LUMINESCENCE OF RARE EARTH VANADATE ASSOCIATES IN SULFATES

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In some divalent metal sulfates (CaSO_4 , PbSO_4) the introduction of trivalent rare earth ions on the metal sites and pentavalent vanadium on the sulfur sites results in the formation of associates $\text{VO}_4^{3-}-\text{RE}^{3+}$. Energy transfer from the vanadate group to trivalent rare earth ions can be studied in these systems. It is shown that the transfer rate is temperature independent, but depends strongly on the choice of the host. In CaSO_4 the transfer rate in the associate is estimated to be $\approx 10^8 \text{ s}^{-1}$, and in $\text{PbSO}_4 \approx 10^4 \text{ s}^{-1}$. The low transfer rate in $\text{PbSO}_4 : \text{RE}, \text{V}$ is ascribed to the influence of the Pb^{2+} ions on the charge distribution in the vanadate group.

1. Introduction

Energy transfer from the vanadate (VO_4^{3-}) group to trivalent rare earth ions (RE^{3+}) has been studied intensively in the host lattice YVO_4 [1–3]. Although excitation into the vanadate group is followed by RE^{3+} emission in many cases, the energy migration through the host lattice also plays an important role. At low temperatures this migration is hampered and no transfer to the RE^{3+} ions occurs. Recently, we have reported a system in which isolated associates consisting of VO_4^{3-} and RE^{3+} occur, namely CaSO_4 with vanadium on sulfur sites and rare earth ions on calcium sites [4–6]. This system throws new light on the energy transfer process between the vanadate group and the trivalent rare earth ions. In MgSO_4 the VO_4^{3-} and RE^{3+} are only partly associated and consequently their luminescence properties are different from those in CaSO_4 [7].

This paper describes the results of a study of the luminescence of VO_4^{3-} and RE^{3+} in PbSO_4 and compares these results with those for VO_4^{3-} and RE^{3+} in CaSO_4 and YVO_4 . Some striking differences were observed. Further, PbSO_4 was found to luminesce at room temperature.

2. Experimental

Samples were prepared as described in ref. [5] using PbO as starting material and

800°C as the final firing temperature. The RE and V concentrations were 0.3 at.%. All samples were checked by X-ray analysis. Excitation and emission spectra were recorded down to 5 K on a Perkin–Elmer MPF-2A spectrofluorimeter. For more details see ref. [5].

3. Results on $\text{Ca}_{1-x}\text{RE}_x\text{S}_{1-x}\text{V}_x\text{O}_4$

In order to facilitate a comparison between the results on PbSO_4 samples with those on CaSO_4 samples we summarize the more important CaSO_4 results:

- (a) RE^{3+} (on Ca^{2+} sites) and VO_4^{3-} (on SO_4^{2-} sites) occur solely as associates.
- (b) If $\text{RE}^{3+} = \text{Y}^{3+}$, Gd^{3+} or La^{3+} , excitation into the vanadate group (with absorption maximum at about 250 nm) is followed by vanadate emission (with maximum at about 465 nm and decay time about 1 μs).
- (c) If $\text{RE}^{3+} = \text{Pr}^{3+}$, Sm^{3+} , Eu^{3+} , Tb^{3+} , Dy^{3+} , excitation into the vanadate group is followed by efficient RE^{3+} emission, even at low temperatures. In YVO_4 no energy transfer from VO_4^{3-} to Pr^{3+} or Tb^{3+} has been observed. This has been ascribed to radiationless decay via a charge-transfer state (see also ref. [8]). In CaSO_4 the rate for energy transfer in the associate from VO_4^{3-} to RE^{3+} is estimated to be about 10^8 s^{-1} .

4. Results on $\text{Pb}_{1-x}\text{RE}_x\text{S}_{1-x}\text{V}_x\text{O}_4$

Unactivated PbSO_4 shows, at room temperature and lower temperatures, a broad emission band peaking at about 360 nm if excited with radiation of $\lambda < 225 \text{ nm}$ (shown in fig. 1 for a doped sample). Diffuse reflection spectra show that the optical

Fig. 1. Relative excitation spectrum of the 500 nm emission of $\text{Pb}_{0.997}\text{La}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ 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 300 nm excitation; broken line for 225 nm excitation).

