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The Luminescence Properties of the Octahedral Uranate Group in Oxides with Perovskite Structure

J. TH. W. DE HAIR* AND G. BLASSE

Solid State Chemistry Department, Physical Laboratory, State University, Sorbonnelaan 4, Utrecht, The Netherlands

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This paper describes how the luminescence properties of the octahedral uranate group in compounds with ordered perovskite structure are influenced by the chemical constitution of its surroundings. The quenching temperature of the emission is more strongly influenced by the neighboring cations in the [100] direction than by those in the [111] direction. This variation of the quenching temperature as a function of the chemical constitution is discussed in terms of a configurational coordinate model.

1. Introduction

The nature of the luminescence transitions within the octahedral uranate group has been described by us in (*1*). The luminescence properties of this group are influenced by the chemical constitution of the surroundings. The most striking example of these effects is the quenching temperature of the emission. A few years ago, Blasse reviewed the effect of the host lattice on the quenching temperature of several activators (*2*).

To study the influence of the surrounding ions on the luminescence properties of the octahedral UO_6^{6-} group we have used host lattices with perovskite structure. This structure has a high symmetry and allows an extensive cation substitution. A survey of compounds with this structure has been given by Goodenough and Longo (*3*). In this laboratory many investigations on the optical properties of compounds with this structure have been performed (*4–6*).

The introduction of uranium on a B' site in cubic perovskites with general formula $A_2BB'O_6$ results in the coordination of uranium by six BO_6 octahedra, which share corners with the UO_6 octahedron. In the [100] direction the UO_6 octahedron is surrounded by B cations; in the [111] direction by eight A cations.

In the host lattices $A_2BB'O_6$ both the A and B ions are divalent. Another charge distribution is provided by the host lattices $A^{2+}La^{3+}B^{+}B'O_6$. Brixner has desribed a few compounds with this composition (*7*). Divalent A and trivalent La ions are distributed among the sites which are occupied by A ions in the host lattices $A_2BB'O_6$. In the compounds $A^{2+}La^{3+}B^{+}B'O_6$ the $B'O_6$ octahedron, and therefore the uranate center, is surrounded not by divalent, but by monovalent B ions in the [100] direction.

We have also studied the luminesence of the uranate group in Ba_2ZnTeO_6. This compound has a hexagonal, perovskite-like structure with two different crystallographic sites for tellurium (*8*).

2. Experimental

All experimental procedures have been described earlier (*1*). If not mentioned otherwise, the U content is 0.3 mole%.

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* Present address: Light Division, N.V. Philips' Gloeilampenfabrieken, Eindhoven, The Netherlands.

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3. Results and Discussion

3a. $A_2BB'O_6$ Host Lattices

The host lattices in which tungsten is used for B' will be considered first. If A and B are alkaline-earth ions, the uranate emission in A_2BWO$_6$–U has at room temperature approximately the same spectral distribution (Fig. 1). The position of the maximum of the emission bands is given in Table I. In this table the position of the excitation band in the long wavelength uv region is also presented (see Fig. 2). The excitation spectra of the compounds have been discussed in (*1*). The uranate emission shifts to longer wavelengths if the cation B as a d^{10} configuration (Cd^{2+} or Zn^{2+}).

At lower temperatures and under short wavelength uv excitation a number of uranium-activated tungstates show host lattice emission. As an example, the emission of Ba_2CaWO_6–U at LNT is given in Fig. 3. The presence of tungstate emission indicates that the energy transfer from tungstate to uranate groups is not efficient enough to quench the host lattice emission completely. At LNT, tungstate emission is also observed for the uranium-activated host lattices Ba_2ZnWO_6, Ba_2SrWO_6, Ba_2CdWO_6, Ba_3WO_6, and Ca_2MgWO_6. The energy transfer from tungstate to uranate groups is discussed in more detail in (*10*).

The quenching temperature $T_{1/2}$ of the uranate emission is very sensitive to the nature of the surroundings ($T_{1/2}$ is defined as the temperature at which the emission intensity has decreased to half of its maximum value). The influence of the host lattice on $T_{1/2}$ is rather regular as can be seen from Table I and Fig. 4, for the alkaline-earth tungstates: The influence of the B ions is considerable, while the A ions do not affect the quenching temperature markedly. To account for this we use the configurational coordinate diagram drawn schematically in Fig. 5.

