

Luminescence in Lanthanum Chlorotungstate (LaWO_4Cl)

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Received August 24, 1982

The luminescence properties of LaWO_4Cl are reported and discussed. The tungstate group occurs as a trigonal bipyramid. Although there is some analogy with the luminescence of the tetrahedral tungstate group, the small Stokes shift reveals the presence of five oxygen ions. The luminescence of the following ions was studied: Mo^{6+} , Eu^{3+} , Sm^{3+} , and Tb^{3+} . The molybdate group shows red emission with a larger Stokes shift than the tungstate group. Energy transfer from the tungstate group to the rare earth ions occurs over nearest-neighbor distances, except for Tb^{3+} . Because of a low-lying $f-d$ transition, the transfer efficiency is much higher for this ion.

1. Introduction

The luminescence of $\text{La}_3\text{WO}_6\text{Cl}_3$, and of several activators therein, has been reported recently (1, 2). The tungstate group in this lattice is trigonal prismatic (3). The crystal structure of LaWO_4Cl has also been described (4). The unusual feature of this structure is the five coordination of tungsten in the form of a trigonal bipyramid. It is the purpose of this paper to report on the luminescence of LaWO_4Cl and activators therein. In view of the similarity with the $\text{La}_3\text{WO}_6\text{Cl}_3$ system, the stress will be on the differences in the luminescence of both host lattices.

2. Experimental

The reader is referred to Refs. (1-4).

3. Results and Discussion

3.1. Unactivated LaWO_4Cl

The compound LaWO_4Cl does not luminesce at room temperature. At lower temperatures, however, a bright, blue luminescence appears under ultraviolet excitation. The quenching temperature is about 230K. Figure 1 presents the emission and excitation spectra at liquid helium temperature. The emission maximum is at 450 nm, the excitation maximum at 300 nm. This yields a Stokes shift of $11,000 \text{ cm}^{-1}$. This value is about equal to that reported for octahedral and trigonal prismatic tungstate groups (2). From this it can be concluded that Stokes shifts of $15,000 \text{ cm}^{-1}$ and more in the case of tungstate emission are only to be expected for tetrahedral tungstate groups (2, 5).

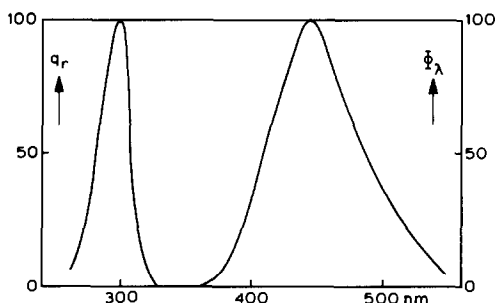


FIG. 1. Emission and excitation spectra of the luminescence of LaWO_4Cl at LHeT.

Figure 2 shows the decay times of the WO_5^{4-} luminescence as a function of temperature. Above 4K the decay curves are exponential. Below 4K, they can be analyzed to give two decay times. The shorter one becomes too short at 4K to be measurable. This behavior differs from that observed for the octahedral and trigonal prismatic tungstate group, for which two radiant decay times were observed, each from a different energy level (2). The fast decay time at very low temperatures with its pronounced temperature dependence is ascribed to a nonradiative transition which feeds the emitting level. Since excitation is into the singlet levels and emission occurs from the triplet levels (5), this nonradiative transition may be the singlet-triplet transition.

The temperature dependence of the longer, radiative decay time is similar to

that reported for the tetrahedral tungstate group in CaWO_4 (6). It can be analyzed using a three-level scheme (5). The energy difference between the two excited states is found to be about 20 cm^{-1} . This value is also observed for CaWO_4 . Unfortunately, no decay time measurements are known for CaWO_4 down to very low temperatures. Our results indicate that the emission in the case of LaWO_4Cl originates from a level which is connected with the ground state by a spin-forbidden, symmetry-allowed transition. The excited level is split by spin-orbit coupling. This splitting yields an optical trap level with a trap depth of 20 cm^{-1} (5). It would be interesting to investigate whether the nonradiative, fast decay can also be observed in the case of CaWO_4 . It has not been found for the WO_6^{2-} groups.

