

Energy Transfer in Mercury-Doped Calcium Tungstate and Molybdate

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The luminescence of $\text{CaWO}_4\text{-Hg}$ and $\text{CaMoO}_4\text{-Hg}$ is reported. The presence of Hg^{2+} ions in the CaWO_4 lattice influences the luminescence of pure CaWO_4 drastically due to efficient energy transfer from host lattice groups to the emitting centre consisting of a tungstate group with a neighbouring mercuric ion. The luminescence characteristics of $\text{CaMoO}_4\text{-Hg}$ do not differ strongly from those of pure CaMoO_4 due to the absence of efficient energy transfer.

1. Introduction

The luminescence of calcium molybdate, CaMoO_4 , and calcium tungstate, CaWO_4 , is well known and has been studied by many investigators. It has also been found that the addition of small amounts of certain impurities may influence the luminescence properties strongly (1-3). The replacement of calcium by lead has become the most well-known example of this phenomenon and has found technical application. Recently we reported on the luminescence of mercuric molybdate, HgMoO_4 , and tungstate, HgWO_4 , and showed that strong analogies exist between the luminescence of the calcium and the mercuric compounds in spite of their structural difference (4). It seemed therefore, interesting to study the substitution of calcium by mercury in CaMoO_4 and CaWO_4 and its influence on their luminescence properties. It was found that these systems present probably the most easily understandable examples of "modified" calcium molybdate and tungstate luminescence.

2. Experimental

Samples of composition $\text{Ca}_{1-x}\text{Hg}_x\text{MoO}_4$ and $\text{Ca}_{1-x}\text{Hg}_x\text{WO}_4$ ($x \leq 0.03$) were prepared by firing intimate mixtures of CaMoO_4 ,

HgMoO_4 , CaWO_4 , and HgWO_4 at 550°C . The mercuric compounds were prepared as described previously (4), the calcium compounds by precipitation from aqueous solutions of Na_2MoO_4 and Na_2WO_4 . Samples were checked by X-ray analysis and appeared to be pure scheelites. We further prepared HgSO_4 (firing the metal oxide with $(\text{NH}_4)_2\text{SO}_4$) and $\text{HgW}_{0.97}\text{Mo}_{0.03}\text{O}_4$ (in the same way as HgWO_4).

The luminescence measurements were performed on a Perkin-Elmer (Hitachi) MPF-2A fluorescence spectrophotometer. These spectra were corrected for spectrophotometer transparency and for photomultiplier response. The cryostat was an Oxford CF 100.

3. Results

Table I gives a qualitative survey of the luminescence response of some of our samples upon short- and long-wavelength ultraviolet excitation at 77 and 300 K. The blue luminescence of CaWO_4 shifts to longer wavelength upon introduction of mercury. This can also be found from Figs. 1 and 2, where the excitation and emission spectra of this luminescence are given. The excitation spectra at 300 K show two excitation bands: one at about 245 nm

TABLE I
LUMINESCENCE CHARACTERISTICS OF SOME OF THE SAMPLES STUDIED^a

Composition	Emission colour and intensity			
	254 nm excitation		365 nm excitation	
	300 K	77 K	300 K	77 K
CaWO ₄	Blue (s)	Blue (s)	—	—
Ca _{0.9} Hg _{0.03} WO ₄	Blue (m)	Blue-green (s)	—	—
Ca _{0.97} Hg _{0.03} WO ₄	Blue (vw)	Blue-green (s)	—	—
CaMoO ₄	Yellow (m)	Yellow (s)	—	—
Ca _{0.97} Hg _{0.03} MoO ₄	Yellow (w)	Yellow (s)	—	Orange (m)
HgSO ₄	—	—	—	Yellow (vw)
HgW _{0.97} Mo _{0.03} O ₄	Yellow-green (m)	Near-White (m)	Orange (vw)	Orange (m)

^a s: strong, m: medium, w: weak, vw: very weak.

coinciding with the excitation band of pure CaWO₄ and another one at about 310 nm, which is not present in the case of pure CaWO₄. The latter band must be due to excitation into a centre in which the mercury ion participates. At lower temperatures this band shows a pronounced shift to shorter wavelengths (about 270 nm). Excitation into the "mercury-induced" excitation band gives rise to luminescence into a broad emission band with a maximum at about 500 nm. This emission is not present in pure CaWO₄. Excitation into the CaWO₄ excitation band results in a complicated luminescence band

consisting of the just-mentioned 500-nm band and the emission band of pure CaWO₄ (maximum at about 410 nm, Refs. (1, 3)). At 5 K the 500 nm band is much stronger, at 300 K the pure-CaWO₄ band is the stronger one (see Fig. 1). Our figures relate to samples with 3% mercury. For lower mercury concentrations the same phenomena are observed, but the intensity of the new bands is weaker.