Fig. 2. Relative excitation spectrum of the 560 nm emission of $\text{PbSO}_4\text{-V}(0.003)$ at 5 K (left-hand side) and spectral energy distribution of the emission at 5 K of this sample (right-hand side: 300 nm excitation).

absorption edge is at about 225 nm at 300 K. The same emission and excitation bands were found in $\text{Ca}_{1-x}\text{Pb}_x\text{SO}_4$ and $\text{Ba}_{1-x}\text{Pb}_x\text{SO}_4$ (x down to 0.01), so that they are ascribed to intrinsic Pb^{2+} transitions. We observed direct energy transfer from the Pb^{2+} ions to RE^{3+} in $\text{Pb}_{1-x}\text{RE}_x\text{S}_{1-x}\text{V}_x\text{O}_4$. Energy transfer from Pb^{2+} to the vanadate group also occurred. These transfers will be discussed elsewhere.

In $\text{PbSO}_4\text{:V,La}$ and $\text{PbSO}_4\text{:V,Y}$ we observed a greenish vanadate emission peaking at about 510 nm with excitation bands peaking at about 290 and 270 nm (see fig. 1). The quenching temperature is situated above room temperature (about 350 K). The decay time of this emission is much longer than in CaSO_4 , namely 35 μs . In $\text{PbSO}_4\text{:V}$ (without RE), however, the vanadate emission and excitation bands are situated at considerably longer wavelengths, namely 580 and 300 nm, respectively (fig. 2). This difference between the RE^{3+} -compensated and the uncompensated sample was also observed for CaSO_4 and is strong evidence for the presence of $\text{VO}_4^{3-}\text{-RE}^{3+}$ associates in PbSO_4 .

Fig. 3. Spectral energy distribution of the emission of $\text{Pb}_{0.997}\text{Sm}_{0.003}\text{S}_{0.997}\text{V}_{0.003}\text{O}_4$ at 5 K for 225 nm excitation (broken line) and 290 nm excitation (drawn line).

Table 1

Ratio of RE^{3+} quantum efficiency to total quantum efficiency for samples $\text{Pb}_{1-x}\text{RE}_x\text{S}_{1-x}\text{V}_x\text{O}_4$ ($x = 0.003$) for vanadate excitation.

RE	$q_{\text{RE}^{3+}}/q_{\text{RE}^{3+}+\text{VO}_4^{3-}}$	
	5 K	300 K
Pr^{3+}	0.08	0.10
Sm^{3+}	0.09	0.10
$\text{Eu}^{3+a)}$	0.1	0.1
$\text{Tb}^{3+b)}$	0.5	0.75
Dy^{3+}	0.15	0.15

a) Samples may contain Eu partly in the divalent state.

b) Excitation may be partly in 4f–5d of Tb^{3+} .

Table 2

Energy transfer probability for associates studied in YVO_4 , CaSO_4 , PbSO_4 (–: no transfer, +: efficient transfer, 0: transfer probability low to medium).

	YVO_4	CaSO_4	PbSO_4
$\text{VO}_4^{3-} \rightarrow \text{Pr}^{3+}$	–	+	0
$\text{VO}_4^{3-} \rightarrow \text{Sm}^{3+}$	+	+	0
$\text{VO}_4^{3-} \rightarrow \text{Eu}^{3+}$	+	+	0
$\text{VO}_4^{3-} \rightarrow \text{Tb}^{3+}$	–	+	0
$\text{VO}_4^{3-} \rightarrow \text{Dy}^{3+}$	+	+	0

