Luminescence of Tungsten-Activated Tellurates

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The luminescence of a number of W^{6+}-activated tellurates (Ca_3TeO_6, Mg_3TeO_6, Ln_2TeO_6 and In_2TeO_6) reported and ascribed to transitions within isolated WO_6 octahedra. The quenching temperature of the lun nescence is related to the position of the maximum of the excitation (absorption) band of the tungstate grou The Mo^{6+} ion also shows luminescence in these tellurates.

1. Introduction

The luminescence of tungstates has been described extensively by Kröger (*1*). His assumption that this luminescence is due to characteristic transitions within the tungstate group is nowadays generally accepted. After Kröger's work further support for this view was given by Kotera et al. (*2*) who described the luminescence properties of $CaSO_4$–W. The luminescence of the isolated WO_4 group in $CaSO_4$ resembles that of the WO_4 group in $CaWO_4$ very closely. This is even true for such a sensitive property as the temperature dependence of the luminescence (*3*).

If sulphates are used as a host lattice for the W^{6+} ion, it is only possible to obtain the tetrahedral WO_4 group (sulphates contain always and only SO_4 groups). Some of the luminescent tungstates, however, contain octahedral WO_6 groups (for example $MgWO_4$). It seemed interesting therefore to try to obtain isolated WO_6 groups. An obvious possibility is to use tellurates as host lattices, since the Te^{6+} ion is always found in octahedral coordination.

Such an approach is analogous to Kröger's work on Ti^{4+}-activated stannates (*1*) and our own work on Nb^{5+}-activated antimonates (*4*). For these materials we found a relation between the quenching temperature of the luminescence and the position of the excitation band of the activator group which could be explained semiquantitatively using a simple configuration-coordinate model (*4*).

From that work W^{6+}-activated tellurates are expected to luminescence and to give a relatic similar to that described for the NbO_6 group. Th paper reports on the results of a study to verify th expectation.

2. Experimental

Samples of W^{6+}-activated tellurates were prepare by usual techniques as described, for example, t Natansohn (*5*). Firing was carried out in O Samples were checked by X-ray analysis (CuK radiation). The performance of the optical measur ments and the measurements of the temperatu dependence of the luminescence has been describe previously (*6*, *7*).

3. Results

The following tellurates were activated by tungste (5% W instead of Te): Ln_2TeO_6 (Ln = La, Gd, ` Lu), In_2TeO_6, Ca_3TeO_6, Mg_3TeO_6 and Y_6TeO_1 The lanthanide tellurates Ln_2TeO_6 and In_2TeC have been described by Natansohn (*5*), Mg_3TeC by Kasper (*8*) and Bayer (*8*) and Y_6TeO_{12} by ou selves (*9*). According to our X-ray diagram tl compound Ca_3TeO_6 is isomorphous with Ca_3WC (ordered, distorted perovskite structure). Tl lattice parameters are $a = 5.55$ Å, $b = 5.77$ Å, ar $c = 7.98$ Å. The structure of Lu_2TeO_6 was recent described by Malone et al. (*10*). The host lattic Ca_3TeO_6 and Y_2TeO_6 were also activated t molybdenum.
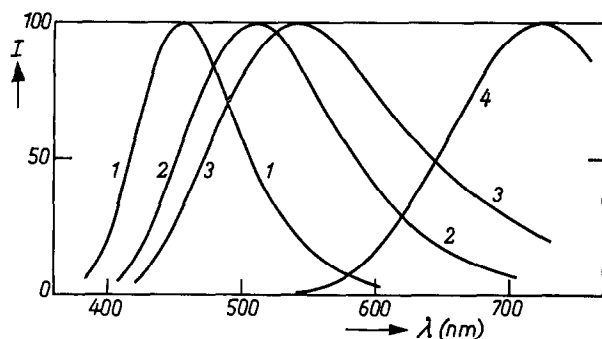
FIG. 1. Spectral energy distribution of the emission at 77°K under 254 nm excitation of 1. Lu_2TeO_6–W; 2. Y_2TeO_6–W; 3. Ca_3TeO_6–Mo; 4. Y_2TeO_6–Mo. I gives the radiant power per constant wavelength interval in arbitrary units.

FIG. 2. Diffuse reflection spectra of Lu_2TeO_6 (broken line) and Lu_2TeO_6–W (drawn line) and relative excitation spectrum of the emission of Lu_2TeO_6–W.

