

ENERGY TRANSFER PHENOMENA IN LEAD SULPHATE

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It is shown that lead sulphate, PbSO_4 , shows Pb^{2+} emission with a large Stokes shift. Energy transfer has been observed from the Pb^{2+} ions to several luminescent centres, viz., tungstate, molybdate, vanadate and rare earths. No transfer occurs to the Pr^{3+} ion.

1. Introduction

Recently we have reported on the luminescence properties of vanadate-rare earth associates in CaSO_4 and PbSO_4 [1,2]. In CaSO_4 efficient energy transfer from the vanadate group to the trivalent rare earth ions was observed, whereas in PbSO_4 this transfer has a much lower probability. This was ascribed to the influence of the Pb^{2+} $6s^2$ electronic charge distribution on the vanadate group. In this paper we wish to report luminescence phenomena that were observed if excitation occurs into the Pb^{2+} ions of lead sulphate (and not in the vanadate group as in ref. [2]). It turns out that PbSO_4 itself is a luminescent compound and that the presence of several luminescent activators in PbSO_4 invoke interesting energy transfer phenomena.

2. Experimental

Sample preparation and optical measurements were performed as described in refs. [1,2]. Activator concentrations varied from 0.1 to 1 atomic percent.

3. Results and discussion

3.1. PbSO_4

Unactivated PbSO_4 shows at room temperature

and lower temperatures a broad emission band peaking at about 360 nm if excited with radiation of $\lambda \leq 225$ nm. Diffuse reflection spectra show that the optical absorption edge is at about 225 nm at 300 K. The same emission and excitation bands were found in $(\text{Ca,Pb})\text{SO}_4$ and $(\text{Ba,Pb})\text{SO}_4$ (independent of the lead concentration), so that they are ascribed to intrinsic Pb^{2+} transitions ($^1\text{S}_0 - ^3\text{P}_1$) [3]. It is quite unusual that lead compounds show characteristic Pb^{2+} emission at room temperature, because concentration quenching is very effective [4]. The Stokes shift of this emission is very large (2 eV) which prohibits energy transfer among the Pb^{2+} ions in lead sulphate due to poor spectral overlap [5,6]. The large Stokes shift may possibly be related to the large sites that are available for the Pb^{2+} ions in the baryte structure, so that a strong contraction upon excitation is possible [7,8]. This situation reminds of a number of bismuth compounds (Bi^{3+} is isoelectronic with Pb^{2+}) where no concentration quenching has been observed due to large Stokes shifts ($\text{Bi}_4\text{Si}_3\text{O}_{12}$ [6], $\text{Bi}_4\text{Ge}_3\text{O}_{12}$ [9] and $\text{Bi}_{12}\text{GeO}_{12}$ [10]).

3.2. $\text{PbSO}_4\text{-W}$ and $\text{PbSO}_4\text{-Mo}$

Tungsten-activated lead sulphate has been studied before for excitation into the tungstate group (≈ 300 nm). A yellow emission was observed and ascribed to a charge-transfer transition between the Pb^{2+} ions and the tungstate group [11]. This has been confirmed further by van Loo [12].

