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Luminescence Properties of Uranium-Activated Lanthanum Halotungstate ($La_3WO_6Cl_3$—U)

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The luminescence properties of $La_3W_{1-x}U_xO_6Cl_3$ ($x \leq 0.01$) are reported. The orange emission is due to a trigonal uranate prism and shows high quantum efficiency. Excitation of the host lattice does not result in uranate emission. The spectra show vibrational structure at low temperatures. An analysis of this structure has been made. For that purpose the vibrational spectra of unactivated $La_3WO_6Cl_3$ were studied also. The decay time of the uranate emission is one of the shortest ever observed. This is primarily due to the absence of an inversion center in the trigonal prism.

1. Introduction

Recently the crystal structure of a new class of compounds with composition $Ln_3WO_6Cl_3$ (Ln = La, Ce, Pr, Nd, Sm, Eu, Gd) has been reported (*1*). In this structure the tungsten ion is in an unusual trigonal prismatic coordination. A preliminary search has shown that several rare earth ions show efficient luminescence in $La_3WO_6Cl_3$ (*1*). The tungstate prism also showed luminescence. A more extensive study will be published in due course. Here we wish to report the luminescence of hexavalent uranium in $La_3WO_6Cl_3$.

Although the U^{6+} ion occurs and emits often as a uranyl (UO_2^{2+}) group, in mixed metal oxides it has been found to occur and emit as a tetrahedral or octahedral uranate group also (*2–4*). A trigonal prismatic uranate group has never been observed before, which made a study of $La_3WO_6Cl_3$–U tempting. We found that this composition presents a very efficient, orange emission. Some of its luminescence properties are rather unusual for a luminescent uranate group.

2. Experimental

Samples were prepared as described in Ref. (*1*) in both laboratories. They were checked by X-ray diffraction. Their composition was $La_3W_{1-x}U_xO_6Cl_3$ with $x \leq 0.01$. We did not investigate higher uranium concentrations, because it is known that spectral characteristics may become complicated due to pair spectra (*5*).

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The performance of the optical measurements has been described before (*2*, *6*).

3. Results

Samples of $La_3WO_6Cl_3$–U show an intense orange luminescence under ultraviolet and visible excitation, at room temperature and below. The quantum efficiency at room temperature is 70–80%.

Figure 1 shows the emission and excitation spectra of this luminescence at room temperature. The emission spectrum consists of a band peaking at about 590 nm. The excitation spectrum consists of three bands with maxima at 565, 440, and 350 nm. It will become clear below that these excitation bands correspond to excitation into the uranate center.

Figure 2 shows the emission spectrum and the lowest energy part of the excitation spectrum at liquid helium temperature (LHeT). A considerable amount of vibrational structure has evolved at this temperature. Note that both spectra are each other's mirror image, apart from minor details. The zero-phonon lines of these spectra coincide within experimental accuracy. They are the most intense lines in the spectra. A list of the vibronic lines is given in Table I. The higher-energy excitation bands also show vibrational structure, but not so sharp as that at 565 nm. In the excitation band at 440 nm we observed a progression in a vibrational mode with frequency 650 cm^{-1}; in the band at 350 nm, a progression in a mode with frequency 620 cm^{-1}.

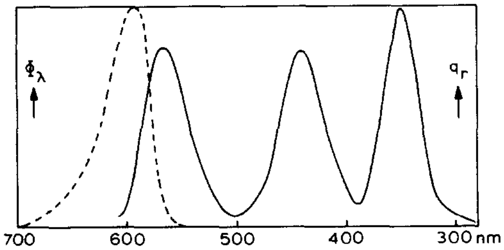

FIG. 1. Emission spectrum (left-hand side) and excitation spectrum (right-hand side) of the uranate luminescence of $La_3W_{0.995}U_{0.005}O_6Cl_3$ at room temperature. Φ_λ gives the spectral radiant power per constant wavelength interval and q_r the relative quantum output, both in arbitrary units.

