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Luminescence in Gadoliniumchlorotungstate ($GdWO_4Cl$)

G. BLASSE

Physical Laboratory, State University, 3508 TA Utrecht, The Netherlands

AND L. H. BRIXNER

E. I. du Pont de Nemours and Company, Inc., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898

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The luminescence of $GdWO_4Cl$, $EuWO_4Cl$, and $GdWO_4Cl$–Eu^{3+} is reported. The tetrahedral tungstate group in these compounds luminesces similarly to those in other host lattices. The Gd^{3+} ions form a luminescent system which is not connected to the tungstate groups. The Gd^{3+} system transfers the greater part of its energy to defective tungstate groups in $GdWO_4Cl$ and to Eu^{3+} in $GdWO_4Cl$–Eu^{3+}.

1. Introduction

In previous papers we have discussed the luminescent properties of $La_3WO_6Cl_3$ (*1, 2*) and $LaWO_4Cl$ (*3*). These are compounds with tungsten in the unusual trigonal prismatic and trigonal bipyramidal coordinations, respectively. In $GdWO_4Cl$ and $EuWO_4Cl$ the tungstate group is tetrahedrally coordinated, a more usual situation (*4*). Efficient luminescence from the WO_4^{2-} tetrahedron is known, e.g., for $CaWO_4$. In view of our foregoing investigations, it seemed interesting to investigate the luminescence properties of $GdWO_4Cl$ and $EuWO_4Cl$. This is the subject of this paper.

2. Experimental

The reader is referred to our previous publications (*1, 2*).

3. Results and Discussion

3.1. $GdWO_4Cl$

At room temperature $GdWO_4Cl$ does not luminesce, but at lower temperatures an efficient photoluminescence develops. The quenching temperature of the luminescence is about 200 K. The tetrahedral tungstate group in $GdWO_4Cl$ shows a broad emission band with a maximum at 485 nm (Fig. 1). The corresponding excitation band has its maximum at 275 nm. The Stokes shift is, therefore, nearly 16.000 cm^{-1}. This is the value to be expected for a tetrahedral tungstate group (*3*).

The situation is more complicated, however. This is due to the fact that $GdWO_4Cl$ contains two different types of luminescent ions in high concentration, viz, the WO_4^{2-} groups and the Gd^{3+} ions. The Gd^{3+} ions can be excited in the range 305–315 nm (^8S

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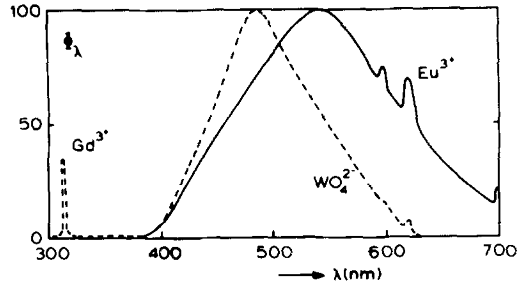

FIG. 1. Spectral energy distribution of the emission of GdWO$_4$Cl at 4.2 K. Broken line is for 277-nm excitation, drawn line is for 312-nm excitation (see text). The sharp line in the ultraviolet is due to Gd^{3+}, those in the red to Eu^{3+}. Note that for 312-nm excitation no Gd^{3+} emission can be monitored. The Φ_λ presents the radiant power per constant wavelength interval in arbitrary units.

$\rightarrow {}^6P_J$) and in the range 275–280 nm ($^8S \rightarrow {}^6I_J$). The emission is at about 313 nm ($^6P_{7/2} \rightarrow {}^8S$). Note that this emission does not overlap the tungstate excitation band (Fig. 2), so energy transfer from Gd^{3+} to WO_4^{2-} is impossible. By the same token, energy transfer from the WO_4^{2-} group to Gd^{3+} is impossible. The two luminescent systems are, therefore, not interconnected.

If we excite into the $^8S \rightarrow {}^6P_J$ transitions, a broad band with a maximum at 540 nm and line emission due to Eu^{3+} ions is observed. The Eu^{3+} ions are present as inadvertant impurity ions in the starting Gd_2O_3. Note, however, that the Eu^{3+} output for Gd^{3+} excitation is much higher than for WO_4^{2-} excitation (Fig. 1).

The excitation spectrum of the 540 nm broad emission band is given in Fig. 2. Note the Gd^{3+} lines, the WO_4^{2-} excitation band at 275 nm, and a new band with a maximum at about 315 nm. This 315-nm band corresponds to the 540-nm emission band. Such an additional band has been observed in other tungstates too. It has been ascribed to a tungstate group near a defect, most probably a tungstate group containing an oxygen vacancy, i.e., $WO_3\square^x$ (5).