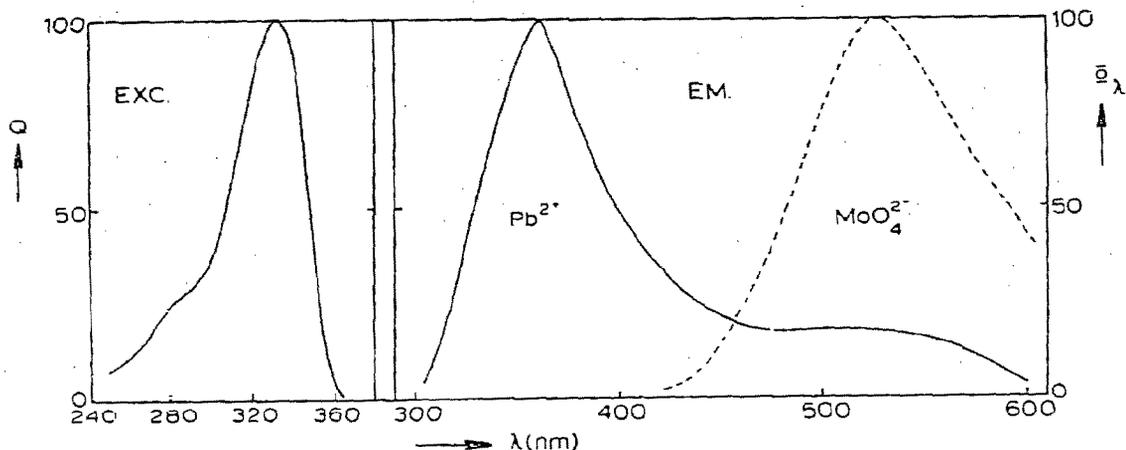


Fig. 1. Relative excitation spectrum of the 510 nm emission of $\text{PbS}_{0.99}\text{Mo}_{0.01}\text{O}_4$ at 5 K (left-hand side; Q gives the relative quantum output) and spectral energy distribution of the emission at 5 K of this sample (right-hand side; Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units; drawn line for 225 nm excitation; broken line for 300 nm excitation).

In fig. 1 we show the emission and excitation spectra of $\text{PbS}_{0.99}\text{Mo}_{0.01}\text{O}_4$. Those for the tungsten-activated samples are very similar. For 225 nm excitation mainly Pb^{2+} emission is observed. For 300 nm excitation the molybdate emission appears. The overall transfer from the lead ions to the molybdate group is not very efficient in the 1% sample. This is rather surprising in view of the considerable spectral overlap between the Pb^{2+} emission and the molybdate excitation band (see fig. 1) and must be ascribed to the absence of energy transfer among the Pb^{2+} ions mu-

tually as a consequence of the large Stokes shift. This shows again that the Pb^{2+} excitation energy is not mobile in this host lattice and further that the Pb^{2+} ion can transfer its excitation energy to nearest neighbour molybdate (or tungstate) groups.

It is noteworthy that the luminescent spectra of the molybdate and tungstate group are very similar in PbSO_4 . This is not the case in the alkaline earth molybdates and tungstates [13] or the Mo- and W-activated alkaline earth sulphates [14] and can be explained by the assumption that the transitions involved

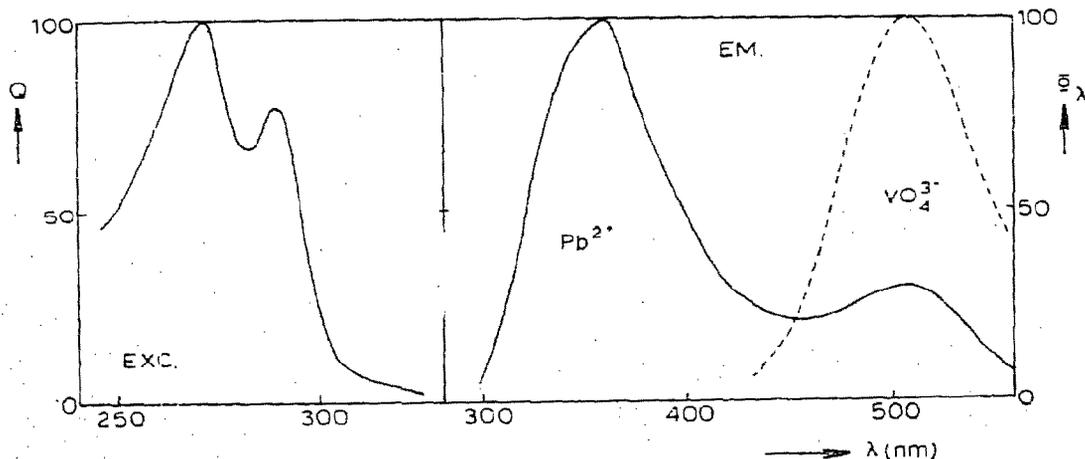


Fig. 2. Same data as in fig. 1 for $\text{Pb}_{0.997}\text{La}_{0.003}\text{So}_{0.997}\text{Vo}_{0.003}\text{O}_4$. Excitation spectrum for 500 nm emission; drawn emission spectrum for 225 nm excitation, broken emission spectrum for 300 nm excitation.

in the lead host lattice are of the metal-metal charge-transfer type [11,12].

