.5 Å. Indeed we did not observe energy migration in $\text{Cs}_2\text{NaGdCl}_6$ –Dy where the shortest Gd^{3+} – Gd^{3+} distance is 7.5 Å. The only transfer process which occurs in this composition, is the one-step Gd^{3+} – Dy^{3+} transfer [11].

Efficient energy migration is only to be expected in gadolinium compounds where the Gd^{3+} – Gd^{3+} distance is less than the value of R_c mentioned above. Exchange interaction is the main interaction mechanism for the Gd^{3+} – Gd^{3+} transfer process. This conclusion holds only at room temperature. At low temperatures the presence of Gd^{3+} traps hampers the migration considerably, as has been discussed elsewhere [5, 12].

5. The trapping process

The trapping process was studied for a large number of A ions in GdAlO_3 [13]. These are Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , Er^{3+} , Tm^{3+} on Gd^{3+} sites and Cr^{3+} on

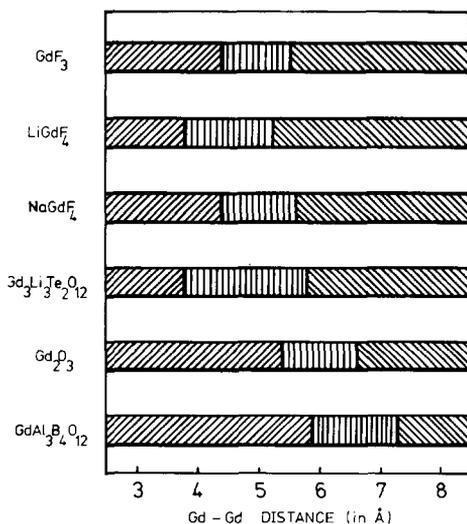


Fig. 5. Estimates of the critical distance (R_c) for Gd^{3+} – Gd^{3+} transfer in several systems at room temperature indicated by the area with vertically hatched lines.

Al^{3+} sites. The results of this study show that the trapping rate increases in the following sequence:



Let us now consider this sequence in some more detail. The latter three ions show broad absorption bands in the spectral region where the Gd^{3+} ion emits: Cr^{3+} and Eu^{3+} a charge-transfer absorption band, Tb^{3+} the spin-forbidden ${}^7\text{F}_6$ (4f^8) \rightarrow ${}^9\text{D}$ ($4\text{f}^75\text{d}$) absorption band. In the case of Eu^{3+} the spectral overlap is with the tail of the charge-transfer band only. This suggests that in these cases trapping is by dipole-dipole interaction. The sequence follows from the spectral details: the case of Cr^{3+} shows maximum overlap with an allowed transition, that of Tb^{3+} maximum overlap with a spin-forbidden transition, and that of Eu^{3+} a smaller overlap with an allowed transition.

The former four ions in the sequence show only narrow and highly forbidden sharp-line transitions in the region where the Gd^{3+} levels (${}^6\text{P}$ and ${}^6\text{I}$) are situated. Spectral overlap seems to be largest in the case of Sm^{3+} , but does not vary much. Tm^{3+} is exceptional, because it has no energy levels which fit the lowest excited level of the Gd^{3+} ion (${}^6\text{P}_{7/2}$). Also the intensities of the transitions do not vary much from ion to ion [14]. It is interesting to note that the standard electrode potentials for the $\text{Ln}^{2+}/\text{Ln}^{3+}$ couples vary in the same way as in the sequence under consideration (see Table 2) with the exception of Tm^{3+} .

TABLE 2

Standard electrode potentials at 298 K for couples $\text{Ln}^{2+}/\text{Ln}^{3+}$ (after ref. 14)

Ln	E° (V)
Eu	-0.35
Sm	-1.56
Dy	-2.6
Tm	-2.3
Er	-3.1

The trapping rate by superexchange interaction will increase if this standard electrode potential increases [15]. It may, therefore, well be that the trapping by the first four ions in the sequence occurs by superexchange interaction. This has to be investigated in further detail.

It is also interesting to note that in GdAlO_3 the Cr^{3+} ion is such an efficient trap that even in compositions $\text{Gd}_{0.99}\text{Ln}_{0.01}\text{AlO}_3$ the Cr^{3+} emission is detected on excitation into the Gd^{3+} ions. The Cr^{3+} ion is present in the samples, since it is an impurity in our starting aluminium compounds.

This observation is of importance if one wishes to prepare efficient gadolinium phosphors for application in luminescent lamps. If Tb^{3+} is used as the activator (or trap), as is often the case, it is essential to prevent every trace of Tb^{4+} . The latter ion has allowed absorption transitions in the UV spectral

region [16] and is, therefore, an efficient trap (in this case even killer) for the migrating excitation energy. Its presence leads to radiationless losses [5, 17].

6. Conclusion

The energy transfer processes in gadolinium compounds, *viz.* sensitization, migration and trapping, have been discussed. There is a reasonable qualitative understanding of these processes, but many aspects, especially the more quantitative ones, warrant further investigation.

Acknowledgments

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