

Influence of Charge-Compensating Ions on the Luminescence of Vanadium-Activated Sulfates

G. BLASSE AND G. P. M. VAN DEN HEUVEL

Physical Laboratory, Sorbonnelaan 4, Utrecht, The Netherlands

Received May 23, 1975

Samples $\text{CaSO}_4\text{-V}^{5+}$, Me^{3+} show mainly unassociated-vanadate emission if Me^{3+} is smaller than the Ca^{2+} ion and mainly associated-vanadate emission if Me^{3+} is about as large as the Ca^{2+} ion. Samples $\text{MgSO}_4\text{-V}^{5+}$, Me^{3+} show efficient yellow emission at room temperature.

Introduction

Recently the presence of associates $\text{V}^{5+}\text{-Ln}^{3+}$ in CaSO_4 and the occurrence of energy transfer in these associates has been reported (1, 2). Vanadium occupies the tetrahedral sulfur site and is charge-compensated by a trivalent lanthanide ion on one of the nearest-neighbor calcium sites. In this paper, we describe the luminescence of $\text{CaSO}_4\text{-V}^{5+}$, Me^{3+} , where Me^{3+} stands for trivalent ions smaller than the lanthanides. In addition, efficient vanadate luminescence in MgSO_4 is reported.

Experimental

Samples were prepared and characterized as described before. Dope concentrations were 0.1 or 0.3 at%. Optical measurements were performed as in (1, 2).

Results and Discussion

(a) $\text{Ca}_{1-x}\text{Me}_x\text{S}_{1-x}\text{V}_x\text{O}_4$ ($\text{Me} = \text{Al, Sc, Fe, Ga}$)

The luminescence properties of these samples do not depend strongly on the nature of Me . Therefore, only the results for $\text{Me} = \text{Ga}$ are given. Below room temperature a greenish emission can be excited by uv excitation. Figure 1 shows some excitation and emission spectra at LHeT. These reveal a rather complex luminescence behavior due to over-

lapping excitation and emission bands; there seem to be at least two excitation bands, one at about 280 nm and the other at about 250 nm. Excitation into the latter yields an extra emission shoulder in the short-wavelength part of the spectrum (see Fig. 1). This shoulder was not detected for the Fe^{3+} -doped sample.

This behavior differs from that observed for $\text{CaSO}_4\text{-V}^{5+}$, Ln^{3+} ($\text{Ln} = \text{Y, La, Gd, Lu}$), where the emission band peaks at 465 nm and the excitation band peaks at 255 nm. The emission band of uncompensated $\text{CaSO}_4\text{-V}^{5+}$ has its maximum at 520 nm (1, 2). A simple explanation for these differences is the following. If the compensating trivalent cation is one of the lanthanides, we have associates $\text{V}^{5+}\text{-Ln}^{3+}$ as shown in (1, 2) with the 465 nm emission band; if the compensating cation is Al, Sc, Fe, or Ga, the degree of association is much lower. The V^{5+} ion occurs partly as a "free" (unassociated) V^{5+} ion with an emission band at 520 nm (and an excitation band at about 280 nm) and partly as an associate $\text{V}^{5+}\text{-Me}^{3+}$ with bluish emission (excitable with 250 nm radiation) as in the case of the $\text{V}^{5+}\text{-Ln}^{3+}$ associates.

A high degree of association in the case of these Me^{3+} ions is improbable, because an associate $\text{V}^{5+}\text{-Fe}^{3+}$ is not expected to luminesce. The "killing-action" of transition metal ions on emissions like those of the vanadate group is well known (3). This also

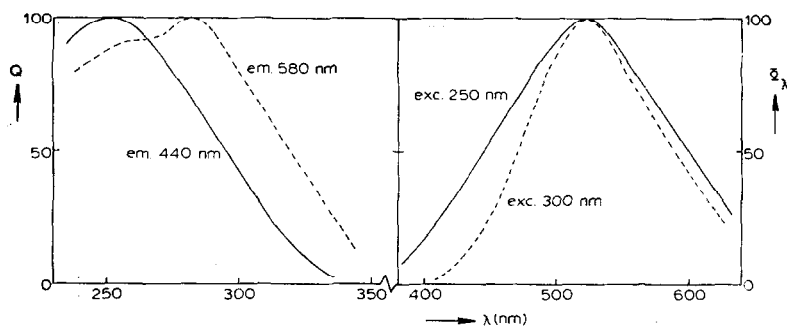


FIG. 1. Left: Relative excitation spectra of the 440 and 580 nm emission of $\text{Ca}_{0.997}\text{Ga}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ at 5°K (Q gives the relative quantum output). Right: Spectral energy distribution of the emission of this sample at 5°K under 250 and 300 nm excitation. (Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units.)

explains the absence of the blue shoulder in the case of the Fe^{3+} -doped sample.

The degree of association of V^{5+} and Me^{3+} ions in CaSO_4 depends, therefore, on the ionic radius of the Me^{3+} ions. If these are of about the same size as or larger than the Ca^{2+} ion, the degree of association is high; if their size is considerably smaller, the degree of association is low. The influence of the association degree on the vanadate luminescence is drastic.