The influence of the mercuric ion on the luminescence of CaMoO₄ is less pronounced. Figure 3 shows the excitation and emission spectra. The excitation spectrum of the emission of CaMoO₄ is also shown (Fig. 3, curve

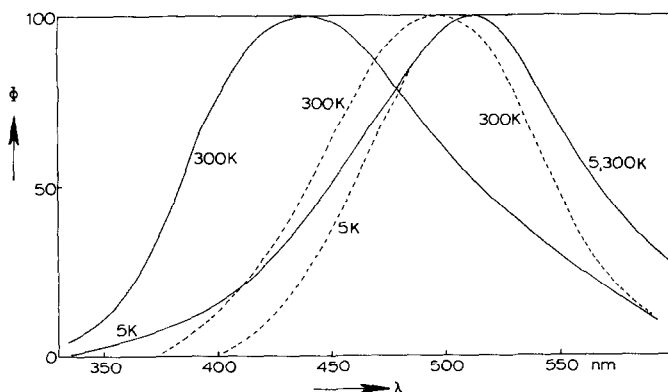


FIG. 1. Spectral energy distribution of the emission of Ca_{0.97}Hg_{0.03}WO₄ under several conditions. Φ gives the radiant power per constant wavelength interval in arbitrary units. — 250 nm excitation; - - - 310 nm excitation.

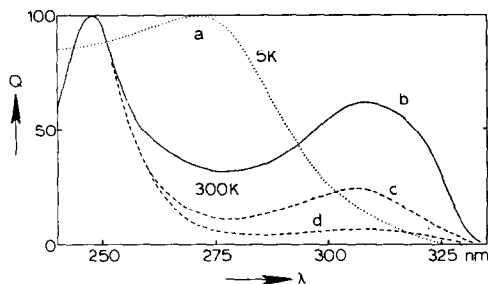


FIG. 2. Excitation spectra of the emission of $\text{Ca}_{0.97}\text{Hg}_{0.03}\text{WO}_4$. Q gives the relative quantum output. Curve (a): 5 K, 420 nm emission (490 nm emission gives an identical curve); curve (b): 300 K, 490 nm emission; curve (c): 300 K, 440 nm emission; curve (d): 300 K, 400 nm emission.

(a). Introduction of mercury yields only intensity variations; new excitation bands do not occur. The emission bands are practically equal to that of pure CaMoO_4 except for excitation into the long-wavelength tail of the excitation band at 5 K. Under these conditions an orange emission is observed.

To find out whether the Hg^{2+} ions would luminesce in crystals without W^{6+} or Mo^{6+} ions we studied HgSO_4 , but no luminescence of reasonable intensity was observed. The weak emission of HgSO_4 may be due to extrinsic defects as has been suggested for other mercuric salts (5). We may therefore conclude that the tungstate and molybdate group are an essential part of the luminescent centre involved.

Finally, $\text{HgWO}_4\text{-Mo}$ behaves more or less

as a mixture of the constituting compounds. Excitation with radiation of wavelengths corresponding to the optical band edge of HgWO_4 results in mainly HgWO_4 emission (as reported in Ref. (4)), whereas excitation with wavelengths corresponding to the edge of HgMoO_4 results in HgMoO_4 emission. This differs typically from molybdenum-doped CaWO_4 where excitation into the tungstate groups results in mainly molybdate emission (1).

4. Discussion

(a) $\text{CaWO}_4\text{-Hg}$.

The luminescent properties of $\text{CaWO}_4\text{-Hg}$ can be explained by assuming two different centres, viz the "undisturbed" tungstate group with an excitation band at about 245 nm and an emission band at about 410 nm and tungstate groups with one or more Hg^{2+} ions as nearest neighbours. Their excitation band peaks at about 310 nm and the corresponding emission band at about 500 nm (all values at room temperature). The position of the bands belonging to the tungstate group with mercury is near to the position of the corresponding bands in HgWO_4 (300 and 510 nm, respectively). This analogy is, of course, not unexpected. At the same time it should be noted that their temperature dependence is different (see Table II) indicating that our samples $\text{CaWO}_4\text{-Hg}$ cannot be considered as a mixture of CaWO_4 and HgWO_4 , but that they are solid solutions.

