The Luminescence of Uranium-Activated Yttrium Tungstate (Y_2WO_6)

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The luminescence of uranium in Y_2WO_6 can be excited with long wavelength ultraviolet radiation at temperatures below room temperature. The emission consists of a fairly narrow band in the orange part of the spectrum. Its characteristics are comparable with the luminescence of uranium in $MgWO_4$ and the scheelites MWO_4 (M = Ca, Sr, Ba). It is possible to relate the thermal quenching temperature of the luminescence to spectral data. Energy transfer from the tungstate group to the uranate group is observed, but its efficiency is not very high compared with other systems.

1. Introduction

Recently, in our laboratory we studied the luminescence of hexavalent uranium ions in tungstates or tellurates which contain isolated WO_6^{6-} or TeO_6^{6-} groups (*1–3*). This means that the uranate group does not have oxygen ions in common with other hexavalent ions. At low enough temperatures the emission spectra of the UO_6^{6-} group in these compounds (e.g., Ba_2MgWO_6, $Y_3Li_3Te_2O_{12}$, Mg_3TeO_6) show extended fine structures consisting of a zero-phonon transition followed by a number of vibronic lines, among which are those that occur by one-phonon emission of the ungerade internal vibrational modes of the UO_6^{6-} octahedron (ν_6, ν_4, ν_3) dominate. In some cases we also observed one-phonon emission of a lower frequency external vibrational mode. Vibronics due to more-phonon coupling always showed a considerably lower intensity than those due to one-phonon coupling (in contradiction with the well-known case of the uranyl ion, UO_2^{2+}).

During the continuation of this study we found apparently different emission spectra for hexavalent uranium in tungstates and tellurates. In this paper we wish to report the luminescence properties of U^{6+}-activated Y_2WO_6. In view of these results we remeasured the luminescence of U^{6+}-activated $MgWO_4$ reported long ago by Kröger (*4*). Since the results of Y_2WO_6–U and $MgWO_4$–U resemble those reported for the U^{6+}-activated scheelites (*5*), a comparison of the luminescence of all these systems is also included.

The luminescence of pure Y_2WO_6 and rare-earth activated Y_2WO_6 has been reported before and is reasonably understood (*6, 7*).

2. Experimental

Samples were prepared as described in the relevant references cited in the introduction. The uranium concentration amounts to 0.3 at%. The firing atmosphere was always oxygen. Samples were checked by X-ray analysis. The way in which the luminescence properties were measured has been described (*1–3*).

3. Results

The sample $Y_2W_{0.997}U_{0.003}O_6$ shows at room temperature the same luminescence as pure Y_2WO_6 but with a lower efficiency: The broad-band emission of the tungstate group peaks at about 485 nm, whereas the maximum of the excitation band is at about 300 nm. Below 275°K, however, this behavior changes. Upon long-wavelength uv excitation, an orange emission occurs. Its spectral energy

distribution at liquid nitrogen and helium temperature is given in Fig. 1. Note the absence of a vibrational fine structure. This emission can be excited in a broad excitation band with two maxima (at 385 and at 335 nm). At low temperatures this emission is very intense. Its efficiency starts decreasing above 220°K, has reduced to 50% at 250°K, and disappears completely at room temperature. If excitation is into the host lattice (tungstate groups), i.e., $\lambda < 300$ nm, the emission consists for the greater part of tungstate emission; the amount of uranate emission in the 0.3% sample, for example, is about 20% (liquid nitrogen temperature, 300 nm excitation). This points to considerably less efficient energy transfer from the tungstate to the uranate group in Y_2WO_6 than in some host lattices reported before, where a critical distance of 25 Å was found (8).

The decay time of the orange luminescence is about 20 μsec at 4.2°K. It decreases at higher temperatures.