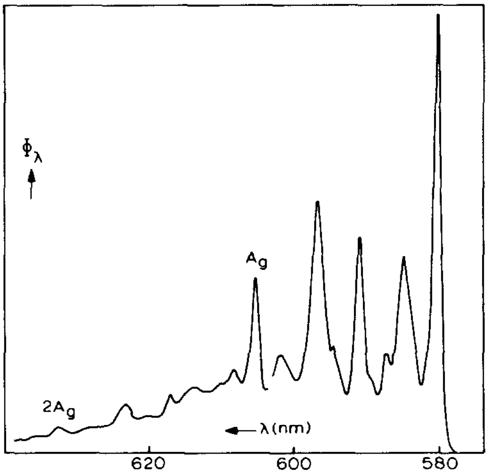

FIG. 2a. Emission spectrum of the uranate emission of $La_3WO_6Cl_3$–U at LHeT. A_g gives the vibronic feature in which the symmetrical U–O stretching mode (712 cm^{-1}) is involved. Compare to Table I. See also Fig. 1.

Under short-wavelength ultraviolet excitation $La_3WO_6Cl_3$–U shows a blue luminescence below room temperature. This is the

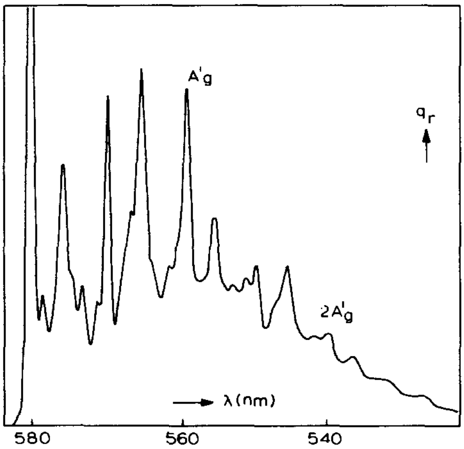

FIG. 2b. Excitation spectrum (lower energy part) of the uranate emission of $La_3WO_6Cl_3$–U at LHeT. Compare to Table I.

TABLE I

VIBRATIONAL STRUCTURE AT 4.2 K IN THE EMISSION BAND AND THE LOWEST ENERGY EXCITATION BAND OF THE LUMINESCENCE OF $La_3WO_6Cl_3$–U (ALL VALUES IN cm^{-1})

Excitation[a]		Emission[b]	
0–0 (vs)	01	0–0 (vs)	01
51 (w)	02		
136 (s)	$01 + \nu'_a$	132 (s)	$01 - \nu_a$
188 (vw)	$02 + \nu'_a$		
211 (w)	$01 + \nu'_b$	202 (w)	$01 - \nu_b$
278 (w)	$01 + \nu'_c$	274 (vw)	$01 - \nu_c$
322 (s)	$01 + \nu'_d$	314 (s)	$01 - \nu_d$
375 (vw)	$02 + \nu'_d$		
418 (m)	$01 + E'_{2g}$	419 (m)	$01 - E_{2g}$
462 (s)	$01 + E'_{1g}$	478 (s)	$01 - E_{1g}$
512 (vw)	$02 + E'_{1g}$		
586 (w)	$01 + A'_u(WO_6)$	617 (m)	$01 - A_u(WO_6)$
664 (s)	$01 + A'_g$	712 (s)	$01 - A_g$
		791 (w)	$01 - A_g(WO_6)$
780 (m)	$01 + A'_g + \nu'_a$	847 (vw)	$01 - A_g - \nu_a$
871 (w)	$01 + A'_g + \nu'_b$	947 (w,br)	$01 - A_g - \nu_{b,c}$
928 (w)	$01 + A'_g + \nu'_c$		
974 (w)	$01 + A'_g + \nu'_d$	1029 (w)	$01 - A_g - \nu_d$
1085 (w)	$01 + A'_g + E'_{2g}$		
1115 (m)	$01 + A'_g + E'_{1g}$	1192 (w)	$01 - A_g - E_{1g}$
1250 (w)	$01 + A'_g + A'_u(WO_6)$		
1311 (w)	$01 + 2A'_g$	1426 (w)	$01 - 2A_g$
1427 (w)	$01 + 2A'_g + \nu'_a$		

[a] Spectral positions are given as $\nu - \nu(0–0)$.