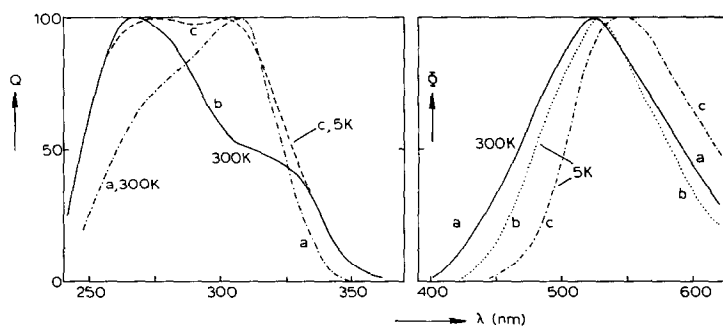


FIG. 3. Excitation (left-hand side) and emission (right-hand side) spectra of $\text{Ca}_{0.97}\text{Hg}_{0.03}\text{MoO}_4$. Q and ϕ as in Figs. 1 and 2. Excitation spectra, curve (a): pure CaMoO_4 , 300 K, 500 nm emission; curve (b) $\text{CaMoO}_4\text{-Hg}$, 300 K, 460 (and also 510) nm emission; curve (c): 5 K, 500 nm emission. Emission spectra, curve (a): 300 K, 290 (and also 340) nm excitation; curve (b): 5 K 250 (and also 280) nm excitation; curve (c): 5 K, 340 nm excitation.

TABLE II

POSITION OF THE EMISSION AND EXCITATION BAND MAXIMA (IN nm) FOR HgWO_4 AND $\text{Ca}_{0.97}\text{Hg}_{0.03}\text{WO}_4$

	5 K	300 K	Remarks
Emission HgWO_4	500	510	300 nm excitation
Emission $\text{CaWO}_4\text{-Hg}$	515	500	300 nm excitation
Excitation HgWO_4	290	300	500 nm emission
Excitation $\text{CaWO}_4\text{-Hg}$	270	310	500 nm emission

The spectral data (Figs. 1 and 2) reveal efficient energy transfer from the undisturbed tungstate centre to the tungstate centre with mercury. Note for example, that excitation into the undisturbed tungstate centre at 5 K results in mainly mercury-tungstate emission (Fig. 1) with less than 10% of undisturbed tungstate emission. At room temperature the mercury-tungstate emission is for the greater part thermally quenched so that at 300 K the emission consists for the greater part of undisturbed tungstate emission, but its intensity is very weak (see Table II).

Conditions for energy transfer in systems of this type have been considered previously by us (6, 7). An important condition is that the emission band of the initial centre should overlap the absorption band of the final centre. In our case the undisturbed tungstate emission band should overlap the absorption (excitation) band of the mercury-tungstate centre. In fact the former extends down to about 325 nm and the latter up to about 335 nm. This overlap is considerably larger than in the case of pure CaWO_4 where transfer is restricted to, on the average, one $\text{WO}_4\text{-WO}_4$ step (8). The influence of small amounts of Hg^{2+} ions on the luminescence of CaWO_4 can therefore be ascribed to two, simultaneously occurring phenomena, viz energy transfer from undisturbed tungstate centres to mercury-tungstate centres, and the strong influence of the Hg^{2+} ion with d^{10} configuration on the electronic transitions within the tungstate group. In a rough approximation this model may be also valid for other impurities in CaWO_4 . Here it turns up very clearly, because the influence of the Hg^{2+} ions upon the electronic transitions of the tungstate group is very

strong. In the case of Pb^{2+} , however, more than two different emission bands are present (1), which does not follow from our model.

Some other properties of the mercury-tungstate centre in CaWO_4 are noteworthy. In the first place the position of the excitation band is strongly temperature dependent. It is not excluded that at low temperatures the Hg^{2+} ion tends to obtain its characteristic linear two-coordination as observed in HgWO_4 (9). A change of coordination number will result in a change of the position of the absorption bands. Furthermore, the quenching temperature of the emission of the mercury-tungstate centre in CaWO_4 (about room temperature) is considerably lower than in HgWO_4 (about 400 K (4)), which can be considered as a certain type of reversed concentration quenching. This fact, however, is not unexpected. The high quenching temperature of the luminescence of HgWO_4 was ascribed by us to a structural peculiarity of the HgWO_4 structure, viz the short strong Hg-O bonds pointing to the tungstate group cause a relatively stiff surrounding around the tungstate group resulting in a high quenching temperature (4). For $\text{CaWO}_4\text{-Hg}$ this argument does not hold. Since the Hg^{2+} ion with d^{10} configuration is more polarizable than the Ca^{2+} ion with noble-gas configuration, we expect a lower quenching temperature for the mercury-tungstate emission than for the undisturbed tungstate emission (10).

We will now show that the situation described above for $\text{CaWO}_4\text{-Hg}$ does not occur for $\text{CaMoO}_4\text{-Hg}$.

(b) $\text{CaMoO}_4\text{-Hg}$.