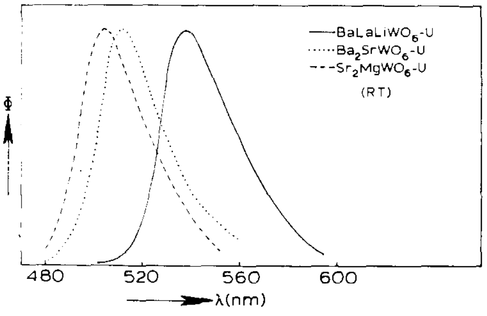

FIG. 1. Emission spectra of $BaLaLiWO_6$–U, Ba_2SrWO_6–U, and Sr_2MgWO_6–U at room temperature under mainly 366 nm excitation. All compounds contain 0.3 mole% uranium. Φ denotes the spectral radiant power in arbitrary units.

In this figure two excited states have been drawn, corresponding to excitation into the long wavelength uv excitation band and an excitation band in the visible region. (The latter band is not shown in Fig. 2). The excited states have been assigned to the $t_{1g} \rightarrow f$ CTS and to the $t_{1u} \rightarrow f$ CTS, respectively (*1*). All compounds have almost the same emission so that the latter charge transfer state, from which the emission takes place, is not much influenced by the surroundings. The quenching temperature, however, is determined especially by the $t_{1g} \rightarrow f$ CTS. The quenching temperature of the emission increases if the excitation band corresponding with this transition shifts to higher energy. This has been concluded from the uranate luminescence in crystallographically different host lattices (*11*).

In this model, the probability for radiationless decay to the ground state increases for higher temperatures. The quenching temperature depends on the position of the cross-over C. In our host lattices $T_{1/2}$, and therefore C, appear to be more sensitive to the surroundings than the long-wavelength uv excitation band (see Table I). The position of the excitation band in the long-wavelength uv region is temperature independent. We have studied the temperature dependence of the emission intensity by exciting into the $t_{1g} \rightarrow f$ CTS.

The displacement Δr (see Fig. 5) corresponds to an expansion of the UO_6^{6-} octahedron upon excitation. Uranium is substituted for tungsten at a lattice site which is somewhat too small to accommodate the uranium ion easily (compare the ionic radii of U^{6+} and W^{6+} for six-coordination, viz., 0.73 and 0.60 Å, respectively (*12*)). The surroundings of the uranate center have to

TABLE I

SOME LUMINESCENCE PROPERTIES OF URANIUM-ACTIVATED OXIDES $A_2BB'O_6$[a]

Host lattice $A_2BB'O_6$	Maximum of the emission band (nm)	Maximum of the long wavelength uv excitation band (nm)	Quenching temperature $T_{1/2}$ (K)	Ionic radii (Å)	
				A Cation 12-coordination	*B* Cation 6-coordination
Ca_2MgWO_6	508	335	340	1.35	0.72
Sr_2MgWO_6	504	340	340	1.40	0.72
Ba_2MgWO_6	514	~365	350	1.60	0.72
Ba_2CaWO_6	507	338	300	1.60	1.00
Ba_2SrWO_6	512	345	230	1.60	1.13
Ba_2BaWO_6	524	340	180	1.60	1.36
Ba_2ZnWO_6	536	380	220	1.60	0.75
Ba_2CdWO_6	532	357	240	1.60	0.95
Ba_2CaMoO_6	510	[b]	210		
Ba_2ZnTeO_6	521	370	260		
				$r(La3^+) = 1.32$ Å	
$SrLaLiWO_6$	535	340	340	1.40	0.74
$SrLaNaWO_6$	518	339	250	1.40	1.02
$BaLaLiWO_6$	538	354	240	1.60	0.74
$BaLaNaWO_6$	545	346	160	1.60	1.02
Ca_2MgTeO_6	502	324			
Sr_2MgTeO_6	495	333			
Ba_2MgTeO_6	509	360			
Ba_2CaTeO_6	504	335			
Ba_2SrTeO_6	508	341			
$SrLaLiTeO_6$	534	332			
$SrLaNaTeO_6$	522	334			
$BaLaLiTeO_6$	548	346			
$BaLaNaTeO_6$	534	340			

[a] Ionic radii of *A* and *B* ions are given following (*12*). The quenching temperature of the emission was determined by exciting into the maximum of the long wavelength uv excitation band.

