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Luminescence and Energy Migration Characteristics of $EuWO_4Cl$

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Luminescence and energy transfer properties of $EuWO_4Cl$ and $Gd_{0.99}Eu_{0.01}WO_4Cl$ are reported. Emission due to a small amount of second phase has been observed for both samples. Energy migration among the Eu^{3+} ions has been observed for $EuWO_4Cl$. The temperature dependence of the migration rate can be explained assuming phonon-assisted energy transfer. The interaction between the Eu^{3+} ions is probably multipole–multipole in character. © 1986 Academic Press, Inc.

Introduction

The luminescence properties of $GdWO_4Cl:Eu^{3+}$ and $EuWO_4Cl$ (*1*) have been reported recently. It was found that the intensity of the europium emission in $EuWO_4Cl$ was temperature independent within the experimental accuracy. The quantum efficiency is high, viz. ≥70%. This means that no pronounced concentration quenching occurs in the system $Gd_{1-x}Eu_xWO_4Cl$. These observations seem to imply, that in spite of the short nearest-neighbor Eu^{3+}–Eu^{3+} distance (~4.4 Å) no energy migration among the Eu^{3+} ions occurs in $EuWO_4Cl$. As announced in Ref. (*1*) the aim of the present investigation is to study by laser spectroscopy, whether energy migration within the Eu^{3+} sublattice of $EuWO_4Cl$ occurs.

2. Experimental

Samples were prepared as described in Ref. (*2*). They were checked by X-ray powder diffraction, which showed them to be single phase. The setup for the optical measurements has been described in Refs. (*3*, *4*).

3. Results

3.1. Spectral Properties

The emission spectrum of $Gd_{0.99}Eu_{0.01}WO_4Cl$ recorded at 4.2 K under high resolution is presented in Fig. 1. A dye laser was used to excite selectively into the lowest-lying $^5D_1$ level at 19015 cm^{-1}. The number of peaks in this spectrum is one $^5D_0 \rightarrow {}^7F_0$, three $^5D_0 \rightarrow {}^7F_1$, and five $^5D_0 \rightarrow {}^7F_2$. Since the site symmetry of Eu^{3+} in $GdWO_4Cl$ is C_s (*2*), and there is only one crystallographic site available for Gd(Eu), this is in agreement with the expected number of lines. In addition to the main peaks corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition, weak peaks in the region between 608 and 614 nm can be observed, which are probably due to a small amount of second phase.

These peaks appear also in the emission spectra of $EuWO_4Cl$, where their relative intensity is stronger than in the spectra of the diluted system. Figure 2 shows the

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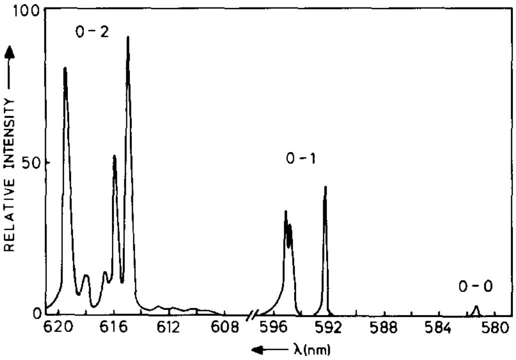

Fig. 1. Emission spectrum of Gd$_{0.99}$Eu$_{0.01}$WO$_4$Cl, recorded at 4.2 K (exc. $^7F_0 \rightarrow {}^5D_1$). The notation $J \rightarrow J'$ refers to the transitions $^5D_J \rightarrow {}^7F_{J'}$.

emission spectrum of EuWO$_4$Cl recorded at 1.2 K under high resolution. From this figure it is clear, that in addition to the so-called satellite peaks that were already observed for Gd$_{0.99}$Eu$_{0.01}$WO$_4$Cl, two extra peaks at 610.2 and 615.8 nm can be observed. Since the number of peaks in the $^5D_0 \rightarrow {}^7F_2$ spectral region (*10*) exceeds the maximum number of possible peaks (*5*), it is obvious that there exist different crystal fields in the samples under study. In passing we note that the number of peaks and their relative intensity do not show noticeable temperature dependence within the experimental accuracy up to 300 K. The integrated intensity of the europium emission in EuWO$_4$Cl remains constant up to approximately 25 K, above which temperature it decreases slowly. At 300 K the emission intensity is about 50% of the value at 4.2 K.