Except for Y_6TeO_{12}–W these compositions luminesce at liquid nitrogen temperatures with medium to high efficiencies for 254 nm excitation. At room temperature the luminescence is usually weaker or even absent. Some of the emission spectra are given in Fig. 1. Table I gives a survey of the luminescence properties measured. Figure 2 shows diffuse reflection spectra of Lu_2TeO_6 and Lu_2TeO_6–W and the excitation spectrum of the luminescence of Lu_2TeO_6–W. Those for the other composition are similar. The excitation spectra consist of two bands. The one at shorter wavelengths corresponds to the absorption edge of the unactivated, nonfluorescent tellurate, whereas the band at longer wavelengths corresponds to excitation into the tungstate group itself. This resembles our results for the Nb^{5+}-activated antimonates (4).
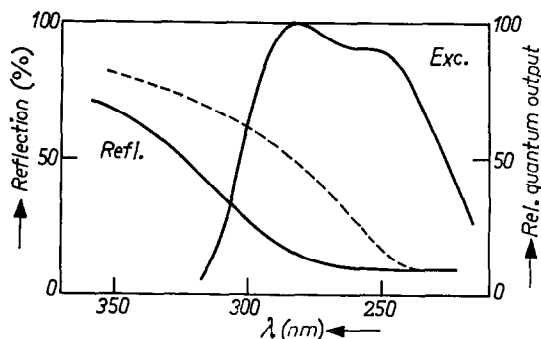
Double activation of Y_2TeO_6 with Bi (on Y sites) and W (on Te sites) gives a material with yellow-green emission under 365 nm excitation and greenish emission under 254 nm excitation. The composition Y_2TeO_6–Bi did not luminesce.

4. Discussion

The first thing to conclude is that the W^{6+} ion as an isolated WO_6 group in the tellurates does indeed fluoresce. In general the luminescence properties of the W^{6+}-activated tellurates resemble those of the tungstates closely. Unfortunately only one of the tellurates, viz., Ca_3TeO_6, is isomorphous with the analogous tungsten compound (Ca_3WO_6). There is hardly any difference between the luminescence properties of Ca_3TeO_6–W described here and those of Ca_3WO_6 described by Kröger (1). This is, how-

TABLE I

SOME LUMINESCENCE PROPERTIES OF W^{6+}-ACTIVATED TELLURATES (TUNGSTEN CONCENTRATION 5%)

Composition	Radiant Efficiency (%) for c.r. Excitation (20 kV)	Maximum Quantum Efficiency (%) in Ultraviolet Region	Position Maximum Emission Band (nm)	Position WO_6 Excitation Band (10^3 cm^{-1})	Quenching Temperature[a] (°K)
Mg_3TeO_6–W	0.5	15	460 (300°K)	38.0	475
Ca_3TeO_6–W	1.5	~ 5	420 (300°K)	34.0	300
La_2TeO_6–W	—	~2	515 (77°K)	34.0	300
Gd_2TeO_6–W	0.5	20	475 (300°K)	34.5	375
Y_2TeO_6–W	0.5	20	480 (300°K)	35.0	400
Lu_2TeO_6–W	0.2	20	450 (300°K)	35.7	425
In_2TeO_6–W	—	—	580 (77°K)	—	~100

[a] According to the definition given by Kröger (1).

ever, not too impressive, because the tungstate groups in Ca_3WO_6 are already far apart (~ 5.5 Å) and do not have oxygen ions in common.

As is to be expected from Kröger's work (1) the MoO_6 octahedron also luminesces in the tellurates, but the luminescence has a considerably lower quenching temperature than that of the tungstate group.

Recently, we have discussed the modifying action of ions with ns^2 configuration on the emission of the tungstate group (11). This can also be found in the tellurates: Y_2TeO_6–W fluoresces blue-green, but Y_2TeO_6–W, Bi fluoresces yellow-green under 365 nm excitation (Bi^{3+}-tungstate centres only) and greenish under 254 nm excitation. This greenish emission consists of two emission bands: the yellow-green band of the Bi^{3+}-tungstate centre and the blue-green band of the isolated tungstate centre. Cations with d^{10} configuration show a similar effect. This is illustrated by the emission of In_2TeO_6–W which shows a shift to considerably longer wavelengths compared with the emission of the isomorphous Lu_2TeO_6–W.