[b] See text.

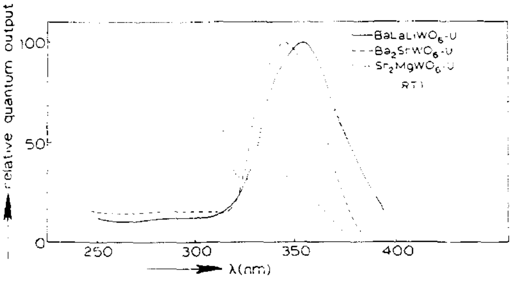

FIG. 2. Relative excitation spectra of the green emission of $BaLaLiWO_6$–U, Ba_2SrWO_6–U, and Sr_2MgWO_6–U at room temperature. All compounds contain 0.3 mole % uranium.

expand to accommodate this center, even if it is in the ground state. A further expansion of the UO_6^{6-} octahedron in the excited state will be strongly resisted by the lattice.

As regards the host lattices with alkaline-earth ions on the *A* and *B* positions the quenching temperature of the emission depends in a regular way on the *B* cations. A small *B* cation will give the host lattice a relatively large bonding strength. In such a rigid lattice Δr will be relatively small. This results in a high quenching temperature. If the size of the *B* cation increases the quenching temperature will decrease. This relation is

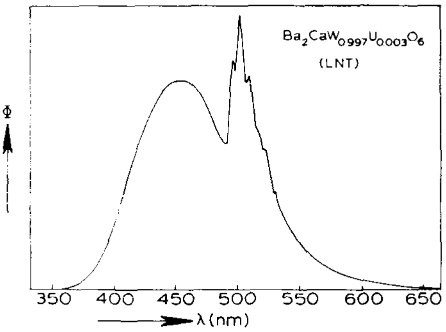

FIG. 3. Emission spectrum of $Ba_2CaW_{0.997}U_{0.003}O_6$ at LNT for 254 nm excitation. Φ gives the spectral radiant power in arbitrary units.

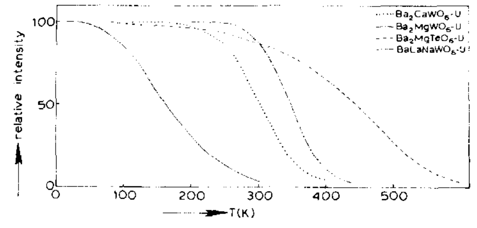

FIG. 4. Temperature dependence of the intensity (in relative units) of the green emission of some uranium-activated compounds for excitation into the uranate group (wavelength about 350 nm). All compounds contain 0.3 mole % uranium.

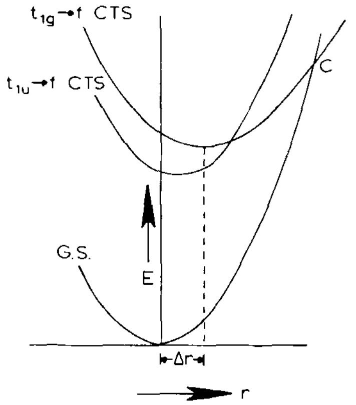

FIG. 5. A schematic configurational-coordinate diagram of the octahedral UO_6^{6-} group. Drawn parabolas refer to some relevant levels, viz., the ground state (G.S.) and two excited states ($t_{1g} \to f$ CTS and $t_{1u} \to f$ CTS).

observed for the emission from the uranate centers in the compounds Ba_2BWO_6–U (B = Mg, Ca, Sr, Ba).

The cations in the A position influence the quenching temperature less markedly. This agrees with the fact that the expansion of the UO_6^{6-} octahedron is more restricted by the ions in the [100] direction than by those in the [111] direction.

