Long-Range Energy Transfer from Gd^{3+} to Pr^{3+}

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Energy transfer from Gd^{3+} to Pr^{3+} is impossible if only the energy levels of the respective $4f^n$ configurations are concerned. In $Gd_2O_2S-Pr^{3+}$, however, this transfer occurs over a long distance (≈ 22 Å). The $4f5d$ configuration of Pr^{3+} is at so low energy in this host lattice that it can accept the excitation energy of the Gd^{3+} ions. © 1988 Academic Press, Inc.

1. Introduction

When gadolinium compounds contain a small amount of other optically active ions, excitation into the gadolinium ions results usually in emission from the dopant ion. The latter is fed efficiently by a process consisting of energy migration over the gadolinium sublattice and subsequent energy transfer from Gd^{3+} to the dopant ion. Examples are $GdB_3O_6-Tb^{3+}$ and $GdB_3O_6-Eu^{3+}$ (*1*), GdF_3-Mn^{2+} (*2*), $Gd_3Li_3Te_2O_{12}-U^{6+}$ (*3*), $GdAlO_3-Dy^{3+}$, $GdAlO_3-Sm^{3+}$, and $GdAlO_3-Cr^{3+}$ (*4*).

The transferring Gd^{3+} ion has its emitting level ($^6P_{7/2}$) at about 32,000 cm^{-1}. This level is at such high energy that the greater part of the luminescent metal–ions have energy levels at the same energy, so that energy transfer is possible. This explains why so many ions are able to trap the gadolinium excitation energy. There is, however, one notorious exception, viz., the Pr^{3+} ion

($4f^2$). The energy levels of the $4f^2$ configuration show a wide gap between $^3P_2$ ($\sim22,500$ cm^{-1}) and $^1S_0$ ($\sim48,000$ cm^{-1}), so that transfer from Gd^{3+} ($4f^7$) to Pr^{3+} ($4f^2$) is clearly impossible. In fact, as far as we are aware, efficient transfer of this type has not been reported previously in the literature.

Here we report effective energy transfer from Gd^{3+} to Pr^{3+} which has necessarily to occur via another configuration of the Pr^{3+} ion, viz., the $4f5d$ configuration. In Gd_2O_2S the lowest component of this configuration turns out to be resonant with the ^6P manifold of the Gd^{3+} ion. In this way long-range transfer is possible.

2. Experimental

A sample of $Gd_2O_2S-Pr^{3+}$ was obtained from M. Tecotzky. The optical measurements were performed as described before (*5*). The Pr concentration amounts to 0.1 at%.
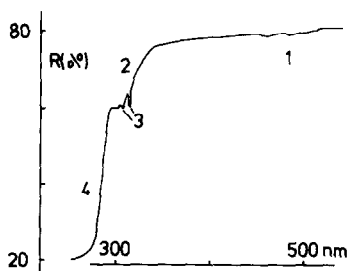
FIG. 1. Diffuse reflectance spectrum of Gd_2O_2S–Pr. 1, Transitions within the Pr^{3+} $4f^2$ configuration; 2, band due to $4f \to 5d$ transition of Pr^{3+}; 3, peaks due to $^8S \to {}^6P$ transitions of Gd^{3+}; 4, host lattice band gap transition.

3. Results and Assignments

The phosphor Gd_2O_2S–Pr^{3+} is an efficient green-emitting X-ray phosphor. Also, under ultraviolet excitation it shows an efficient green emission.

Figure 1 shows the diffuse reflectance spectrum at room temperature. The weak absorption in the area 450–500 nm corresponds to the Pr^{3+} intra-$4f^2$ transitions ($^3H_4 \to {}^3P_{0,1,2}$ and $^1I_6$). The Gd^{3+} $^8S \to {}^6P$ transitions are found as lines around 310 nm. The Gd_2O_2S host lattice absorption appears as the strong band at wavelengths shorter than 290 nm. This agrees with earlier observations (6–8).

These assignments are obvious. We are left with a weak band with a maximum at about 300 nm just below the host lattice absorption. This is assigned to the $4f^2 \to 4f5d$ transition on Pr^{3+}. It has been argued elsewhere (5) that the Pr^{3+} ($4f5d$) levels are, within one and the same lattice, about 12,500 cm^{-1} above the corresponding Ce^{3+} levels. Since the Ce^{3+} $f \to d$ absorption in Gd_2O_2S is at 21,500 cm^{-1} (8), our present assignment agrees with this rule of thumb.