The luminescent properties of $MgW_{0.997}U_{0.003}O_4$ are very similar. There is also a bluish tungstate luminescence and an orange uranate luminescence. The spectral energy distribution of the latter at 4.2°K is given in Fig. 2. This emission consists of two subbands peaking at about 585 and 610 nm, each showing some structure. The present apparatus is not accurate enough to resolve this pattern reliably. To present an impression of the frequencies involved we give the (inaccurate) values of the vibronics of the stronger subband relative to the one at the highest energy: 90, 170, 240, 310, and 380 cm^{-1}. The wavenumber difference between the two subbands is about 700 cm^{-1}.
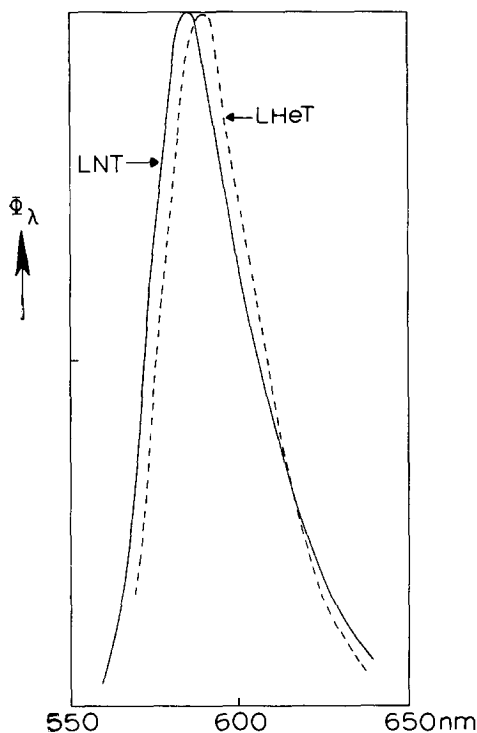

FIG. 1. Spectral energy distribution of the uranium emission of $Y_2W_{0.997}U_{0.003}O_6$ under 380 nm excitation at liquid nitrogen and helium temperature. Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units.
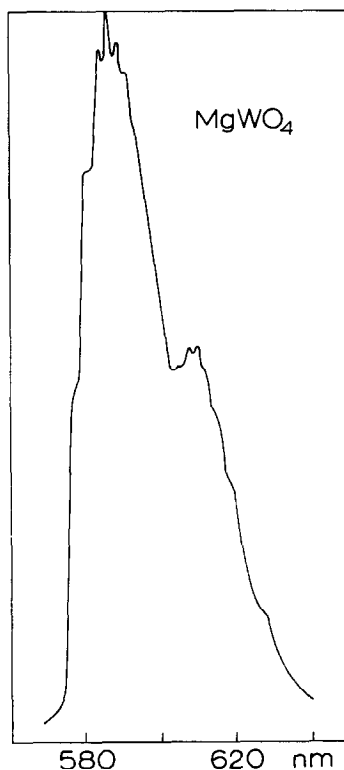
FIG. 2. Spectral energy distribution of the uranium emission of $MgW_{0.997}U_{0.003}O_4$ under 315 nm excitation at liquid temperature. Uncorrected recorder curve.

This orange emission can be excited in the long-wavelength uv region. Again we find two maxima in the excitation spectrum (at 420 and at 385 nm). If excitation is into the tungstate group ($\lambda > 300$ nm), the emission consists mainly of the bluish tungstate emission. The quenching temperature of the uranate luminescence of $MgWO_4$–U is lower than that of Y_2WO_6–U. The luminescence intensity decreases strongly above $100°K$ and has disappeared at about $200°K$. The decay time of the orange luminescence of $MgWO_4$–U amounts to 35 μsec at $4.2°K$, but decreases rapidly at higher temperatures. This decrease is mainly due to the thermal quenching of the luminescence.

4. Discussion

Unfortunately, the crystal structure of Y_2WO_6 has not yet been solved. Using vibrational spectra it has been proposed that the structure contains WO_6 octahedra (9). We will stick to this proposal. As will become clear below, the tungsten (uranium) coordination does not play a decisive role in our discussion. The vibrational spectra further revealed the presence of a considerable number of crystallographically different tungsten ions. This includes the fact that the activating uranium ion can also be considered to occupy several different sites in the lattice of Y_2WO_6.

The absence of vibrational fine structure in the emission spectra of Y_2WO_6 (see Fig. 1) can be partly ascribed to the presence of uranium in crystallographically different sites. The half-width value of the emission band (about 1000 cm^{-1}) excludes the presence of intense vibronics due to more-phonon coupling. In comparison with our previous results (1–3) it seems rather improbable at first sight that the present emission spectrum consists of only broadened vibronics due to one-phonon coupling with the internal v_6, v_4, and v_3 mode and with an external mode.

Since the overall luminescence properties of Y_2WO_6–U resemble those of $MgWO_4$–U (4), we decided to remeasure the latter. Results were given above. The crystal structure of $MgWO_4$ contains WO_6 octahedra also, but they are crystallographically equivalent

(10). The appearance of the emission spectrum of $MgWO_4$–U is different, because the several vibronics cannot be resolved as distinctly from each other as in the compounds investigated before (1–3). Nevertheless the one-phonon vibronics dominate. The large number of phonon frequencies in the vibronic structure can probably be related to the complexity of the crystal structure: The WO_6 groups form zig-zag chains, whereas in the compounds studied before (1–3) they occur as isolated groups. The second subband in the emission spectrum, some 700 cm^{-1} after the first one, must be a repetition of the first band due to coupling with the symmetrical U–O valence vibration (v_1).