[b] Spectral positions are given as $\nu(0–0) - \nu$. Relative intensities are indicated as follows: vs: very strong; s: strong; m: medium; w: weak; vw: very weak. Stretching modes W(U)–O are indicated by the representations in Table II; the other modes are indicated alphabetically. A prime relates to excited state modes.

tungstate emission which has been reported before (*1*). Remarkably enough, we did not observe efficient energy transfer from the tungstate to the uranate group. The tungstate excitation band is not observed in the excitation spectrum of the uranate emission. Small dips in the emission band of the tungstate group at the position of the uranate excitation vibronics indicate radiative energy transfer from the tungstate to the uranate group, but its total efficiency is small.

If the temperature was increased, the intensity of the tungstate emission started to decrease below 125 K. The uranate emission did not benefit from this decrease, as also follows from the room-temperature excitation spectrum of the uranate emission which does not contain the tungstate excitation band. This observation shows that the tungstate excitation energy does not become mobile at higher temperatures. This will be discussed in more detail in a forthcoming paper on rare earth-activated halotungstates. Note that in the uranium-activated ordered perovskites A_2BWO_6–U the tungstate excitation energy starts to migrate through the host lattice at not too low temperatures, so that these materials are efficient uranium-activated phosphors not only for activator, but also for host lattice, excitation. The compound $La_3WO_6Cl_3$–U is an efficient phosphor for activator excitation only.

The decay time of the uranate emission is about 0.5 μsec. All decay curves are exponential. The decay time is slightly dependent on temperature: at LHeT its value is 320 nsec; this value increases to about 600 nsec at room temperature.

For the interpretation of the vibronics in the uranate spectra we measured the infrared and Raman spectra of $La_3WO_6Cl_3$. Figure 3 presents the spectra in the region of the W–O stretching frequencies.

4. Discussion

4.1. Vibrational Spectra

For purposes which will become clear be-

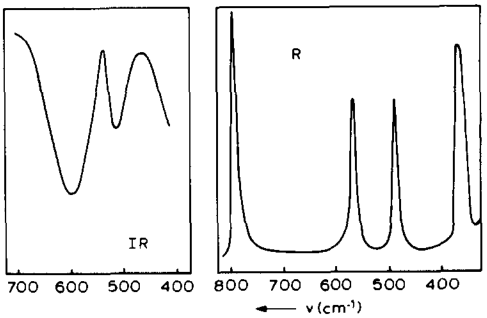

FIG. 3. Infrared (left-hand side) and Raman (right-hand side) spectrum of $La_3WO_6Cl_3$. The ir spectrum was taken in a KBr pellet.

low we analyzed the vibrational spectra of the compound $La_3WO_6Cl_3$ as far as the W–O stretching modes are concerned. The lower frequency range of the spectra is hard to analyze, because the W–O bending modes will mix with the La–O(Cl) stretching modes.

The representations of the W–O stretching modes of a WO_6 trigonal prism with D_{3h} symmetry are given in Table II, together with their spectral activity. The site symmetry of the W^{6+} ion in $La_3WO_6Cl_3$ is a little lower than D_{3h}, viz., C_{3h}. This does not change the results of the spectral activity (see Table II). Note that there are three Raman lines and two infrared bands to be expected and that one of each of these groups should coincide. Although the experimental number of lines agrees with expectation, none of the Raman lines coincides with the infrared bands.

However, the unit cell of $La_3WO_6Cl_3$ (space group $P6_3/m$) contains two WO_6 groups, so that factor group splitting should be taken into account. This has been performed in Table II. From the results, the assignment of the vibrational spectra in the W–O stretching region is obvious, if one assumes that the most intense and highest frequency Raman line has A_g representation (totally symmetric stretching frequency) and the factor group splitting is 25 cm^{-1} (E_{2g} and E_{1u}) which does not seem an unreasonable value.

TABLE II

ANALYSIS AND ASSIGNMENT OF W–O STRETCHING FREQUENCIES IN $La_3WO_6Cl_3$ (R: RAMAN; IR: INFRARED)

Site symmetry	Representation
D_{3h}	$A_1'(R) + E'(IR + R) + A_2''(IR) + E''(R)$
C_{3h}	$A'(R) + E'(IR + R) + A''(IR) + E''(R)$
$La_3WO_6Cl_3$: two WO_6 prisms (C_{3h}) in space group $P6_3/m$ (C_{6h}^2)	
$2A' \rightarrow A_g(R) + B_u$	780 cm^{-1} (R)
$2E' \rightarrow E_{2g}(R) + E_{1u}(IR)$	490 cm^{-1} (R) + 515 cm^{-1} (IR)
$2A'' \rightarrow B_g + A_u(IR)$	600 cm^{-1} (IR)
$2E'' \rightarrow E_{1g}(R) + E_{2u}$	560 cm^{-1} (R)