The emission spectra consist of Pr^{3+} emission from the $^3P_0$ level, independent of excitation wavelength. At 300 K there is a very small contribution from Pr^{3+} $^1D_2$ emission (lower than 1%), which is absent at 4.2

K. At the latter temperature there is also present the $^6P_{7/2} \to {}^8S$ emission transition on the Gd^{3+} ion (Fig. 2). Its relative intensity is some 3%. This Gd^{3+} emission is present for host lattice, Pr^{3+} ($f \to d$), and Gd^{3+} excitation.

The excitation spectrum of the Pr^{3+} $^3P_0$ emission at 4.2 K is given in Fig. 3. It consists of the $f \to d$ absorption transition of the Pr^{3+} ion, the intra-$4f^7$ transitions of Gd^{3+} ($^8S \to {}^6P$ and ^6I), and the host lattice absorption band. This shows that the Pr^{3+} ($4f^2$) emission can be excited in the Gd^{3+} ions and in the host lattice, and in the Pr^{3+} $f \to d$ transition. Since the emission spectra contain mainly Pr^{3+} ($4f^2$) transitions, the transfer efficiencies are high. At 300 K the excitation spectrum is not essentially different from that at 4.2 K apart from some line broadening.

The excitation spectrum of the Gd^{3+} emission at 4.2 K is also shown in Fig. 3. It consists of the host lattice band. The Gd^{3+}
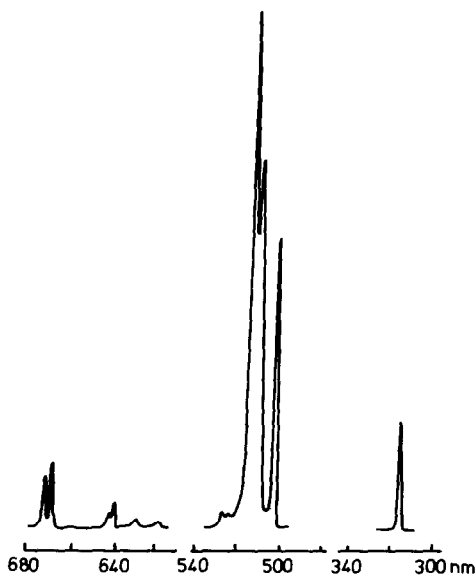

FIG. 2. Emission spectrum of Gd_2O_2S–Pr at 4.2 K under 280 nm excitation. Note breaks in wavelength scale. The three parts are on the same intensity scale. The ultraviolet emission is due to Gd^{3+}; the visible emission is due to Pr^{3+}.
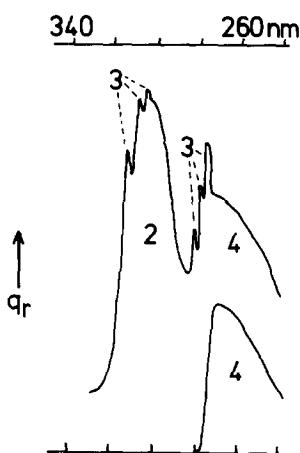
FIG. 3. Above: excitation spectrum of the Pr^{3+} emission (515 nm) of $Gd_2O_2S-Pr^{3+}$ at 4.2 K. Below: excitation spectrum of the Gd^{3+} emission (315 nm) of $Gd_2O_2S-Pr^{3+}$ at 4.2 K. The quantity q_r indicates the relative quantum output. The peaks numbered 3 are due to excitation in the Gd^{3+} ion; the bands numbered 2 and 4 are due to excitation in the $4f-5d$ band of Pr^{3+} and the host lattice absorption band, respectively.

excitation lines are not observed, since the emission is near the excitation region concerned.

4. Discussion

From the results it is clear that the $4f5d$ state of Pr^{3+} in Gd_2O_2S relaxes to the levels of the $4f^2$ configuration of this ion, without yielding $f \rightarrow d$ emission as observed in some other host lattices (9, 10). This fast relaxation is related (5) to the low-energy position of the $4f5d$ state in the oxysulfide and to the large relaxation of this state as can be derived from the data for Ce^{3+} in Y_2O_2S where the Stokes shift is 7300 cm^{-1} (8).