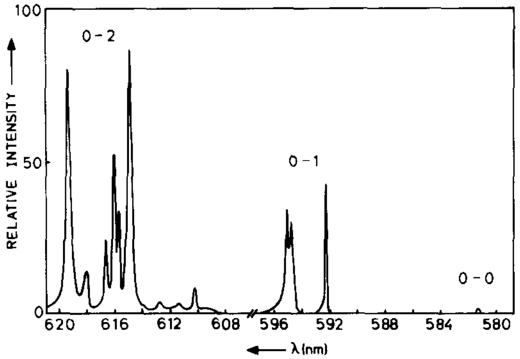

Fig. 2. Emission spectrum of EuWO$_4$Cl, recorded at 1.2 K (exc. $^7F_0 \rightarrow {}^5D_1$). The notation $J \rightarrow J'$ refers to the transitions $^5D_J \rightarrow {}^7F_{J'}$.

In order to obtain information on the different types of Eu^{3+} ions, we recorded the excitation spectra for the $^5D_0 \rightarrow {}^7F_2$ main (intrinsic) emission peak at 618.9 nm and a satellite (extrinsic) emission peak at 612.4 nm of EuWO$_4$Cl in the $^7F_0 \rightarrow {}^5D_1$ spectral region at 4.2 K. The excitation spectrum of the intrinsic emission peak at 618.9 nm consists of two lines at 525.9 and 526.3 nm (see Fig. 3). The $^7F_0 \rightarrow {}^5D_1$ transition is expected to be split into three lines. The reason for this discrepancy is not clear, but may be accidental. The excitation spectrum of the satellite peak consists of three main peaks and two weak peaks, which resemble the ones in the excitation spectrum of the intrinsic emission peak (compare Fig. 4 to Fig. 3). Their occurrence is probably due to overlap of the intrinsic emission peaks with the satellite peaks under the experimental conditions.

We used a tuneable dye laser to excite selectively the Eu^{3+} ions with the $^7F_0 \rightarrow {}^5D_1$ peak at 524.9 nm. Figure 5 shows the emission spectrum recorded at 4.2 K. It is clear that this spectrum differs strongly from the spectrum recorded after excitation into the

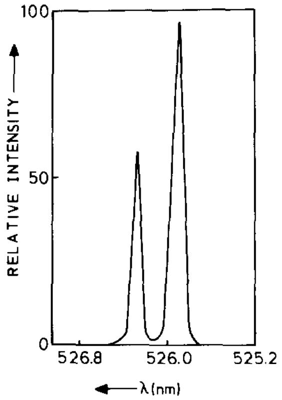

Fig. 3. Excitation spectrum of the emission of EuWO$_4$Cl, recorded at 4.2 K in the $^7F_0 \rightarrow {}^5D_1$ spectral region (emission wavelength: 618.9 nm).

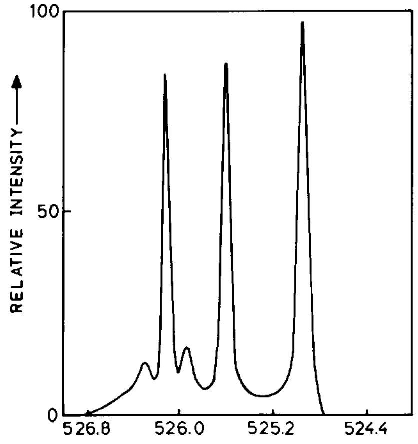

Fig. 4. Excitation spectrum of the extrinsic emission of $EuWO_4Cl$, recorded at 4.2 K in the $^7F_0 \rightarrow {}^5D_1$ spectral region (emission wavelength: 612.4 nm).

intrinsic Eu^{3+} ions (see Fig. 2). The intrinsic peaks in the spectral region between 614 and 622 nm can be distinguished. The spectrum of the extrinsic emission resembles that of the Eu^{3+} emission in $La_3WO_6Cl_3$ (5). From this, and the fact that the relative intensity of the extrinsic emission does not show noticeable temperature dependence, we conclude that we are probably dealing with a second phase of $Eu_3WO_6Cl_3$.

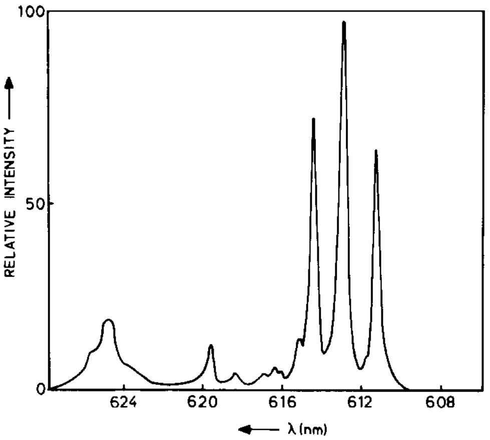

Fig. 5. Emission spectrum of $EuWO_4Cl$, recorded at 4.2 K upon excitation into the extrinsic Eu^{3+} ions (exc. 524.9 nm).