The luminescence of $\text{CaMoO}_4\text{-Hg}$ can also be described with two different centres, viz an undisturbed molybdate centre and a mercury-molybdate centre. Their excitation and emission bands are very near to each other. In fact the yellow emission of the undisturbed molybdate group, as observed in pure CaMoO_4 (1), dominates in all our emission spectra except if excitation takes place in the long-wavelength tail of the excitation spectrum at low temperature (see Fig. 3). Under these conditions an orange lumines-

scence results with an emission band peaking at longer wavelength than that of the undisturbed molybdate group (550 and 525 nm, respectively). It is impossible to separate these two emission bands completely; the excitation bands are even closer together.

Nevertheless, it is possible to draw the following conclusions from these observations.

- a. In this case we are dealing with a mixed crystal $(\text{Ca,Hg})\text{MoO}_4$ and not with a mixture of CaMoO_4 and HgMoO_4 . The latter compound shows an emission band peaking at 600 nm at 5 K (4).
- b. The quenching temperature of the emission of the mercury-molybdate centre is lower than the quenching temperatures of the emission of CaMoO_4 and HgMoO_4 (4). This is analogous to the situation in the tungstate system (see above).
- c. There is no energy transfer from the undisturbed molybdate centre to the mercury-molybdate centre in contradiction to the situation in the tungstate system. This follows from the fact that excitation at low temperatures into the undisturbed molybdate group (i.e., excitation with about 300 nm radiation) results in emission consisting of mainly undisturbed molybdate emission. In the case of the tungstate system the emission under these circumstances consists of mainly mercury-tungstate emission.

The efficiency of the energy transfer in the molybdate system must be due to the lack of spectral overlap of the emission band of the undisturbed molybdate centre (extending down to about 400 nm) and the excitation band of the mercury-molybdate centre (extending up to about 360 nm).

From this we may conclude that energy transfer in systems like these under consideration occurs only, if the influence of the "modifying" ions on the electronic transitions in the tungstate or molybdate group is drastic. The Hg^{2+} ion does not influence the spectral position of the electronic transitions in the molybdate group strongly, possibly due to

the fact that the electronic transitions within the Hg^{2+} ion are at considerably higher energy than those in the molybdate group.

The excitation spectra (Fig. 3) contain at least two subbands (at about 310 and 265 nm). It is impossible to discuss the intensity ratio of these two bands which varies with the mercury content, because we have no data on the absorption strengths. It is not excluded that the presence of Hg^{2+} ions influences this strength strongly due to spin-orbit coupling effects. Such phenomena cannot be observed in the tungstate samples due to the restricted spectral range of our apparatus. The presence of two bands is, however, not unexpected, especially in view of the work by Müller and co-workers (11). These authors observed in the absorption spectra of the MoO_4^{2-} group in aqueous solutions three absorption bands at 43.2 kK ($t_1 \rightarrow 2e$), 48.0 kK ($3t_2 \rightarrow 2e$) and ~ 55 kK ($t_1 \rightarrow 4t_2$). For the WO_4^{2-} group they give only the lowest transitions, viz at 50.3 kK ($t_1 \rightarrow 2e$). It seems not unreasonable to assume that the corresponding transitions in the solid are shifted to lower energy by about 10 kK. Then the two excitation bands of the molybdates can be assigned to the transition $t_1 \rightarrow 2e$ (310 nm, 32 kK) and $3t_2 \rightarrow 2e$ (265 nm, 38 kK) within the undisturbed molybdate group. The 245 nm excitation band of the tungstates corresponds to the $t_1 \rightarrow 2e$ transition.

Finally, we will show that the luminescence of tungstates containing small amounts of molybdate can be described similarly as that of the calcium compounds containing mercury.

(c) $\text{HgWO}_4\text{-Mo}$

From our results on samples $\text{HgWO}_4\text{-Mo}$ that were mentioned above it is clear that energy transfer from the tungstate to the molybdate group in $\text{HgWO}_4\text{-Mo}$ does not have a high efficiency. This is contradictory to the system $\text{CaWO}_4\text{-Mo}$ (1), where this transfer occurs with such an efficiency that the tungstate emission disappears at the cost of the molybdate emission. In the calcium system the tungstate emission overlaps the molybdate absorption as shown earlier (6). This occurs as a consequence of the difference in spectral

position of the tungstate and molybdate bands.

In the mercury system this difference is much smaller (4). At room temperature the emission band of the tungstate group extends down to about 420 nm, whereas the excitation band of the molybdate group extends up to about 390 nm which fact is prohibitive for efficient energy transfer in view of the results discussed above.

We conclude that energy transfer in systems like those under consideration can be reasonably understood, but note simultaneously that the mechanism of this transfer is unknown up till now as is the exact character of the electronic transitions in tungstate or molybdate groups surrounded by mercuric ions.

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