We introduced in PbSO_4 those rare earth ions that showed efficient emission in CaSO_4 , namely Pr^{3+} , Sm^{3+} , Eu^{3+} , Tb^{3+} and Dy^{3+} . Remarkably, excitation into the vanadate absorption band did not result in efficient RE^{3+} emission: we observed mainly vanadate emission. In table 1 we have tabulated the ratio of the RE^{3+} quantum efficiency and the total emission quantum efficiency for excitation into the vanadate group. Fig. 3 shows the emission spectrum of $\text{Pb}_{1-x}\text{Sm}_x\text{S}_{1-x}\text{V}_x\text{O}_4$ for excitation into the vanadate excitation band. We note that excitation into the Pb^{2+} ions (225 nm) result in a higher ratio of RE^{3+} and vanadate emission than into the vanadate group itself.

In table 2 we have given a qualitative survey of the efficiency of energy transfer from the vanadate group to RE^{3+} ions in YVO_4 , CaSO_4 and PbSO_4 . It is evident that the influence of the host lattice on this transfer efficiency is drastic.

5. Discussion

Energy transfer from the vanadate group to the trivalent rare earths is now considered to occur via exchange interaction with a relatively short critical distance. Consequently, the transfer probability is mainly determined by two factors, namely the spectral overlap and an exchange integral [9]. The broad vanadate emission usually overlaps one or more $f-f$ absorption lines, so that transfer occurs, albeit with a relatively slow rate.

From this model it does not become clear why there is no transfer from the vanadate group to Tb^{3+} and Pr^{3+} (in YVO_4 and YPO_4) and why at low temperatures there is no energy transfer to the lanthanides in YVO_4 . In $CaSO_4:V,RE$, however, there is efficient transfer to Tb^{3+} and Pr^{3+} . This has been explained by the presence of effective charges on the RE^{3+} ions (on Ca^{2+} sites) and the V^{5+} ions (on S^{6+} sites) [5,6] which displace the interfering charge-transfer state $V^{4+}-RE^{4+}$ to higher energies. Further, the study on the $CaSO_4:V,RE$ systems shows that the transfer is independent of temperature as is to be expected from theory. Temperature-dependent transfer phenomena in YVO_4 are due to the temperature dependence of the vanadate-vanadate energy transfer which is hampered at low temperatures.

From the radiant decay time of the vanadate emission in $CaSO_4:V,Y$ ($\approx 1 \mu s$) the rate of energy transfer from the vanadate group to the rare earth ions can be estimated as about $10^8 s^{-1}$.

We now turn to the results for the $PbSO_4:V,RE$ system and consider first $RE = La$ (or Y), i.e. non-luminescing RE ions. The vanadate emission in these systems differs from that in uncompensated $PbSO_4:V$ (see figs. 1 and 2) which we consider as strong evidence for association of V^{5+} and RE^{3+} as in $CaSO_4$ where the situation is similar. This is sustained by the larger halfwidth of the emission band in the case of the uncompensated $PbSO_4-V$ sample (compare figs. 1 and 2).

If $PbSO_4:V, La$ (or Y) is excited with ≈ 220 nm radiation, mainly 360 nm emission is observed. This is considered to be the well-known $^3P_1-^1S_0$ emission of Pb^{2+} which will not be considered here. Excitation with radiation with λ between 260 and 300 nm results in a quite different emission peaking at 510 nm. We assume that this is the vanadate emission (it is absent for pure $PbSO_4$). In $CaSO_4$ this emission peaks at shorter wavelength, namely 465 nm. In addition the radiant decay time of the vanadate emission in $PbSO_4:V, La$ is much longer than in $CaSO_4:V,Y$.

We explain this difference by the assumption that in $CaSO_4$ the vanadate absorption and emission is a pure charge-transfer transition within the vanadate group [10], whereas in $PbSO_4$ it has much more the character of a metal-metal ($Pb^{2+}-V^{5+}$) charge-transfer transition [11]. Ample evidence for transitions of this type have been put forward for $Bi^{3+}-V^{5+}$ in YPO_4 [11,12] and for $Pb^{2+}-W^{6+}$ (Mo^{6+}) in $PbWO_4$ and $PbMoO_4$ [13,14]. This explains at the same time why the transitions are at lower energies in $PbSO_4$ than in $CaSO_4$ and why the radiant decay time in $PbSO_4$ is much longer (less wave-function overlap) than in $CaSO_4$.