4.2. Luminescence Properties

The U^{6+}-activated $La_3WO_6Cl_3$ is undoubtedly a very efficient, orange-emitting phosphor. This is valid only for direct excitation of the uranate group, because excitation with wavelengths shorter than 330 nm results in tungstate excitation and energy transfer from the tungstate to the uranate group does not occur effectively.

Since the uranyl group, and often also the octahedral uranate group, luminesces green, the emission color may seem unusual. However, Ba_2TeO_5–U (with unknown crystal structure) (*7*) and Y_2WO_6–U (*8*) also luminesce orange, whereas the tetrahedral uranate group in the scheelite structure emits in the far red (*4*). The emission transition is of the charge-transfer type with some *f–f* character (*3*).

This emission transition could be analyzed in more detail for the case of the uranate octahedron, since for the isoelectronic UF_6 not only the spectra but also reliable theoretical studies of the electronic energy level scheme are available (*3, 9*). For a UO_6^{6-} trigonal prism such a comparison is not possible. In what follows we will show that the present experimental results agree with prismatic coordination of the U^{6+} ion.

First we draw attention to the extremely short decay time of the luminescence of $La_3WO_6Cl_3$–U. In view of the high quantum efficiency the short value of the decay time cannot be due to nonradiative losses. For the uranyl group, radiative decay times of milliseconds have been reported; for the octahedral uranate groups, values of up to 400 μsec (*2, 3*). In these compounds the emission is assigned to a zero-phonon magnetic dipole transition, followed by vibronically allowed transitions. By all means the pure electronic transition is forbidden as electric dipole transition. If small distortions from pure inversion symmetry occur, the decay times become somewhat shorter (*2, 3*). A different situation occurs if inversion symmetry is completely absent, as in the tetrahedral uranate group. Obviously the parity selection rule is then strongly relaxed resulting in decay times of the order of 10 μsec (*4*).

Our experimental value of ~0.5 μsec indicates that the uranate group in $La_3WO_6Cl_3$ lacks inversion symmetry and is reasonably electric-dipole allowed. This corroborates with the trigonal prismatic coordination. It seems to us that the highly covalent character of the bands in this group, as suggested in Ref. (*1*), may be responsible for the very short decay time, the mixing of several wave functions being effective in relaxing the parity selection rule.

In agreement with the allowed character of the transition the zero-phonon line dominates the emission spectrum and its spectral counterpart in the excitation spectrum. Note further that in the vibronic spectra the one-phonon lines are by far the more intense lines. This is similar to the situation for the octahedral uranate group (*2, 3*). It shows that the relaxation of the excited state of the uranate prism is small. This also results in the small Stokes shift and the narrow bandwidth of the emission of $La_3WO_6Cl_3$–U (see Fig. 1).

We do not understand why the energy transfer from the tungstate to the uranate group in $La_3WO_6Cl_3$–U is so ineffective. For the ordered perovskites a critical transfer distance of about 20 Å has been observed (*10*). The spectral overlap between the tungstate emission and the uranate absorption band is so favorable that even radiative transfer occurs. Further, the absorption strength in the uranate prism is considerably higher than that in the uranate octahedron as argued above, and the W–W distance in $La_3WO_6Cl_3$ is hardly longer than in A_2BWO_6.

4.3. The Vibrational Structure in the Spectra

An analysis of the vibrational structure in the emission and excitation spectra reveals several interesting facts. First, the zero-phonon lines of the emission and excitation spectrum coincide. This shows that luminescence is from the same center as where excitation occurred and that no energy transfer between uranate groups occurs.

Although none of the bands involved shows a long progression, it is nevertheless clear that the emission spectrum contains a progression in the mode with 712-cm^{-1} frequency, whereas the lowest excitation band shows a progression in the 664-cm^{-1} frequency mode. The mode involved must be the totally symmetric U–O vibration (A_g symmetry). Its frequency does not differ much from that observed for the octahedral uranate group (*2, 3*) and is lower than that for the uranyl group (*2*). In the lowest excited state the frequency is about 7% lower than that in the ground state. In the higher excited states the progression frequencies are lower (650 and 620 cm^{-1}), indicating a decreasing bonding strength in the uranate group for higher excited states.