We also tried to record the excitation spectra of the satellite peaks at 610.2 and 615.8 nm. However, probably due to overlap with other extrinsic or intrinsic emission peaks, respectively, we were not able to record these spectra. On account of the same temperature argument as mentioned above, we assume that the occurrence of these two lines is due to another second phase.

3.2. *Time Dependence of the Luminescence*

In order to obtain information about any possible excitation energy migration through the Eu^{3+} sublattice, we investigated the decay characteristics of the intrinsic $^5D_0$ emission as a function of temperature for $Gd_{0.99}Eu_{0.01}WO_4Cl$ and $EuWO_4Cl$. For the diluted system the decay curves of the intrinsic emission after excitation into the $^5D_1$ level are exponential in the whole temperature region under study (1.2–300 K). The decay time at 1.2 K was 1.39 msec and remained constant up to room temperature. The decay curves of the intrinsic emission in $EuWO_4Cl$ show a deviation from exponential behavior for short times after the excitation pulse, but they become exponential after a long time. The exponential tail of the decay curve recorded at 1.2 K corresponds to a decay time of 1.34 msec. Above 20 K the decay time starts to decrease slowly (0.57 msec at 300 K). In Fig.

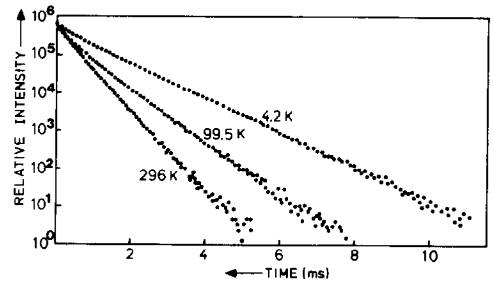

Fig. 6. Decay curves of the intrinsic Eu^{3+} emission (618.9 nm) in $EuWO_4Cl$ at various temperatures (excitation wavelength: 525.9 nm).

6 some semilogarithmic plots of the decay curves of the intrinsic emission at various temperatures are shown.

We also measured the decay characteristics of the extrinsic $^5D_0$ emission. The decay curves are exponential in the whole temperature region. The decay time for the extrinsic emission at 612.4 nm was 500 μsec at 4.2 K and 340 μsec at 100 K. Even at 1.2 K no build-up of the extrinsic emission upon excitation with 525.9-nm light could be observed. This, again, suggests that the occurrence of extrinsic emission peaks after excitation into the intrinsic Eu^{3+} ions is due to overlap of the excitation peaks.

4. Discussion

Both from the emission spectra and from the excitation spectra it is clear that in $Gd_{0.99}Eu_{0.01}WO_4Cl$ and $EuWO_4Cl$ a small amount of the Eu^{3+} ions is extrinsic. From the fact that the relative intensity of the extrinsic emission is temperature independent and from the absence of a buildup of the extrinsic emission decay curve after excitation into the intrinsic ions it follows that the extrinsic Eu^{3+} ions do not function as traps for the intrinsic excitation energy. As stated above, the extrinsic ions are probably due to a small amount of second phases.

The decrease of the integrated intensity of the europium emission in $EuWO_4Cl$ above 25 K suggests a thermally activated loss of excitation energy at quencher sites. A comparable, though more drastic effect has been observed for $NaEuTiO_4$ (*3*) and EuOCl (*6*), where it could be explained by phonon-assisted energy migration through the Eu^{3+} sublattice. A striking difference with these two compounds, however, is the high quantum efficiency of $EuWO_4Cl$.

If we assume energy transfer to quencher sites, the time development of the intrinsic emission following pulsed excitation can be used to distinguish between several cases of energy transfer. In general, if one knows the intrinsic radiative decay rate, information about the transfer between intrinsic ions (donors) and transfer from intrinsic ions to acceptor ions can be obtained by fitting the decay curve to the appropriate theoretical expressions. A general theory for the time development of the intrinsic luminescence in the presence of a random distribution of acceptors is given in Refs. (*7–9*). Exact solutions for the decay curves are only possible in two limiting cases: no donor–donor transfer (*10*) and rapid donor–donor transfer (*7*).

As stated above, the decay curves of the intrinsic Eu^{3+} emission in $EuWO_4Cl$ approach a single exponential a long time after the pulse. Since the exponential tail of the decay curves recorded at higher temperatures corresponds to a decay rate which is faster than the radiative rate of the intrinsic emission (719 sec^{-1}), direct energy transfer to acceptors can be ruled out as the only transfer mechanism (*10*). For the case of three-dimensional diffusion-limited energy migration the decay is predicted to be nonexponential for short times after the excitation pulse due to direct transfer to acceptor ions. For long times after the pulse the decay becomes exponential (*7, 11*). The decay time derived from this exponential part of the decay curve is shorter than the radiative decay time. This suggests three-dimensional diffusion-limited energy migration in $EuWO_4Cl$ (see Fig. 6).