Vibrational spectra were measured to compare the W-O stretching frequencies of the WO_5^{4-} bipyramid with those of the tungstate tetrahedron and octahedron. The Raman spectrum was given in Ref. (4). In Table I, the infrared and Raman frequencies for LaWO_4Cl in the W-O frequency range are given. For an isolated WO_5^{4-} group, the symmetry should be D_{3h} . In LaWO_4Cl , the W^{6+} ion moves off the basal plane. Although the exact site symmetry is C_s , C_{3v} is a good approximation. The W-O stretching frequencies have the following representations in this approximation: $3A_1 + E$. All of them are allowed in infrared and Raman.

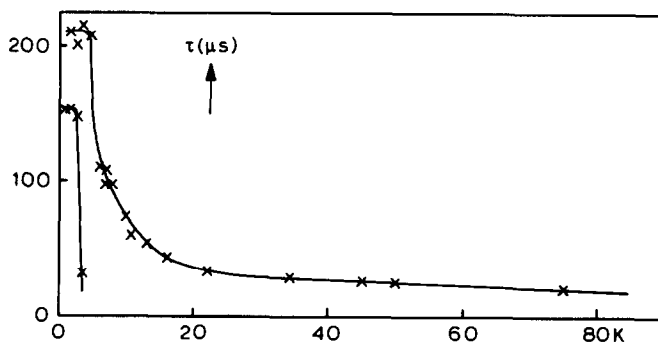


FIG. 2. Decay times (τ) of the luminescence of LaWO_4Cl as a function of temperature. Also see text.

TABLE I
INFRARED AND RAMAN
FREQUENCIES OF LaWO₄Cl IN THE
W-O STRETCHING REGION (ALL
VALUES IN cm⁻¹)

Infrared ^a	Raman
950 (m) + 920 (sh)	925 (s)
850 (m)	825 (m)
760 (s)	765 (w)
730 (s)	730 (m)
710 (s)	715 (m)

^a Abbreviations: s = strong, m = medium, w = weak, sh = shoulder.

However, more than four lines are observed. Under C_s symmetry, the representations become $4A' + A''$. The subcell described in Ref. (4) contains four W^{6+} ions, and has space group $Pnma (D_{2h}^{16})$. A detailed analysis becomes difficult. We assume that the five main frequencies (Table I) correspond to the five W-O frequencies expected for C_s site symmetry. The two highest frequencies do not coincide in infrared and Raman, which indicates factor group splitting.

The values of the W-O frequencies of LaWO₄Cl are in the same region as those for CaWO₄ (7). Those for the WO_6^{6-} groups are considerably lower (1, 8).

Although the crystallographic and vibrational spectroscopy data suggest a close analogy between the W-coordination in LaWO₄Cl and that in a tungstate tetrahedron,

it seems to us that the value of so sensitive a parameter as the Stokes shift clearly indicates the presence of a fifth oxygen ion. Probably the W^{6+} ion is more off-center in the ground state than in the excited state.

3.2. LaW_{1-x}Mo_xO₄Cl

Samples with a few percent of molybdenum could be prepared easily. Emission and excitation spectra are presented in Fig. 3. The molybdate emission peaks at about 650 nm. The excitation spectrum shows two bands, viz., one at about 330 nm corresponding to molybdate absorption and one at 300 nm corresponding to tungstate absorption. The latter indicates energy transfer from tungstate to molybdate, but because of its low intensity this transfer is of limited importance.

The Stokes shift of the molybdate emission of LaWO₄Cl:Mo is about 14,500 cm⁻¹, which is much larger than that for the tungstate emission (see above). Usually the Stokes shift of similar molybdate and tungstate groups has the same value, e.g., for CaWO₄ and CaMoO₄ (9). The larger Stokes shift for LaWO₄Cl:Mo may well indicate that the smaller Mo⁶⁺ ion has moved even further away from the basal plane of the pyramid than the W⁶⁺ ion, so that a tetrahedral coordination occurs.