The ground state value of 712 cm^{-1} is to be compared with the 780-cm^{-1} value of the trigonal tungstate prism found in the Raman spectrum (Table II). The corresponding values for Ba_2MgWO_6–U, for example, are 790 and 818 cm^{-1}, respectively (*3*).

For $La_3WO_6Cl_3$–U we have assumed, therefore, that the frequency of the U–O stretching modes is somewhat lower than that of the W–O stretching modes. It is then impossible to assign the 617-cm^{-1} mode found in the emission spectrum, whereas it is obvious to assign the 478-cm^{-1} mode to E_{1g} (560 cm^{-1} in the case of tungstate) and the 419 cm^{-1} to E_{2g} (490 cm^{-1} for tungstate) and/or E_{1u} (515 cm^{-1} for tungstate). The 617-cm^{-1} line is then ascribed to coupling with the A_u tungstate mode. This line is also relatively broad, which may be due to the fact that it cannot be interpreted in terms of the $k = 0$ internal modes of the uranate group. A similar observation has been made in the system Cs_2SiF_6–Mn^{4+}, where the Mn^{4+} emission spectrum shows coupling with a SiF_6^{2-} vibrational mode (*11*), and in the system Rb_2SnBr_6–Re^{4+}, where the Re^{4+} emission shows coupling with the internal modes of the $SnBr_6^{2-}$ group (*12*).

In view of the assignment of the 617-cm^{-1} feature we assigned the 791-cm^{-1} feature in the emission spectrum to coupling with the totally symmetric W–O stretching vibration (780 cm^{-1} in the Raman spectrum). Such couplings have not been observed in the spectra of the uranium-activated ordered perovskites (*5*), but here the frequencies of the W–O and U–O stretching modes are about equal. These lines, however, were rather broad, as is the 617-cm^{-1} feature in the emission spectrum of $La_3WO_6Cl_3$.

The features below 400 cm^{-1} (see Table I) are assigned to coupling with deformational modes and lattice vibrations without further specification. Let us now compare the emission and excitation spectra (see Table I). There are only some minor differences to note. The excitation spectrum contains a very weak second zero-phonon line, at some 50 cm^{-1} above the lower one. Splittings of this magnitude are well known from studies on the octahedral uranate group (*3*). It is obvious that the transition from the ground state to the higher level is considerably less intense than that to the lower level (see Fig. 3). Further, we observed coupling with the A_u tungstate mode also in the excitation spectrum.

The increase of the decay time of the luminescence with temperature can be explained by taking into account this second level. For a three-level scheme we have the general formula for the decay time τ: $\tau^{-1} = p_{31}(1 + e^{\epsilon/kT})^{-1} + p_{21}(1 + e^{-\epsilon/kT})^{-1}$ (*13*). Here ϵ is the energy difference between the two excited levels which are assumed to be in thermal equilibrium. Further, p_{31} and p_{21} are the radiative transition probabilities from the highest and the lowest excited state to the ground state, respectively. If we take $\epsilon = 50$ cm^{-1} (from the excitation spectrum), $p_{31}/p_{21} = 10^{-2}$ (from the intensities in the excitation spectrum) and $p_{21} = 3 \times 10^6$ sec^{-1}, we get a reasonable fit to the experimental data. From 0 to 300K τ increases in this model from 330 to 590 nsec in good agreement with experiment. The temperature dependence of τ can be followed nicely in this system, because thermal quenching occurs only above room temperature.

Measurements of the present spectra under higher resolving power would certainly reveal many more details. We feel, however, that the real bottleneck for a further analysis is the fact that the energy level scheme of the trigonal uranate prism is not known. The studies on the octahedral uranate group are illustrative in this aspect.

5. Conclusions

Uranium-activated $La_3WO_6Cl_3$ is a very efficient, orange-emitting luminescent material. The emission is due to the trigonal uranate prism UO_6^{6-}. Energy transfer from the host lattice to the activator is negligible. The uranate decay time is one of the shortest ever observed.

Acknowledgment

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