A regular influence of the surroundings on the luminescence quenching temperature has not yet been reported in such detail. This is due to the aforementioned advantages, which are offered by the crystal structure of the host lattice. Kröger has reported the temperature quenching of the luminescence of tungstates with scheelite structure (*13*). We give these quenching temperatures together with our results in Fig. 6 as a function of the ionic radius of the B cation. Note that the ionic radii for eight- and six-coordination have been used for the scheelites and the perovskite host lattices, respectively. Obviously, the quenching temperature of the tungstate emission of scheelites is more sensitive to the surroundings than the uranate emission in perovskites.

As mentioned previously, the emission of the octahedral uranate group shows vibrational fine structure at lower temperatures (*1*). Under identical experimental circumstances, the pattern is not always equally well resolved. The lines are equally well resolved in the emission of the magnesium-containing compounds, but they are less sharp in those of the other compounds. The fine structure is fading away for the compounds with lower quenching temperatures. This may be correlated with the expectation that vibrational fine structure will be less resolvable, the larger the value of Δr (*14*). An additional feature of the vibrational fine structure, viz., a repetition of the one-phonon part as an extra coupling with the $\nu_1(A_{1g})$ vibrational mode suggests that Δr is greater in the [100] direction (*15*). This corresponds to the observed dependence of the quenching temperature.

Let us now compare the quenching temperature of the emission from the uranate centers in Ba_2ZnWO_6 and Ba_2CdWO_6 with those in Ba_2MgWO_6 and Ba_2CaWO_6, respectively. The ionic radii of Zn^{2+} (0.75 Å) and

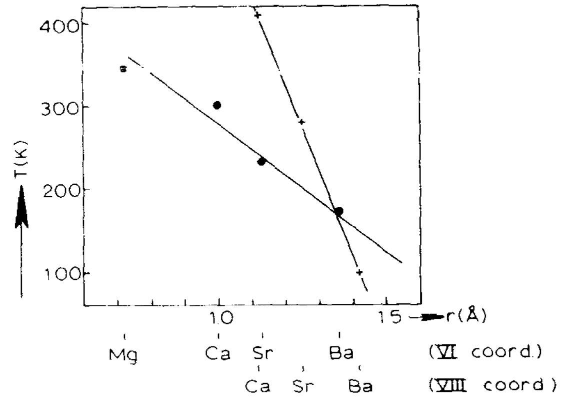

FIG. 6. Quenching temperatures of the tungstate emission of compounds AWO_4 (A = Ca, Sr, Ba) (*13*) and of the uranate emission of compounds $Ba_2BW_{0.997}U_{0.003}O_6$ (B = Mg, Ca, Sr, Ba) (this work) as a function of the radii of the ions A and B, respectively. Ionic radii for eight- and six-coordination have been used (*12*).

Mg^{2+} (0.72 Å) and those of Cd^{2+} (0.95 Å) and Ca^{2+} (1.00 Å) are comparable (*12*). In view of this, the differences between the quenching temperatures cannot be explained by the values of the ionic radii of the B cations. These are illustrative examples that the quenching temperature is not only influenced by the ionic radius of the surrounding ions, but also by the polarizability of these ions. This is larger for the Zn^{2+} and Cd^{2+} ions with a d^{10} configuration than for the Mg^{2+} and Ca^{2+} ions, respectively. A highly polarizable surroundings will not resist the expansion of the uranate group effectively.

This description of the influence of the surroundings on the quenching temperature cannot be complete. In particular, $T_{1/2}$ for Ba_2ZnWO_6–U is too low. Up to now we have assumed that the quenching temperature is influenced only by Δr and that the energy differences between the ground and excited states remain constant. From the experiments, however, we find that the emission and the excitation band in the long wavelength uv region lie at lower energies if the host lattice contains a cation with d^{10} configuration so that probably the $t_{1g} \rightarrow f$ CTS will be closer to the ground state. The crossover C will also be influenced. This may be the reason that the quenching temperature of the luminescence of the uranate center in Ba_2ZnWO_6 is relatively low.

