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The Temperature Dependence of the Luminescence of Gd_2O_2S–Pr^{3+} Upon 4f–5d Excitation

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Abstract

Upon excitation into the 4f5d configuration of Pr^{3+} in Gd_2O_2S the ion relaxes rapidly to the $4f^2$ configuration, from where $^3P_0$ and $^1D_2$ emission occurs. Their temperature dependence is reported and interpreted in terms of $^3P_0$–$^1D_2$ multiphonon emission.

Introduction

Recently the $4f5d \rightarrow 4f^2$ emission of Pr^{3+} in $ScBO_3$ has been reported [1]. It consists of four spin-allowed transitions (to $^3H_4$, $^3H_5$, $^3H_6 + {}^3F_2$, and $^3F_3 + {}^3F_4$) and one spin-forbidden transition (to $^1G_4$). The latter is of considerably weaker intensity. In $ScBO_3$–Pr^{3+} the $4f5d \rightarrow 4f^2$ transition is completely radiative. In Gd_2O_2S–Pr^{3+}, however, this transition is only nonradiative, due to a larger offset and a lower energy position of the 4f5d configurational states [2]. It seemed interesting to us to investigate whether in this nonradiative transition there would also be a rate difference between the $\Delta S = 0$ and $\Delta S = 1$ transitions, where ΔS gives the change in the spin quantum number. Here it should be realized that the lowest level of the 4f5d configuration is a triplet level [1], whereas the $4f^2$ configuration contains triplets and singlets in the energy range of importance.

Our results indicate that there is some evidence for a slow $\Delta S = 1$ transition, but that the $^3P_0$–$^1D_2$ multiphonon emission is the dominating process.

Experimental

The sample of Gd_2O_2S–Pr^{3+} used has been described in ref. 2. The optical measurements were performed using a Perkin-Elmer spectrofluorometer MPF-44 equipped with a high-temperature cell.

Results

At room temperature Gd_2O_2S–Pr^{3+} is an efficiently emitting green phosphor upon ultraviolet excitation. At higher temperatures the emission starts to quench gradually and the emission colour shifts to the red. This means that the $^1D_2$ emission appears next to the $^3P_0$ emission which is observed at room temperature. In this paper we include under the heading $^3P_0$ emission also the emission from higher levels (viz. $^3P_1$, $^1I_6$ and $^3P_2$) which become populated thermally at higher temperatures.

Figure 1 presents the total emission intensity, the $^3P_0$ emission intensity and the $^1D_2$ emission intensity of Gd_2O_2S–Pr^{3+} as a function of temperature above 300 K for excitation into the $4f^2 \rightarrow 4f5d$ transition of the Pr^{3+} ion at 300 nm [2]. At 300 K the relative amount of $^1D_2$ emission is about 2%. Figure 1 shows, therefore, that the $^1D_2$ emission never becomes the dominating emission. The data presented were obtained by monitoring the emission spectrum as a function of temperature.

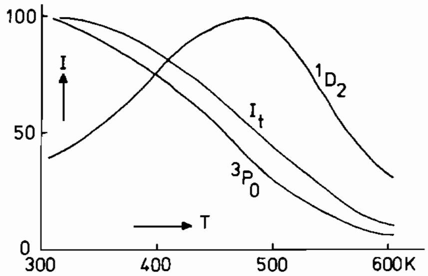

Fig. 1. Temperature dependence of the emission intensity of Gd_2O_2S–Pr^{3+}. Excitation 300 nm (4f5d configuration). All curves are normalized to 100. The curve I_t gives the total emission intensity, the curve $^3P_0$ that of the $^3P_0$ emission, the curve $^1D_2$ that of the $^1D_2$ emission. At 300 K the $^1D_2$ emission contributes about 2% to the total emission intensity.

Discussion

Before analysing the data of Fig. 1, it is instructive to estimate the rates of multiphonon emission in the $^3P_0 \rightarrow {}^1D_2$ and the $^1D_2 \rightarrow {}^1G_4$ transitions (see also Fig. 2). We use the van Dijk and Schuurmans approach [3]. The energy gaps in the two transitions are at least 3000 and 6000 cm^{-1}, respectively. The