In Fig. 3 we have plotted the quenching temperature of the tungstate luminescence [determined according to Kröger (1)] versus the frequency of the excitation band that corresponds to direct excitation of the tungstate centre. We have also included data on $MgWO_4$ [after Ref. (12)] and unpublished data on Sr_3WO_6 and Gd_2WO_6. The relation obtained in this way is analogous to that which we described earlier for niobates (4), viz. about linear down to a certain frequency of the excitation band. For compositions with excitation bands at lower
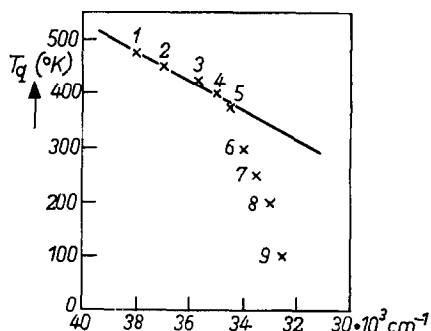
frequencies there is a sharp drop of T_q, so that at still lower-frequency absorption bands no luminescence is expected. From Fig. 3 we may predict that octahedral tungstate centres with absorption bands situated at frequencies corresponding to a value lower than about 32,500 cm^{-1} do not luminesce (for the niobates this value was 34,000 cm^{-1}). This is indeed the case: Y_6WO_{12} (32,500 cm^{-1}) luminesces only weakly at 77°K; $Ba_3Gd_2WO_9$ (31,000 cm^{-1}) does not luminesce; WO_3 (25,000 cm^{-1}) does not luminesce (13).

The slope of the linear part of the relation amounts to about 25°K per 1000 cm^{-1}. It is noteworthy that within the experimental error this value is equal to that found for the niobates.

In Ref. 4 we have shown that it is possible to account for a relation such as in Fig. 3 using a simple configuration–coordinate diagram. For the linear part of the relation the normal Seitz–Mott model is valid and high quantum efficiencies are expected for $T \rightarrow 0°K$ (Fig. 4a). For excitation bands located below about 34,500 cm^{-1} (i.e., where the deviation from linearity occurs) the Dexter, Klick, and Russell model is valid. In this model nonradiative losses are possible for $T \rightarrow 0°K$, so that low quantum efficiencies may be expected (Fig. 4b). For the niobates this was found to be the case. Unfortunately, the interpretation of the quantum efficiencies of the W^{6+}-activated tungstates is complicated, since a considerable amount of the exciting radiation (250–270 nm) is absorbed by the host lattice and not by the tungstate groups (see Fig. 2). The quantum efficiencies given in Table I were determined assuming that all quanta are absorbed by or transferred to the tungstate centres. Since this is probably not the case, the values given in Table I are lower limits for the quantum efficiency. Moreover, all samples mentioned in Table I are in
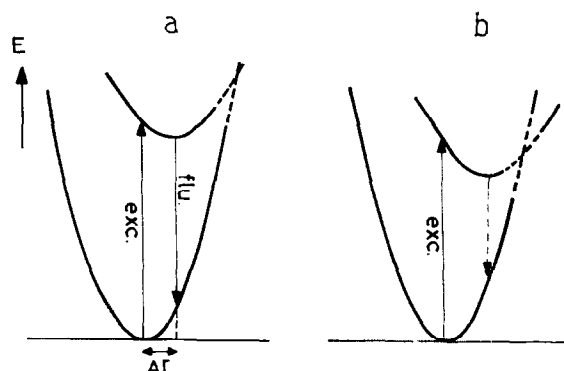

FIG. 3. Quenching temperature T_q of some tungstates and W^{6+}-activated tellurates (all with WO_6 octahedra) versus the position of the maximum of the excitation band of the WO_6 group.

1. Mg_3TeO_6–W;   2. $MgWO_4$;   3. Lu_2TeO_6–W;
4. Y_2TeO_6–W;   5. Gd_2TeO_6–W;   6. La_2TeO_6–W and Ca_3TeO_6–W;   7. Sr_3WO_6;   8. Gd_2WO_6;   9. In_2TeO_6–W.

FIG. 4. Configuration coordinate diagrams—a gives the Seitz–Mott model and b the Dexter–Klick–Russell model.

the quenching region at room temperature. The quantum efficiencies of the samples with T_q above 300°K are, for $T \to 0$°K, probably three to four times higher than those given in Table I. Therefore, the samples that obey the linear part of the relation of the relation probably have high quantum efficiencies for $T \to 0$°K. From the present data it is difficult to give a reliable estimate of the low-temperature efficiency of the other samples. Nevertheless it can be said that the results for the WO_6 octahedron are similar to those for the NbO_6 octahedron.

From the foregoing it follows that nonradiative losses from an excited charge-transfer state are probable if this state lies at relatively low energies (Fig. 4b). This corroborates our earlier model for the low efficiency of the Eu^{3+} luminescence of those Eu^{3+}-activated oxides that have the Eu^{3+}-charge-transfer band at relatively low energies. It was assumed that the nonradiative energy losses occur by transitions from the charge-transfer state to the ground state (and not via excited 4f-levels) (14). For the oxysulphides a similar mechanism has been proposed (15).

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