The quenching temperature of the molybdate luminescence is 140K. In contradistinction with the molybdate emission in La₃WO₆Cl₃, that in LaWO₄Cl has a high

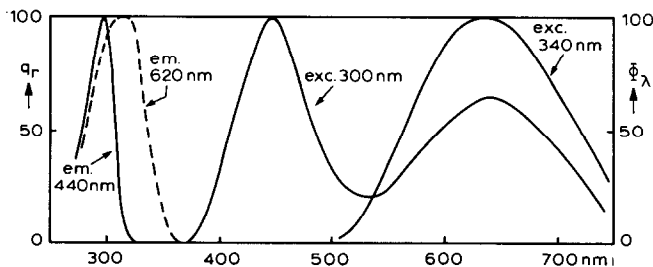


FIG. 3. Emission and excitation spectra of the molybdate luminescence of LaW_{0.97}Mo_{0.03}O₄Cl at LHeT.

quantum efficiency at low temperatures. This made it possible to perform decay time measurements. Figure 4 presents the decay time as a function of temperature. There is a maximum at 20K. At higher temperatures the decay time decreases as a result of thermal quenching. At lower temperatures, the decay time goes to a value of 160 μsec . Note that the values at 20K and higher are 1 order of magnitude larger than for the corresponding tungstate luminescence. This phenomenon was also observed for the tetrahedral groups and is due to a weaker spin-orbit coupling in the case of molybdenum. The weaker coupling makes the triplet-singlet emission transition more forbidden.

The level splitting responsible for the low-temperature behavior is different in the molybdate and the tungstate. This splitting is due to spin-orbit effects in the latter case (5). The energy difference between the two levels involved is estimated to be 5 cm^{-1} , which agrees reasonably well with the value for CaMoO_4 (5). For details of analysis and interpretation, the reader is referred to a recent review paper (5).

It is hard to explain why the red emission of $\text{La}_3\text{WO}_6\text{Cl}_3\text{:Mo}$ (2) has a low quantum efficiency at LHeT, whereas that of $\text{LaWO}_4\text{Cl:Mo}$ does not. For an explanation, it is necessary to know the complicated level structure of the excited state. Note, in addition, that the quenching temperature of the luminescence of $\text{La}_3\text{WO}_6\text{Cl}_3$ is higher than

that of LaWO_4Cl , which makes the problem even more difficult.

3.3. $\text{LaWO}_4\text{Cl-Sm}$

Several rare earth ions show luminescence in LaWO_4Cl (4). Here the luminescence properties are reported in more detail, stressing the energy transfer from host lattice to the rare earth ions.

First, we consider the Sm^{3+} ion. Results presented here are for the composition $\text{La}_{0.98}\text{Sm}_{0.02}\text{WO}_4\text{Cl}$. At room temperature, the characteristic Sm^{3+} emission can be excited in the Sm^{3+} lines (4). The excitation spectrum at 300K does not show the tungstate absorption band at 300 nm, so that at 300K energy transfer from the WO_4^{2-} group to the Sm^{3+} ion does not occur. At LHeT, the situation is different. Upon tungstate excitation a complicated emission spectrum is observed consisting of the characteristic Sm^{3+} lines (for about 12%) and the tungstate emission band (for about 88%). The tungstate emission band shows a number of sharp dips coinciding with the sharp Sm^{3+} excitation lines. From this, we conclude that nonradiative as well as radiative energy transfer occurs. An analysis is given in Ref. (2) and shows that the nonradiative transfer occurs only over nearest-neighbor distances. Each tungstate group has six nearest-neighbor La^{3+} sites. For a Sm^{3+} concentration of 2 at%, this means that $0.98^6 = 89\%$ of the tungstate groups have no Sm^{3+} neighbors and decay radiatively. However, 11% of the tungstate groups see one or more Sm^{3+} ions and transfer their excitation energy, so that Sm^{3+} emission occurs. From the emission spectrum, it is estimated that about 1% of the tungstate emission is, in addition, transferred radiatively. In this model, the Sm^{3+} -tungstate emission ratio is predicted to be 0.14, in excellent agreement with the experimental value.

It is interesting to follow the emission spectrum under tungstate excitation as a

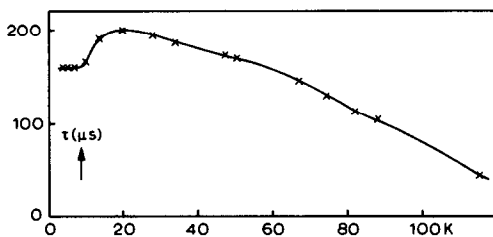


FIG. 4. Decay times of the molybdate luminescence of $\text{LaW}_{0.97}\text{Mo}_{0.03}\text{O}_4\text{Cl}$ as a function of temperature.

function of temperature. Up to 100K nothing changes, but at higher temperatures the tungstate emission band loses intensity. Above 230K, it has disappeared. Also the Sm^{3+} emission intensity decreases, but not as strongly as the tungstate emission intensity. At 300K, about 30% of the low-temperature intensity is left.