Excitation into the $^8S \rightarrow {}^6P_J$ transition of Gd^{3+} results, therefore, in a number of processes. In the first place we excite the defective tungstate groups directly, because their excitation band coincides with these transitions. We also excite the Gd^{3+} ions. It is well known that in concentrated Gd^{3+} systems the excitation energy migrates among the Gd^{3+} sublattice (6). Only a small part of this excitation energy is lost radiatively as Gd^{3+} emission. The greater part is trapped by the defective tungstate groups. This trapping must be an effective process, since the Gd^{3+} emissions overlaps with the absorption band of the defective tungstate group. The trapped excitation energy appears as 540-nm band emission. The Eu^{3+} ions act also as traps for the migrating Gd^{3+} excitation energy.

Some of our samples contained a small amount of $Gd_3WO_6Cl_3$ which was not detectable in the X-ray diffraction pattern. This complicated the situation even more, because its 440-nm broad band emission is also excited in the region of the Gd^{3+} $^8S \rightarrow {}^6P_J$ transitions. The fact that the excitation spectrum of the 580-nm emission also con-

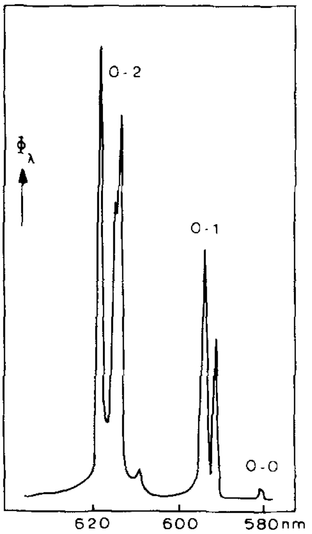

FIG. 2. Excitation spectrum of the 480- and 580-nm emission of GdWO$_4$Cl at 4.2 K. See also text. The q_r gives the relative quantum output.

tains the WO_4^{2-} 275-nm excitation band is due to the fact that in monitoring the 580-nm emission, we also pick up some 480-nm band emission which is much stronger than the defect emission.

Excitation into the higher Gd^{3+} $^8S \rightarrow {}^6I_J$ transitions will mainly excite the regular WO_4^{2-} groups directly. Note that these Gd^{3+} transitions occur as a dip in the excitation spectrum of the 480-nm emission (Fig. 2). This means that the Gd^{3+} transition absorbs energy which does not result in 480-nm emission. This appeared from Fig. 1: Gd^{3+} excitation gives mainly the 540-nm emission band.

The intensity of the Gd^{3+} emission line (Fig. 2) is extremely sensitive to sample history and temperature. The former is immediately clear, because the sample history determines the concentration of defects which trap the Gd^{3+} emission. For a given sample the amount of Gd^{3+} emission varies with temperature as follows: 9.5 K, 20%; 15 K, 11%; 20 K, 1.5%; 25 K, 0%. This indicates that Gd^{3+} traps are effective at low temperatures and compete with the defective tungstate groups and Eu^{3+} ions for the migrating energy. At higher temperatures, back transfer from the Gd^{3+} traps occur. They have become too shallow. A similar situation has been observed for other rare earth ions in high concentrations (see, e.g., Ref. (*7*)). Our data suggest a trap depth of about 30 cm^{-1}.

The quenching temperature of the defective tungstate groups is about 100 K. It is general practice that this temperature is lower than the value for the regular groups.

Let us now compare these results with those for gadolinium compounds of similar groups. In $GdTaO_4$ and $GdNbO_4$, the tantalate and niobate emission is situated at higher energies than the tungstate emission in $GdWO_4Cl$. Consequently, the tantalate (niobate) system and the Gd^{3+} are strongly connected. Excitation into the tantalate (niobate) host lattice groups is followed by immediate energy transfer to the Gd^{3+} system. The excitation energy migrates among the Gd^{3+} ions and is trapped by defective tantalate (niobate) groups which show only emission at low enough temperatures (*8*). In $GdVO_4$, however, the vanadate absorption lies below and on the Gd^{3+} transitions. Here the Gd^{3+} system transfers excitation energy to the regular vanadate groups which emit, after excitation, below 200 K. At higher energies, the vanadate excitation energy becomes mobile (*8*, *9*). Therefore, the compound $GdWO_4Cl$ is between $GdTaO_4$ ($GdNbO_4$) and $GdVO_4$.

For completeness and for comparison with the other chlorotungstates, the Raman and infrared spectra of $GdWO_4Cl$ were also recorded. The infrared spectrum in a KBr pellet showed four absorption bands in the W–O stretching region, viz., 975 (sharp, m), 935 (s), 835 (s) and 795 (s). Other absorptions are situated below 400 cm^{-1}. These W–O stretching frequencies were not observed in the Raman spectrum, so the exclusion principle seems to be effective. In the same spectral region the Raman spectrum shows a large number of lines, peaking at 994 (s), 950 (w), 937 (m), 907 (vw), 867 (s), 839 (s), 824 (m), 803 (m), 750 (w), 730 cm^{-1} (w). According to the crystal structure determination (*4*), the site symmetry of tungsten is C_s, $Z = 4$, and the space group symmetry is C_{2h}^3. This agrees with the observation of the exclusion principle and predicts even more lines than observed in our spectra. An assignment in terms of the tetrahedral ν_1 and ν_3 stretching modes is clearly impossible. The frequency region in which these vibrational features are observed agrees with common experience with tungstate tetrahedra (*10*).