The quenching curves of the emission of uranium-activated tellurates have a very long quenching range (see Fig. 4). This emission, however, is still observed at much higher temperatures than the quenching temperature of the corresponding uranium-activated tungstates. Summarizing the results concerning the spectra of the uranium-activated tellurates it can be remarked that the emission and excitation bands have been observed in the same spectral regions as for the corresponding uranium-activated tungstates. The bands observed in the spectra of the former compounds, however, are shifted somewhat to shorter wavelengths (see Table I). This difference may possibly contribute to the fact that the emission of the uranate center in the tellurates is still observed at much higher temperatures than the quenching temperature of the corresponding uranium-activated tungstates.

The host lattice absorption of the tellurates A_2BTeO_6 could not be well established. The absorption spectra show a long tail to the visible, which is probably due to the presence of defects. The extended portion of the emission intensity vs temperature curve suggests nonequivalent sites for the activator. For these reasons we have not used the tellurate host lattices as model compounds.

The quenching temperature of the emission of the uranate center in Ba_2CaMoO_6 is lower than expected from the value obtained for uranate in Ba_2CaWO_6. The ionic radii of Mo^{6+} and W^{6+} are equal (*12*). So, this does not explain the difference between the quenching temperatures. The absorption edges of Ba_2CaMoO_6 and Ba_2CaWO_6, however, are rather different. The absorption edge of Ba_2CaMoO_6 is shifted to considerably longer wavelength, so that the molybdate absorption overlaps the uranate absorption in the long wavelength uv region. Energy transfer from the host lattice to the uranate group is very improbable, since the host lattice shows only a very weak luminesence, situated in the red (*16*). In conclusion the greater part of the absorbed radiation will be lost by radiationless processes in the molybdate groups. Since the uranate group absorbs in a region where the host lattice absorption at RT is very high, the value of $T_{1/2}$ cannot be interpreted in terms of radiationless decay in the uranate group.

3b. $A^{2+}LaB^{+}B^{6+}O_6$ *Host Lattices*

In this type of host lattices the La^{3+} and A^{2+} cations (A = Sr or Ba) are distributed in a disordered way among the lattice sites with 12-coordination (*17*). Due to this disorder we may expect the presence of several, slightly different uranate centers. This is reflected in our observations. The decay curve of the emission must be described by more than one exponential. The decay time will be shorter if the deviation from inversion symmetry is larger. This has been pointed out elsewhere (*18*).

In the region where the host lattice tungstate absorption is strong, no clear excitation band is observed (Fig. 2). So, the energy transfer from tungstate to uranate groups is not as efficient as in some A_2BWO_6–U compounds. Accordingly, at lower temperatures the emission spectra of $ALaBWO_6$–U all show intense tungstate emission under short wavelength uv excitation. Moreover, the uranate emission does not show a pronounced fine structure. This may be due to the presence of several, different uranate centers. The emission of these compounds is shifted to longer wavelengths compared to that of the compounds A_2BWO_6–U (see Fig. 1 and Table I).

The quenching temperature of the emission depends on the host lattice in the same way as mentioned previously (Fig. 4 and Table I). The emission is quenched at higher temperatures if the B cation is smaller, i.e., the emission from the uranate center in the lithium-containing compounds quenches at higher temperatures than in the sodium-containing compounds. Note that the influence of the A cation is more pronounced than in the case of the $A_2BB'O_6$ host lattices. But again a smaller cation results in a higher quenching temperature.

The compounds $SrLaNaWO_6$ and $SrLaNaTeO_6$ have not been reported in the literature before. Both have an orthorhombically distorted, ordered perovskite structure. From X-ray powder patterns we found the following lattice constants: For $SrLaNaWO_6$, $a = 5.90$ Å, $b = 5.67$ Å, $c = 8.08$ Å, and for $SrLaNaTeO_6$, $a = 5.85$ Å, $b = 5.70$ Å, $c = 8.12$ Å. At RT the emission from the uranate centers in these host lattices is shifted to the short wavelength side (Table I). At lower temperatures the emission of $SrLaNaW_{0.997}U_{0.003}O_6$ shows a considerably more pronounced fine structure (see Fig. 7) than the emission of the uranate centers in the other $ALaBB'O_6$ host lattices. This is not in accordance with the quenching temperatures, a relation we mentioned in 3a. At LHeT this emission has a vibrational pattern which differs completely from the vibrational patterns observed in the other ordered perovskites. This pattern (Fig. 7) shows a striking similarity with that of the uranyl emission as described by Hoffman for uranium in $SrZnP_2O_7$ (*19*). At LHeT the emission of