(b) $\text{Mg}_{1-x}\text{Me}_x\text{S}_{1-x}\text{V}_x\text{O}_4$ ($\text{Me} = \text{Al}, \text{Cr}, \text{Fe}$)

In view of the results of the calcium system and the small difference between the ionic radii of Al^{3+} and Mg^{2+} we expected that Al^{3+} and V^{5+} would be associated in MgSO_4 . At 300°K , samples $\text{MgSO}_4\text{-V}^{5+}$, Al^{3+} , and $\text{MgSO}_4\text{-V}^{5+}$ show efficient yellow emission under long as well as shortwave uv excitation. At 300°K , samples $\text{MgSO}_4\text{-V}^{5+}$, Cr^{3+} and $\text{MgSO}_4\text{-V}^{5+}$, Fe^{3+} show yellow emission under shortwave uv excitation only. $\text{MgSO}_4\text{-V}^{5+}$, Cr^{3+} shows strong red emission under longwave uv excitation at liquid N_2 temperature.

In Fig. 2 we have drawn some representative excitation spectra and in Fig. 3 emission spectra. The following facts are noteworthy.

(i) The spectra for $\text{MgSO}_4\text{-V}^{5+}$, $\text{MgSO}_4\text{-V}^{5+}$, Cr^{3+} and $\text{MgSO}_4\text{-V}^{5+}$, Fe^{3+} are practically the same.

(ii) The excitation spectra of $\text{MgSO}_4\text{-V}^{5+}$, Al^{3+} show an excitation band with a maximum at 330 nm that is not present in the

spectra of samples with other compensating ions.

It seems probable that in MgSO_4 a large number of different luminescent vanadate centers is present. Our samples crystallize in the low-temperature MgSO_4 structure (the CrVO_4 structure) with Mg^{2+} in octahedral and S^{6+} in tetrahedral coordination (4). There is only one crystallographic position for Mg as well as for S. From our results we deduce the following approximate model. The emission and excitation spectra observed for $\text{MgSO}_4\text{-V}^{5+}$ and the Cr^{3+} and Fe^{3+} compensated samples are due to "free" V^{5+} ions. In fact these spectra show an analogy with the spectra for the "free" V^{5+} ions in CaSO_4 . (Compare Fig. 1 with Figs. 2 and 3.) Any associates $\text{V}^{5+}\text{-Cr}^{3+}$ and $\text{V}^{5+}\text{-Fe}^{3+}$ are not

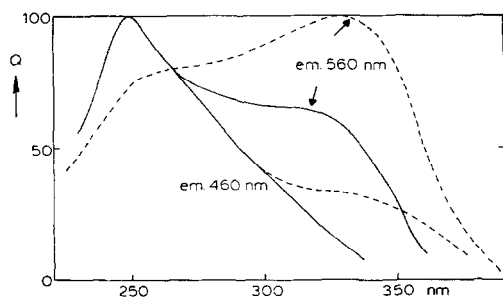


FIG. 2. Relative excitation spectra of the 460 and 560 nm emission of $\text{Mg}_{0.997}\text{Al}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ (broken lines) and $\text{Mg}_{0.997}\text{Cr}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ (solid lines) at room temperature. Curves for $\text{MgSO}_4\text{-V}$ (0.3 at%) are identical to the curves for the Cr^{3+} sample.

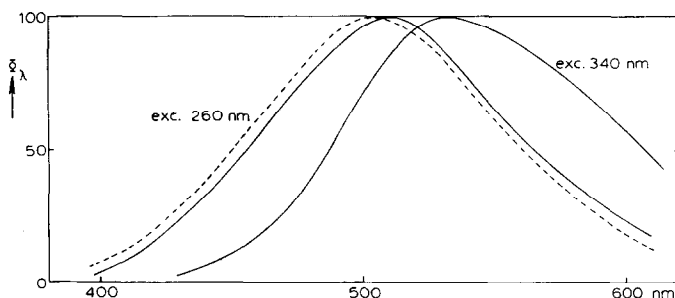


FIG. 3. Spectral energy distribution of the emission of $\text{Mg}_{0.997}\text{Cr}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ (broken line) under 260 nm excitation and of $\text{MgSO}_4\text{-V}$ (0.3 at %) (solid lines) under 260 and 340 nm excitation at room temperature.

expected to luminesce. The V^{5+} center in $\text{MgSO}_4\text{-V}^{5+}$, Al^{3+} with the excitation band at 330 nm is then probably a V^{5+} ion associated with Al^{3+} . Evidence for this follows from the observation that at 300°K, 330 nm excitation yields efficient luminescence for the Al^{3+} sample, but not for the Cr^{3+} and Fe^{3+} samples. At lower temperatures, however, the Cr^{3+} emission (red) can be excited into this band (energy transfer in a possible $\text{V}^{5+}\text{-Cr}^{3+}$ associate). Direct excitation of the Cr^{3+} ion, however, cannot be excluded.

It is remarkable that in MgSO_4 the associate has its spectra (especially the excitation band) at longer wavelengths than the free V^{5+} ion, whereas in CaSO_4 the situation is reversed. This may indicate that the associate in MgSO_4 is different from that in CaSO_4 where the compensating ion in the associate occupies a

regular (calcium) lattice site. It seems impossible to achieve in MgSO_4 an association that is so complete as in CaSO_4 .

Finally, we may add that the yellow emission of V^{5+} in MgSO_4 is probably the same as mentioned in (5) for $\text{V}_2\text{O}_7^{4-}$ in MgSO_4 .

References

1. W. HORDIJK AND G. BLASSE, *J. Luminescence* **6**, 137 (1973).
2. W. T. DRAAI AND G. BLASSE, *Phys. Stat. Sol.* **21**, 569 (1974).
3. F. A. KRÖGER, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam (1948).
4. R. W. G. WYCKOFF, "Crystal Structures," 2nd ed., Vol. 3, Interscience, New York (1965).
5. Y. KOTERA, M. YONEMURA, AND T. SEKINE, *J. Electrochem. Soc.* **108**, 540 (1961).