From this, we can conclude the following: (1) energy migration among the tungstate groups in LaWO_4Cl does not occur. A similar observation was made for $\text{La}_3\text{WO}_6\text{Cl}_3$ (2). At higher temperatures the nonradiative processes in the tungstate group are so fast that they compete with the $\text{WO}_5^{4-} \rightarrow \text{Sm}^{3+}$ transfer probability.

3.4. $\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$

Samples with Eu^{3+} concentrations below 1 at% did not show Eu^{3+} luminescence. A sample with 5% Eu^{3+} , i.e., $\text{La}_{0.95}\text{Eu}_{0.05}\text{WO}_4\text{Cl}$, showed efficient Eu^{3+} emission and was studied in more detail. At room temperature, the results are similar to those for Sm^{3+} , i.e., only Eu^{3+} emission and excitation lines were observed in the spectra. At LHeT, the emission spectrum under Eu^{3+} excitation shows a complete splitting of all the emission transitions in accordance with the low site symmetry (C_2), i.e., ${}^5D_0 \rightarrow {}^7F_0$ 1, ${}^5D_0 \rightarrow {}^7F_1$ 3, ${}^5D_0 \rightarrow {}^7F_2$ 5, etc. (Fig. 5).

Upon tungstate excitation at LHeT, this sample shows mainly tungstate emission, viz., 94% of the total emission. Only 6% of the emission originates from the Eu^{3+} ions. A small amount of radiative transfer could just be observed. In the simple model described above for $\text{LaWO}_4\text{Cl}:\text{Sm}^{3+}$, we predict 26% of Eu^{3+} emission. Since it does not seem realistic to assume an inefficient energy transfer from tungstate to Eu^{3+} , we conclude that the real concentration of Eu^{3+} ions is less than 5 at%. This was also observed for $\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$ (2) and has been ascribed to a slight amount of reduction in the preparation procedure. It may be

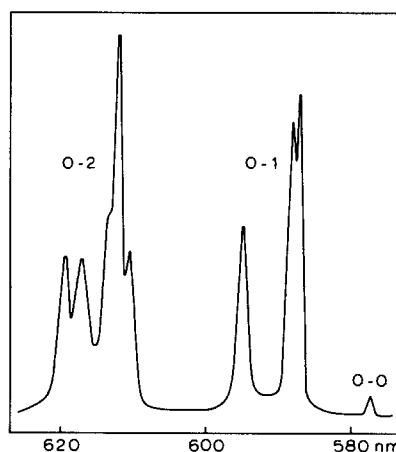


FIG. 5. Emission spectrum of $\text{La}_{0.95}\text{Eu}_{0.05}\text{WO}_4\text{Cl}$ under Eu^{3+} excitation at LHeT in the ${}^5D_0 \rightarrow {}^7F_{0,1,2}$ region.

that the absence of Eu^{3+} emission in the lower-concentration samples is due to the same reason. An amount of Eu^{3+} emission of 6% points to a concentration of 1 at% using our energy-transfer description.

As in the case of $\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$, the charge-transfer band of Eu^{3+} in $\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$ is at relatively low energy. Figure 6 shows the excitation spectra of the Eu^{3+} and the tungstate emission of $\text{LaWO}_4\text{Cl}:\text{Eu}^{3+}$. The extra broadband on the low-energy side of the tungstate band is the Eu^{3+} charge-transfer band. This phenomenon is similar to that observed for $\text{La}_3\text{WO}_6\text{Cl}_3:\text{Eu}^{3+}$, where the charge-transfer band is at even lower energy.

3.5. $\text{LaWO}_4\text{Cl}:\text{Tb}^{3+}$

For Tb^{3+} activation, an efficient, green phosphor is obtained. It turns out that there are striking differences to Sm^{3+} and Eu^{3+} . Data given here refer to the composition $\text{La}_{0.98}\text{Tb}_{0.02}\text{WO}_4\text{Cl}$. At room temperature, there is efficient, green emission. The excitation spectrum consists not only of the characteristic Tb^{3+} lines, but also of a broadband which coincides partly with the tungstate excitation band. This shows that at room temperature energy transfer from