3.2. $GdWO_4Cl$–EU

A sample of composition $Gd_{0.99}Eu_{0.01}WO_4Cl$ was studied to confirm the description given above and before (*1*–*3*). The main difference with the undoped sample is

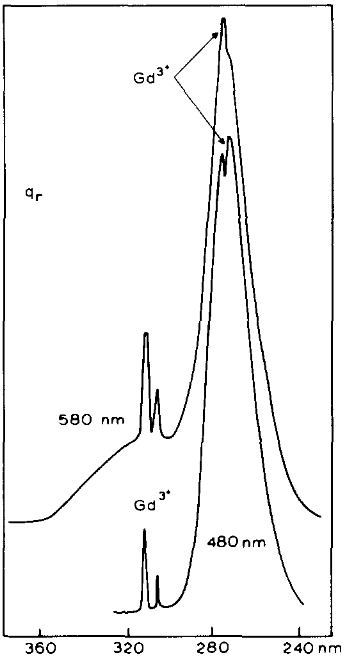

FIG. 3. Spectral energy distribution of the emission of EuWO$_4$Cl at 4.2 K. Excitation wavelength is 395 nm. The notation 0–J relates to the transitions $^5D_0$ – ^7F_J.

expected to be the 1 at.% Eu^{3+} ions which will act as traps for the migrating Gd^{3+} excitation energy. Because the Eu^{3+} concentration is now much higher than in the undoped sample, trapping by Eu^{3+} ions should be much more effective, so that Gd^{3+} excitation is expected to result in Eu^{3+} emission. Energy transfer from tungstate to Eu^{3+} is also to be expected, but only up to a minor amount, because the tungstate excitation energy is not mobile and the transfer occurs only over a restricted distance (*2*, *3*).

These expectations are substantiated. Upon 275-nm excitation at LHeT, the emission of Gd$_{0.99}$Eu$_{0.01}$WO$_4$Cl consists of 90% tungstate emission (485-nm band) and of 10% europium emission. Emission from Gd^{3+} was detectable, but contributed less than 0.2% to the total emission intensity. Without Eu^{3+} present, the Gd^{3+} contribution was much higher. This shows that the Eu^{3+} traps compete successfully with the Gd^{3+} traps because of their higher concentration. The 10% Eu^{3+} emission originates, therefore, partly from tungstate excitation followed by one-step transfer to Eu^{3+} and partly from Gd^{3+} excitation followed by migration through the Gd^{3+} sublattice until the energy is trapped by Eu^{3+}.

The excitation spectrum of the Eu^{3+} emission is quite complicated. It consists of Eu^{3+} absorption lines (direct excitation of the activator), an Eu^{3+} charge-transfer band at about 300 nm as observed before in the lanthanum chlorotungstates (*2*, *3*), the Gd^{3+} absorption lines (migration through the Gd^{3+} sublattice followed by trapping at the Eu^{3+} ions), and the tungstate absorption band at 275 nm. All this is in line with expectation and, therefore, does not need to be discussed in detail.

Because of the presence of the Eu^{3+} charge-transfer band, it is no longer possible to excite the Gd^{3+} ions in the $^8S \rightarrow {}^6P_J$ transition or the defective tungstate group in a selective way.

3.3. EuWO$_4$Cl

The compound EuWO$_4$Cl has the same crystal structure as GdWO$_4$Cl and luminesces bright red (*10*). Its emission spectrum is given in Fig. 3 in the $^5D_0$ – $^7F_{0,1,2}$ region. The number of lines in this spectrum is $^5D_0$ – $^7F_0$1, $^5D_0$ – $^7F_1$2, $^5D_0$ – $^7F_2$4. Since the site symmetry of Eu^{3+} in EuWO$_4$Cl is C_s (*4*), the expected number of lines is 1, 3, 5, respectively. An approximate site symmetry would be C_{2v}, but then we come to 1, 3, 4. The $^5D_0$ – $^7F_1$ transition is expected to split into three lines. The reason for this discrepancy is not clear, but may be accidental.

No tungstate emission is observed at any temperature. This confirms our earlier model (*2*, *3*) that the probability for energy transfer from the tungstate group to the Eu^{3+} ion exceeds the radiative probability in the tungstate group. The excitation spectrum of the Eu^{3+} emission consists, accordingly, of the characteristic Eu^{3+} lines, an Eu^{3+} charge-transfer band, and the tungstate absorption band.

The emission intensity at 4 and 300 K is the same within the experimental accuracy. The quantum efficiency is high, viz., $\geq 70\%$. This means that no pronounced concentration quenching occurs in the system $Gd_{1-x}Eu_xWO_4Cl$. It remains to be investigated whether energy migration in the Eu^{3+} sublattice of $EuWO_4Cl$ occurs (*11*). Such an investigation using dye-laser excitation is planned for the near future.

4. Acknowledgments

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