If we assume a three-dimensional diffusion model for the energy migration in $EuWO_4Cl$, the decay rate due to migration (τ_m^{-1}) can be obtained from the exponential part of the decay curves by the expression

$$1/\tau = 1/\tau_r + 1/\tau_m \qquad (1)$$

where $1/\tau$ is the observed decay rate and $1/\tau_r$ is the radiative decay rate. Using Eq. (1) we can calculate the rate of migration with the Eu^{3+} system ($\tau_m^{-1} \equiv p_m$). The calculated rate of migration showed a temperature dependence, which is probably due to

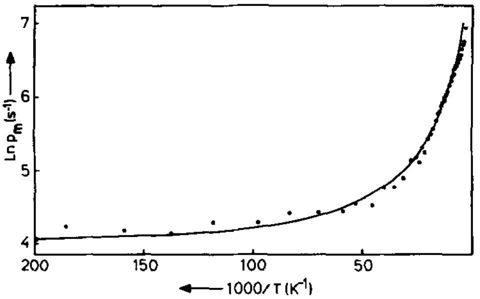

Fig. 7. The temperature dependence of p_m. See text for explanation of the theoretical line.

a temperature dependence of the diffusion constant (*3*, *4*, *6*). Figure 7 shows a plot of $\ln p_m$ against 1000/T. The temperature dependence of the migration rate in $Eu(PO_3)_3$ (*12*) and $EuAl_3B_4O_{12}$ (*13*) has been explained by thermal population of $^7F_1$ and $^7F_2$ levels. Since the lowest $^7F_1$ level of Eu^{3+} in $EuWO_4Cl$ lies at relatively high energy (316 cm^{-1}), this process is not very likely below 100 K. However, for $EuWO_4Cl$ the increase of p_m starts at lower temperatures (~20 K). The temperature dependence of p_m is probably due to the fact that the energy transfer interactions within the $^5D_0$ level are phonon-assisted.

The theory of phonon-assisted energy transfer was first developed by Orbach (*14*) and then worked out in detail by Holstein *et al.* (*15*, *16*). The best fit for the experimental data is presented in Fig. 7 and was obtained by using the equation for the one-phonon-assisted process:

$$p_m = A \coth (\Delta E/2kT) \qquad (2)$$

with $A = 57.7\ sec^{-1}$ and $\Delta E = 12.3\ cm^{-1}$. The value of ΔE equals approximately the halfwidth of the $^7F_0 \rightleftarrows {}^5D_0$ transition (~12 cm^{-1}). It has been discussed in Ref. (*3*) that the one-phonon process is not very probable for transfer among nearest-neighbor identical rare-earth ions. However, as found earlier for $NaEuTiO_4$ (*3*) and for EuOCl (*6*), the temperature dependence of the migration up to ~100 K seems to suggest that the one-phonon process occurs. In Fig. 7 a deviation from the theoretical fit can be observed above ~100 K. This is probably due to thermal population of the $^7F_1$ levels above this temperature.

Compared to p_m found for EuOCl at 1.2 K (1420 sec^{-1}), p_m found for $EuWO_4Cl$ at 1.2 K (27 sec^{-1}) is very small. Even at 300 K p_m for $EuWO_4Cl$ (1035 sec^{-1}) is still smaller than for EuOCl (8100 sec^{-1}). It has been shown that the interaction between the Eu^{3+} ions in EuOCl is, at least partly, exchange in character (*17*). The interaction occurs via the europium-anion charge transfer state. The only anions to give rise to such a superexchange interaction in $EuWO_4Cl$ are the Cl^- ions. However, the Cl^- ions are shared between two Eu^{3+} ions in a pair, which is not connected to another pair by Cl^- ions (*2*). This excludes energy migration among the Eu^{3+} ions via superexchange interaction in $EuWO_4Cl$, and implies that the observed energy migration is due to multipole–multipole interaction. The relatively small values found for p_m at low temperatures are then explained by the fact that for multipolar coupling the probability of energy transfer depends on the probability of the multipolar transitions on the ions involved: $^5D_0 \leftrightarrows {}^7F_0$. Due to the forbidden character of this transition, the probability for energy transfer between two Eu^{3+} ions is low.

In conclusion we have evaluated the energy migration process in $EuWO_4Cl$. It has been shown that energy migration to quenching centres occurs. The energy transfer between the Eu^{3+} ions occurs via multipole–multipole interaction. This explains the low migration probability and the high quantum efficiency.

Acknowledgments

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