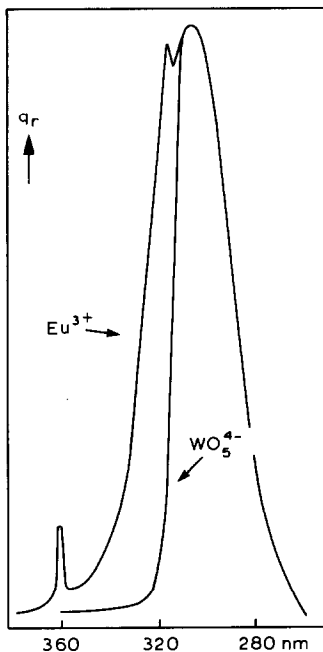


FIG. 6. The excitation spectra of the Eu^{3+} and the tungstate emission of $\text{La}_{0.95}\text{Eu}_{0.05}\text{WO}_4\text{Cl}$ at LHeT. Note the additional broadband in the case of Eu^{3+} , which corresponds to the charge-transfer transition.

tungstate to Tb^{3+} occurs, whereas it does not to Sm^{3+} and Eu^{3+} .

At LHeT, the emission spectrum under tungstate excitation consists of a weak tungstate emission band (50% of the total emission intensity) and sharp Tb^{3+} lines ($^5D_4\text{--}^7F_1$), which also contribute 50%. The total emission intensity is as strong as in the case of Sm^{3+} - and Eu^{3+} -activated samples. For the Tb^{3+} concentration concerned, we expect the same Tb^{3+} -tungstate emission ratio as derived above for $\text{LaWO}_4\text{Cl}:\text{Sm}^{3+}$, i.e., 0.14. The experimental value, viz., 1.0, is much higher. From this, we have to conclude that the tungstate- Tb^{3+} transfer proceeds over considerably longer distances than those between nearest neighbors.

The reason for this may become clear from Fig. 7, which gives the excitation spectrum of the Tb^{3+} emission at LHeT. Note the broad tail on the low-energy side

of the tungstate excitation band. This tail is due to direct Tb^{3+} excitation. We have to ascribe it to one of the components of the $4f \rightarrow 5d$ transitions on the Tb^{3+} ion. This is an allowed optical transition. A comparison between Figs. 1 and 7 shows that there is spectral overlap between the tungstate emission and the broad Tb^{3+} tail, i.e., the tungstate emission overlaps an allowed Tb^{3+} absorption band. In the case of Sm^{3+} and Eu^{3+} , there is only overlap with forbidden $4f\text{--}4f$ transitions. This gives the tungstate- Tb^{3+} transfer a considerably higher range. A similar situation exists in $\text{YTaO}_4:\text{Tb}$ (10).

In the LaWO_4Cl structure, the La^{3+} ions are situated on rows along the b axis (Ref. (4), Fig. 2). A $5d$ orbital oriented along this direction will have a very low energy because of the attractive forces of the La^{3+} ions. This seems to be an obvious explanation

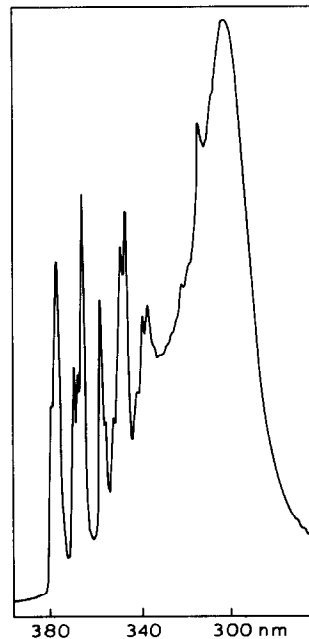


FIG. 7. The excitation spectrum of the Tb^{3+} emission of $\text{La}_{0.98}\text{Tb}_{0.02}\text{WO}_4\text{Cl}$ at LHeT. Sharp peaks are Tb^{3+} $f\text{--}f$ transitions, the band peaking at 300 nm is the tungstate excitation band, and the broad tail from 390 up to 300 nm is the Tb^{3+} $f\text{--}d$ transition.

tion for the exceptionally low position of one of the $4f-5d$ components in the spectra.

3.6. Other Ions

The U^{6+} as well as the Bi^{3+} ion were found to luminesce efficiently in $\text{La}_3\text{WO}_6\text{Cl}_3$ (1, 2). Therefore, we also tried these ions in LaWO_4Cl , but no emission of any intensity could be observed.

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