3.3. $PbSO_4-V, Ln$ ($Ln = La, Pr, Y$)

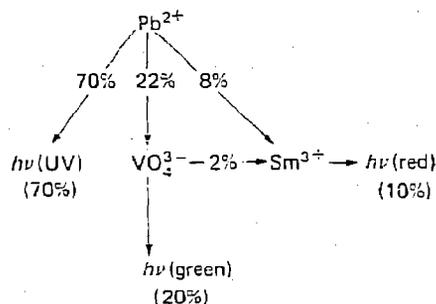
The compositions show mutually similar luminescent behaviour. For excitation into the Pb^{2+} ions (225 nm) we observe Pb^{2+} emission (360 nm) as well as vanadate emission (510 nm) (see fig. 2). This can be interpreted along the same lines as for the molybdate-activation. Energy transfer from the Pb^{2+} ions to the vanadate group occurs. The spectral overlap is not very large, but the relevant transitions are only slightly forbidden. Usually vanadates, tungstates, etc. are used as host lattices in which activators are introduced. In the present system the situation is reversed which is probably the reason that transfers of this type have not been observed before.

There is no transfer to the Pr^{3+} ion in $PbSO_4-V, Pr$. Transfer from the vanadate group to Pr^{3+} is inefficient as has been shown in ref. [2]. But neither does transfer from the Pb^{2+} ions to Pr^{3+} occur. This was also found for the composition $PbSO_4-P, Pr$. The phosphate group has no energy levels in the spectral region concerned. Also in this sample excitation into the Pb^{2+} ions does not result in Pr^{3+} emission. There is a simple explanation for this absence of energy transfer, viz., the absence of spectral overlap of the Pb^{2+} emission and Pr^{3+} absorption. The energy level scheme of Pr^{3+} [15] shows a large gap between the 3P_2 level at $\approx 22500\text{ cm}^{-1}$ and the 1S_0 level at $\approx 48000\text{ cm}^{-1}$, and the Pb^{2+} emission of $PbSO_4$ peaks exactly in this gap.

3.4. $PbSO_4-V, Ln$ ($Ln = Sm, Tb, Dy$)

The results for these compositions are mutually similar, apart from the characteristic Ln^{3+} emission. We shall, therefore, restrict ourselves to the case of $PbSO_4-V, Sm^{3+}$. If a sample of composition $Pb_{0.997}Sm_{0.003}S_{0.997}V_{0.003}O_4$ is excited at 5 K with 225 nm excitation, the emission exists for about 70% of Pb^{2+} emission, 20% of vanadate emission and 10% of samarium emission. From our earlier studies [2] we found that excitation into the vanadate group yields about 90% vanadate emission and only 10% samarium emission. This means that in $PbSO_4-V, Sm$ excitation of the Pb^{2+} ions at 5 K is followed by a

number of processes indicated in the following scheme:



In accordance with this a similar sample with P instead of V yields 90% of Pb^{2+} emission and 10% of Sm^{3+} emission (the path way via the vanadate group is no longer available).

It should be realized that the vanadate group and the Sm^{3+} ion occur as an associate in $PbSO_4$. We find that the transfer from Pb^{2+} to the vanadate group is somewhat more efficient than to the Sm^{3+} ion. It seems hard to account quantitatively for this effect. Nevertheless this result indicates that, comparing $Pb^{2+} \rightarrow VO_4^{3-}$ and $Pb^{2+} \rightarrow Sm^{3+}$ transfer, the smaller spectral overlap in the case of $Pb^{2+} - VO_4^{3-}$ transfer is more than compensated by the stronger interaction (electric dipole-dipole); in the case of $Pb^{2+} - Sm^{3+}$ transfer the Pb^{2+} emission overlaps favourably with many Sm^{3+} absorptions, but the interaction is either of the electric dipole-quadrupole or of the exchange type in view of the forbidden nature of the Sm^{3+} transitions [16].

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