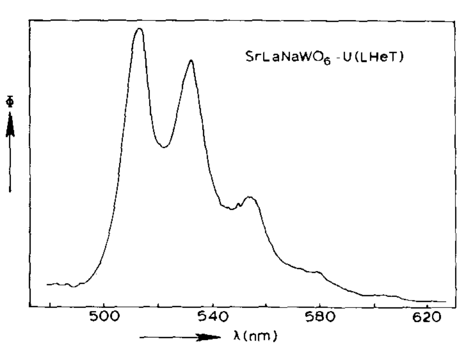

FIG. 7. Emission spectrum of $SrLaNaW_{0.997}U_{0.003}O_6$ at LHeT under mainly 366 nm excitation. Φ denotes the spectral radiant power in arbitrary units.

$SrLaNaTe_{0.997}U_{0.003}O_6$, however, does not show a clear vibrational fine structure. The nature of the emitting center in the tellurate is unknown; in the tungstate it is probably a uranyl center. It is not clear why this center occurs in this specific host lattice.

3c. Ba_2ZnTeO_6

In contrast with the $A_2BB'O_6$ host lattices which have the cubic perovskite structure, as mentioned previously, this compound has a hexagonal perovskite-like structure (*8*). Two rather different types of TeO_6 octahedra are present:

(1) The first type of TeO_6 octahedra is surrounded by six ZnO_6 octahedra, the TeO_6 and ZnO_6 octahedra being linked by corners and the Zn–O–Te bonds being collinear. This situation corresponds to that in the cubic perovskites.

(2) The second type of TeO_6 octahedra shares faces with two ZnO_6 octahedra in a linear row with sequence Zn–Te–Zn. A large trigonal field will be present at the center of these TeO_6 octahedra.

This host lattice offers, therefore, a possibility for the uranium ion to occupy two different crystallographic sites.

The decay time measurements, however, reveal only one decay time. Its temperature dependence is the same as described in (*18*), corresponding to the presence of inversion symmetry at the uranium site. The value of the decay time at LHeT is 300 μsec. This agrees with the fact that both Te-sites have inversion symmetry. The emission spectrum (Fig. 8) does not depend on the excitation wavelength at all. The difference between the emission spectra of Ba_2ZnWO_6–U and Ba_2ZnTeO_6–U is not very large. Probably a trigonal field would induce a larger difference. The quenching temperature of Ba_2ZnTeO_6–U is higher than that observed for Ba_2ZnWO_6–U, in accordance with arguments given above. Since the luminesence properties of Ba_2ZnTeO_6–U correspond well with those of Ba_2ZnWO_6–U and the compound Ba_2ZnUO_6 has the cubic perovskite structure (*3*), and not the hexagonal structure of Ba_2ZnTeO_6 we presume that the uranium ion occupies preferably those octahedra which share corners with neighboring ZnO_6 octahedra. This is in accordance with rules given before (*9*).

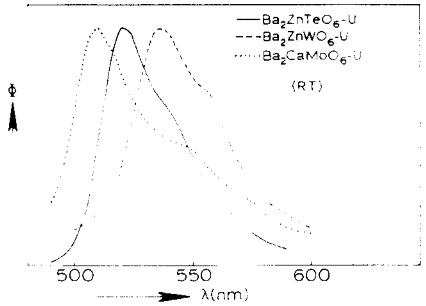

FIG. 8. Emission spectra of Ba_2ZnTeO_6–U, Ba_2ZnWO_6–U, and Ba_2CaMoO_6–U at room temperature under mainly 366 nm excitation. All compounds contain 0.3 mole% uranium. Φ denotes the spectral radiant power in arbitrary units.

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