The analogy between the fine-structure pattern of the uranium luminescence of $MgWO_4$–U and of that of the scheelites MWO_4–U ($M = $ Ca, Sr, Ba) (5) is striking. In the case of the scheelites two subbands also have been observed (at a distance of about 725 cm^{-1}); each of these bands shows fine structure with phonon frequencies of the same order of magnitude as in the case of $MgWO_4$–U. The position of the subbands is at much lower energies in the case of the scheelites ($\simeq 650$ nm for the stronger band). Russian workers report estimated decay times of 10–20 μsec between 4.2 and $300°K$. This is of the same order of magnitude as observed for $MgWO_4$–U. In view of the crystal structure there is not much doubt that the U^{6+} ion in the scheelites is present in four-coordination (5).

This analogy may be due to the fact that the WO_6 group in $MgWO_4$ is distorted in such a way that four oxygen ions are nearer to the central ions than the other two. Also the vibrational spectra of the tungstate group in these crystal structures show some resemblance (11). The emission spectrum of the uranium luminescence in Y_2WO_6 can be described along the same lines, but due to the presence of different U^{6+} ions the fine structure has been lost completely.

In the case of host lattices with isolated WO_6^{6-} groups, the decay time of the uranium luminescence was very long (300–350 μsec) (1, 2). This is due to the fact that in this case the purely electronic transition is parity forbidden as follows from the coupling with ungerade

vibrational modes. In the crystal structure of $MgWO_4$ and scheelite there is no inversion symmetry present at the tungsten site. As a consequence, the coupling with vibrational modes is less selective and the decay time is considerably shorter.

In our laboratory we have recently found that in tellurates the progression in v_1 in the emission spectrum of the uranium luminescence can be much longer than in the present case (four to five subbands instead of two), each subband showing additional fine structure at low temperatures. From the presence of a progression in v_1 in the uranium emission spectra some authors have concluded that uranium occurs as uranyl in the solid state (12, 13). From the present work we conclude that this is not necessarily true. At least it is necessary to have at one's disposal high-resolution emission spectra at low temperatures in combination with decay times. The present study shows that there is no essential difference between the structure in the uranium emission spectra of the tungstates dealt with and the structure in the spectra of the tungstates (tellurates) containing isolated groups UO_6^{6-}.

Let us now consider the thermal quenching temperature of the uranium luminescence in Y_2WO_6 and $MgWO_4$. Elsewhere (1) we have suggested that the energy difference between the position of the first allowed absorption band (i.e., the long-wavelength uv excitation band) and that of the emission band is proportional to the value of the quenching temperature. This follows from a model in which thermal quenching of the emitting state is assumed to occur via another state, viz. the one corresponding to the first allowed absorption band. This energy difference is about 9 kK for Y_2WO_6 and 7 kK for $MgWO_4$ (1 kK = 1000 cm^{-1}). The smaller difference corresponds with the lower quenching temperature, as expected from the model proposed before. From the work on MWO_4–U ($M =$ Ca, Sr, Ba) (5) it can be found that for the case of Sr and Ba this difference is at least 10 kK. In fact, the quenching temperature of the uranium luminescence in $SrWO_4$ and especially $BaWO_4$ is above room temperature (14), i.e., at higher temperatures than for

Y_2WO_6. Unfortunately, Ref. (5) does not give the position of the first allowed absorption band in the case of $CaWO_4$–U. Since its quenching temperature is about equal to that of $MgWO_4$–U (14), this position is estimated to be at 22 kK (emission maximum at 15 and 7 kK as found for $MgWO_4$–U). In Ref. (14) the variation of the quenching temperature of the uranium luminescence is explained with the virtual exchange mechanism (15). Our model seems to give a more straightforward explanation.

Finally, energy transfer from the host lattice to the activator is discussed. In a phosphor like Ba_2MgWO_6–U, the tungstate–uranate transfer is extremely efficient due to the high value of the critical distance for energy transfer ($R_c > 25$ Å (8)) and the possibility of tungstate–tungstate energy transfer (8, 16). The latter possibility is absent in Y_2WO_6 and $MgWO_4$ (7). But also the tungstate–uranate transfer will have a much lower probability in the present systems than in Ba_2MgWO_6–U. The reason for this is the fact that the spectral overlap between the tungstate emission (of Y_2WO_6 and $MgWO_4$) and the allowed uranium absorption band is considerably less than in Ba_2MgWO_6. For Y_2WO_6–U the critical distance for the tungstate–uranate transfer was estimated to be 12 Å using the experimental value of the spectral overlap (as in (8)). This is in fact considerably shorter than for Ba_2MgWO_6–U.

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