It might be argued that the crystal structure of $PbSO_4$ (baryte) is different from

CaSO_4 (anhydrite) and that this might cause the difference in the vanadate emissions. In $\text{BaSO}_4 : \text{V}, \text{Y}$, however, the vanadate luminescence is very much like that in $\text{CaSO}_4 : \text{V}, \text{Y}$ [7], although BaSO_4 and PbSO_4 are isomorphous.

Note in passing that metal–metal charge-transfer transitions of this type often have a relatively high quenching temperature of their luminescence, e.g. $\text{CaWO}_4 : \text{Pb}$ [15] and $\text{PbSO}_4 : \text{V}, \text{La}$ (350 K, whereas the Ca and Ba sample have 200 and 150 K, respectively).

We now turn to samples $\text{PbSO}_4 : \text{V}, \text{RE}$ with luminescing RE ions. From table 1 it is obvious that the transfer rate is so low that excitation into the vanadate group is followed by mainly vanadate emission (see fig. 3). From the radiant decay time of the emission of $\text{PbSO}_4 : \text{V}, \text{La}$ (35 μs) the transfer rate in the associate can be estimated as about 10^3 – 10^4 s^{-1} . This is a factor 10^4 less than in the CaSO_4 system.

It seems improbable that the spectral overlap integral is responsible for this drastic reduction. Although the vanadate emission in PbSO_4 is at longer wavelength than in CaSO_4 there is always overlap with levels from the $4f^n$ configuration of the rare earth ions. This means that the exchange integral in the expression for the transfer rate must be responsible for the large difference in transfer rate in PbSO_4 and CaSO_4 . An obvious explanation is that the wave-function overlap of a pure-vanadate excited charge transfer state (involving $2p \text{ O}^{2-}$ and $3d \text{ V}^{5+}$ wave functions) and the $4f^n$ state will be larger than the overlap in the case of a $\text{Pb}^{2+} - \text{VO}_4^{3-}$ excited charge-transfer state (involving $6s \text{ Pb}^{2+}$ and $3d \text{ V}^{5+}$ wavefunctions) and a $4f^n$ state. Overlap with the $4f$ orbitals will occur mainly via the oxygen anions ("super-exchange interaction"); these anions play a more important role in CaSO_4 than in PbSO_4 . This argument runs parallel with an explanation previously given to explain the low energy transfer rate from VO_4^{3-} to Eu^{3+} in InVO_4 [12].

A more quantitative elucidation seems difficult at the moment. Nevertheless it is striking and unexpected to find how the rate of transfer from VO_4^{3-} to RE^{3+} is influenced by the choice of the host lattice.

Finally, the variation of the transfer rate in $\text{PbSO}_4 - \text{V}, \text{RE}$ with the nature of RE is intriguing. Two effects may play a role here:

- (a) if the fourth ionization potential of the RE is relatively low it will be easier to admix into the $\text{Pb}^{2+} - \text{VO}_4^{3-}$ excited charge-transfer state;
- (b) the RE^{3+} ions are considerably smaller than Pb^{2+} [16], probably the 12-coordinated site of Pb^{2+} in the baryte structure is too large for them, so that they are displaced from the centre of the Pb^{2+} site to the V^{5+} ion. This effect will be more important for the smaller RE^{3+} ions and results in a larger wave-function overlap.

The former effect favors transfer to Pr^{3+} and Tb^{3+} , the latter Tb^{3+} and Dy^{3+} . Our results (table 1) do not contradict such an explanation. It should be realized that the Tb^{3+} results may be influenced by the fact that the VO_4^{3-} excitation band may overlap the $4f$ – $5d$ excitation band of Tb^{3+} . Perhaps this is also the reason why the temperature dependence (table 1) in the case of Tb^{3+} is anomalous.

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