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maximum vibrational frequency of the host lattice is about 500 cm^{-1} [4]. The multiphonon emission rate is given by

$$W_{MPE} = \beta \exp\{-(\Delta E - 2h\omega_{max})\alpha\}$$

where α and β are constants, and ΔE is the energy gap involved [3]. For $\beta = 10^7$ s^{-1} and $\alpha = 4.10^{-3}$ cm we arrive at $W_{MPE}(^3P_0 \rightarrow {}^1D_2) = 3 \times 10^3$ s^{-1} and $W_{MPE}(^1D_2 \rightarrow {}^1G_4) = 2 \times 10^{-2}$ s^{-1}. Using the temperature dependence given by $W(T) = W(0)(n+1)^p$ [5], these values at 600 K are 2×10^4 s^{-1} and 1 s^{-1}. In the formula $W(T)$ denotes the rate at temperature T, n the phonon occupation number and p the number of phonons involved in the transition, i.e. $p(^3P_0 - {}^1D_2) = 3000/500 = 6$, and $p(^1D_2 - {}^1G_4) = 6000/500 = 12$.

The results of our estimation show that nonradiative decay from $^1D_2$ to $^1G_4$ will not occur, its rate being considerably lower than the radiative rate. This conclusion cannot be drawn for the $^3P_0$–$^1D_2$ transition. The $^3P_0$ radiative decay is about 10^5 s^{-1} [6] which is not much larger than the estimated nonradiative rate at higher temperatures. However, the temperature dependence of the $^3P_0$ emission intensity could not be fitted to the formula $W(T) = W(0)(n+1)^p$. Note also that the decrease of the $^3P_0$ emission intensity does not result in an equally large increase of the $^1D_2$ emission intensity. This seems to exclude multiphonon emission as the dominant nonradiative decay process.

Struck and Fonger have discussed the sequential quenching of the luminescence of different, subsequent energy levels of lanthanide ions via higher-energy offset states. The case of Eu^{3+} was treated in detail [7], but comparable results are known for other rare earth ions [8]. However, the present results do not follow the sequential quenching model at all, since quenching occurs mainly from $^3P_0$ leaving $^1D_2$ unoccupied.

Figure 2 presents a configurational coordinate diagram for Pr^{3+} in Gd_2O_2S. The position of the excited 4f5d state has been drawn in such a way that it fits the maximum of the $4f^2 \rightarrow 4f5d$ excitation band and the offset corresponds to the Stokes shift given for Ce^{3+} in the oxysulphides [9]. Elsewhere it has been shown that the offsets for Ce^{3+} and Pr^{3+} in the same lattice are nearly the same [10]. Further we took into account that up to 300 K excitation of the 4f5d level results in the $^3P_0$ emission of high quantum efficiency, i.e. the minimum of the 4f5d parabola should be closer to the $^3P_0$ parabola than to the parabolae of $4f^2$ levels that lead to other emissions or quenching. All these arguments give not much freedom to draw the 4f5d parabola in Fig. 2 in a strikingly different way.

Figure 2 shows what are the nonradiative processes of importance upon excitation of the 4f5d level. The nonradiative rate 4f5d $\rightarrow$ $^3P_0$ (and $^3P_1$, $^1I_6$, $^3P_2$) is obviously very fast, so that at temperatures below 300 K this is the dominant process. At higher temperatures this emission is quenched. The diagram of Fig. 2 does not offer any acceptable possibility for this.

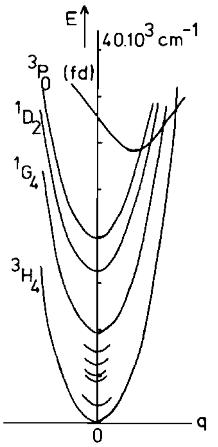

Fig. 2. Schematic configurational coordinate diagram for Gd_2O_2S–Pr^{3+}. The parallel parabolae refer to the $4f^2$ configuration. Not all of these have been drawn. The curve (fd) refers to the lowest 4f5d state. See also text.

It turns out that the quenching must be ascribed to a trivial effect. Upon increasing the temperature, the host lattice absorption shifts to lower energy. At 300 K the excitation band corresponding to the host lattice absorption peaks at 280 nm [2]. It is known from data in other sulphides [11], that this absorption edge may shift some 10 nm to longer wavelengths if the temperature increases from 300 to 600 K. It is also known that the Pr^{3+} emission quenches in the temperature range 300–450 K if excitation is into the host lattice [12].

Upon increasing the temperature of the sample, the 4f5d excitation and the host lattice excitation will overlap more and more. The higher the temperature, the higher the amount of excitation energy that is lost nonradiatively after host lattice absorption. Therefore we corrected our data assuming that up till 600 K there are no radiationless losses if excitation had occurred completely in the 4f5d configuration.