Excitation into the Gd^{3+} ion results in Pr^{3+} ($4f^2$) emission. This is a clear example of efficient energy transfer from Gd^{3+} to Pr^{3+}. Let us consider this transfer in more detail. It is clear that the Gd^{3+} $^6P_{7/2} \rightarrow {}^8S$ emission line peaks into the absorption maximum of the Pr^{3+} $f-d$ transition. This

results in a large spectral overlap, necessary for efficient energy transfer. The $f-d$ transition is an allowed one, so that the interaction will be relatively strong.

The critical distance for energy transfer from Gd^{3+} to Pr^{3+} was calculated from the expression $R_c^6 = 0.6 \times 10^{28} \cdot (4.8 \times 10^{-16} \times f) \cdot E^{-4} \cdot S.O.$ (11). This expression follows from the Förster–Dexter theory for energy transfer by dipole–dipole interaction. R_c gives the critical transfer distance (in Å), f the oscillator strength of the Pr^{3+} $f \rightarrow d$ transition (10^{-2}), E the energy of maximum spectral overlap (4 eV), and S.O. the spectral overlap (~ 1 eV^{-1} from the spectral results). In this way we find $R_c = 22$ Å, which is a respectable distance for transfer between two rare-earth ions.

Since the Pr^{3+} concentration (0.1 at%) and the crystallographic data of Gd_2O_2S learn that every Pr^{3+} ion has available a sphere of radius 28 Å, it may be thought at first glance that the $Gd^{3+} \rightarrow Pr^{3+}$ transfer is mainly a one-step process. Further analysis shows that this is by no means the case. The reason for this is the rapid migration over the Gd^{3+} sublattice with $Gd^{3+}-Gd^{3+}$ transfer steps with the rate 10^7 sec^{-1} (12, 13).

The long-range $Gd^{3+}-Pr^{3+}$ transfer occurs by electric dipole–dipole interaction and its rate is 5×10^2 sec^{-1} for a $Gd^{3+}-Pr^{3+}$ distance of 22 Å. Here we assume the Gd^{3+} radiative rate to be 5×10^2 sec^{-1}. This rate becomes equal to the $Gd^{3+}-Gd^{3+}$ transfer rate (10^7 sec^{-1}) for a distance of 4.3 Å, which is close to the nearest-neighbor distance. This shows that the $Gd^{3+}-Pr^{3+}$ transfer occurs via $Gd^{3+}-Gd^{3+}$ transfers with a final $Gd^{3+}-Pr^{3+}$ transfer step over nearest neighbors.

At 4.2 K we find 3% Gd^{3+} emission. Since the Gd^{3+}/Pr^{3+} intensity ratio is equal to the product of the Gd^{3+} and Pr^{3+} concentration ratio and the ratio of the Gd^{3+} radiative rate and the $Gd^{3+} \rightarrow Pr^{3+}$ transfer rate, we estimate as 1.5×10^7 sec^{-1}, in good

agreement with the calculation performed above.

This type of $Gd^{3+} \rightarrow Pr^{3+}$ transfer was also observed in $Y_2GdAl_5O_{12}$–Pr (5), but there it was not very efficient due to a poor spectral overlap.

The presence of a small amount of $^1D_2$ emission at room temperature may be due either to a nonradiative $^3P_0 \rightarrow {}^1D_2$ decay (multiphonon emission) or to $^3P_0 \rightarrow {}^1D_2$ decay via the low-energy offset $4f5d$ level (14).

What happens under host lattice excitation is not clear from these experiments. The charge carriers created may be trapped directly by the Pr^{3+} ions, but it cannot be excluded that they are trapped by Gd^{3+} ions, since the Gd^{3+} excitation spectrum contains the host lattice absorption band. The Gd^{3+} excitation is transferred efficiently to Pr^{3+} as we have shown above.

In conclusion, efficient energy transfer from Gd^{3+} to Pr^{3+} is possible in Gd_2O_2S due to the favorable spectral position of the $4f5d$ level of the Pr^{3+} ion.

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