This procedure is justified by considering a model calculation by Struck and Fonger [13]. They calculated nonradiative rates for an outside crossover which is very similar to the situation of the 4f5d parabola in Fig. 2 relative to the non-emitting parabolae, i.e. $^1G_4$ and lower ones. The 4f5d–$^3P_0$ transition is clearly of the fast bottom crossover type [13] with a practically temperature independent rate 10^{11-12} s^{-1}. The 4f5d–X transition rate, where X is the $^1G_4$ and/or lower levels, at 600 K is about 3×10^6 s^{-1}. In spite of its inaccuracy, this estimate

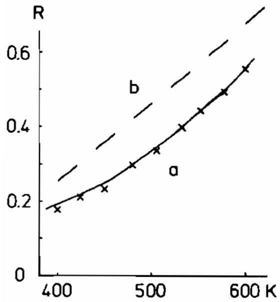

Fig. 3. The ratio of the $^3P_0$ and $^1D_2$ emission intensities (R) as a function of temperature after correction for host lattice excitation (see text). Crosses are experimental points. Curve a is a fit to $(n + 1)^p$, i.e. multiphonon emission. The broken curve b is a fit to eqn. (1), i.e. crossover via 4f5d. See also text.

shows that nonradiative losses are negligible up to 600 K.

In Fig. 3 we have plotted the results as the ratio of the $^1D_2$ and $^3P_0$ emission intensities in the range 400–600 K. This range was considered, because in this range host lattice excitation yields less than 3% of the emission intensity at 300 K [12].

We are now left with the problem to interpret the results in Fig. 3. One possibility is to fit these data to a temperature dependence given by $(n + 1)^p$. The reason for this is the following. If the increase of the $^1D_2/^3P_0$ emission intensity ratio is due to $^3P_0$–$^1D_2$ multiphonon emission, the intensity ratio is given by

$$\frac{I(^1D_2)}{I(^3P_0)} = \frac{W(0)(n + 1)^p}{p_r}$$

where p_r is the radiative life time of the $^3P_0$ level. Since $W(0)$ and p_r may be considered as temperature independent, the temperature dependence is given by $(n + 1)^p$. Figure 3 shows a fit curve with $\hbar\omega = 500$ cm^{-1} and $p = 7$. This curve accounts for the results. This shows also that the energy gap is larger than 3000 cm^{-1} in agreement with the literature data [6].

At high temperatures the $^1D_2$ level may also be fed by the $^3P_0$ level via the 4f5d state. In this case we may expect that the $^1D_2/^3P_0$ intensity ratio is given by

$$\frac{g_2}{g_0} \exp(-\Delta E/kT) \qquad (1)$$

where g_i denotes the degeneracy of the level ^nX_i, and ΔE the energy difference between the crossing points of the $^1D_2$ and $^3P_0$ parabolae with the 4f5d parabola. ΔE is found from Fig. 2 to be about 800 cm^{-1}, and $g_0 = 1$ and $g_2 = 5$. Using these data, eqn. (1) has also been plotted in Fig. 3. Its temperature dependence is weaker than that of $(n + 1)^p$ and does not agree with experiment. Consideration of the levels just above $^3P_0$ (viz. $^3P_1$, $^1I_6$ and $^3P_2$) would effectively increase the value of g_0, but not change the temperature dependence. Therefore, the feeding of $^1D_2$ by $^3P_0$ via 4f5d does not seem to contribute in the amount predicted by eqn. (1).

An obvious explanation for this is that the rate constant $W(0)$ in the expression $W(T) = W(0) \times f(T)$ is different for the 4f5d → $^3P_0$ and the 4f5d → $^1D_2$ transitions. Equation (1) assumes these to be equal. Since the latter is an $\Delta S = 1$ transition, its rate constant is probably smaller than for an $\Delta S = 0$ transition. Here we use the fact that the lowest 4f5d state is a triplet [1]. In this way the 4f5d–$^1D_2$ transition is comparable to the intersystem-crossing transition in organic molecules [14], although the difference between the rates of the spin-allowed and spin-forbidden transitions will be less in Pr^{3+} due to a stronger spin–orbit coupling.

The $\Delta S = 1$ radiative rate is one order of magnitude smaller than that for $\Delta S = 0$ [1]. If this holds also for the corresponding nonradiative rate constants $W(0)$, eqn. (1) yields only a negligible amount of $^1D_2$ emission in comparison with multiphonon emission.

The dominating nonradiative processes in Gd_2O_2S–Pr^{3+} upon 4f5d excitation are, therefore, 4f5d–$^3P_0$ by fast bottom crossover, and $^3P_0$–$^1D_2$ by multiphonon emission. The latter is only effective at temperatures above room temperature.

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