

LUMINESCENCE OF CALCIUM HALOPHOSPHATE-Sb³⁺,Mn²⁺ AT LOW TEMPERATURES

G. BLASSE

Physical Laboratory, State University, P.O. Box 80000, 3508 TA Utrecht, The Netherlands

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The luminescence spectra of calcium halophosphate co-doped with Sb³⁺ and Mn²⁺ at liquid-helium temperature are reported. The Stokes shift increases considerably upon decreasing the temperature. The consequence for the energy-transfer phenomena are discussed. The red-shift of the Sb³⁺ emission is related to the off-centre position of this ion.

Calcium halophosphate co-doped with Sb³⁺ and Mn²⁺ is a well-known luminescent material which has been used for many years in fluorescent lamps [1,2]. Several detailed investigations have been performed on this material. It was found that the Sb³⁺ ions occupy Ca(II) sites with an O²⁻ ion on the nearest-neighbour halide-ion site to provide for charge compensation [3,4]. This centre is responsible for the blue emission. The Mn²⁺ ion substitutes for calcium ions with a strong preference for the Ca(I) site [5]. This centre yields the yellow emission.

Excitation of the Sb³⁺ ion yields blue as well as yellow emission, so that energy transfer from Sb³⁺ to Mn²⁺ occurs. This transfer has been analyzed by Soules et al. [6]. These authors present strong evidence that the transfer occurs by exchange interaction.

No liquid-helium-temperature measurements have been reported in the literature as far as we are aware. We were interested in investigating the temperature dependence of the Sb³⁺ → Mn²⁺ transfer rate. Our results are presented in this note.

A sample of calcium halophosphate co-doped with Sb³⁺ and Mn²⁺ was kindly put at our disposal by Ir. R.C. Peters, Philips Lighting Division, Eindhoven, The Netherlands. Its composition was Ca_{9.61}Cd_{0.04}Mn_{0.2}Sb_{0.1}(PO₄)₆(F_{0.9}, Cl_{0.1})₂. The optical instrumentation has been described elsewhere [7]. It consists of a Perkin-Elmer spectrofluorometer MPF-3, equipped with an Oxford CF 100 helium cryostat.

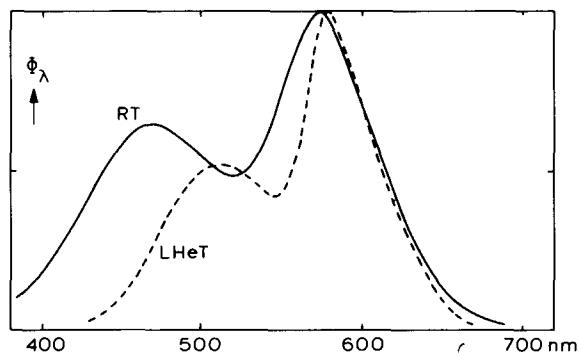


Fig. 1. Spectral energy distribution of the emission of calcium halophosphate-Sb³⁺,Mn²⁺ at RT and LHeT for 280 nm excitation. Φ_λ gives the spectral radiant power per constant wavelength interval in arbitrary units.

Fig. 1 presents the emission spectrum of our sample at liquid-helium temperature (LHeT) and room temperature (RT). The amount of blue (Sb³⁺) and yellow (Mn²⁺) emission in the total output is temperature-independent within the experimental accuracy. The Mn²⁺ emission maximum shifts from 575 to 585 nm from RT to LHeT. The Sb³⁺ emission maximum shifts from 470 to 515 nm from RT to LHeT. This is in line with the liquid-nitrogen data of Davis et al. [8].

Fig. 2 shows the excitation spectrum of the Sb³⁺ and the Mn²⁺ emission in the region 320 > λ > 240 nm. This band corresponds to the lowest absorption band of the Sb³⁺ centre. It is clear that this transition shifts to higher energy upon lowering the tempera-

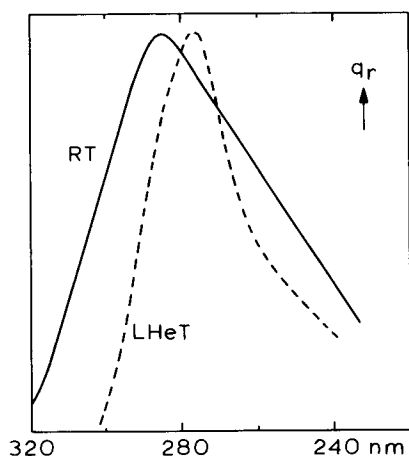


Fig. 2. Relative excitation spectra of the Mn^{2+} emission of calcium halophosphate- Sb^{3+} , Mn^{2+} at RT and LHeT in the Sb^{3+} excitation region. q_r gives the relative quantum output in arbitrary units.

ture, i.e. contrary to the shift of the emission band. Consequently, the Stokes shift increases when the temperature is decreased. For RT its value amounts to $\approx 14000 \text{ cm}^{-1}$, for LHeT 17000 cm^{-1} . It should be realized that the sensitivity of our spectrometer decreases drastically towards the shorter-wavelength side of fig. 2, since it is equipped with a xenon lamp. The accuracy of the excitation spectra is, therefore, not very high in this spectral range. This explains the discrepancy with the 300 and 77 K excitation spectra given in ref. [4] and ref. [8].

The excitation spectrum of the Mn^{2+} emission shows in addition the well known Mn^{2+} transitions, viz. ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2, {}^4\text{E}$ around 350 nm, ${}^6\text{A}_1 \rightarrow {}^4\text{E}, {}^4\text{A}_1$ around 410 nm and ${}^6\text{A}_1 \rightarrow {}^4\text{T}_2$ and ${}^4\text{T}_1$ around 500 nm. The latter transitions could not be measured with any accuracy due to the presence of the xenon lines in this spectral region. Although the Mn^{2+} excitation lines sharpen somewhat at LHeT, their integrated intensity did not change markedly as the temperature was lowered from RT to LHeT.

From these measurements, we have to conclude that the total energy transfer rate is practically temperature-independent. A contribution from $\text{Sb}^{3+} \rightarrow \text{Sb}^{3+}$ transfer seems to be negligible in view of the large Stokes shift [9]. For LHeT this contribution will vanish; from the temperature invariance it follows that at RT also its importance is negligible, in contrast to early suggestions [10].

Let us now consider the $\text{Sb}^{3+} \rightarrow \text{Mn}^{2+}$ transfer. Our experiments suggest that the absorption strength of the Mn^{2+} transitions does not depend strongly on temperature. This is not unexpected, since the Ca(I) site lacks inversion symmetry [2]. In that case, the temperature dependence of the transfer rate is determined by the spectral overlap, irrespective of the transfer mechanism. In view of the considerable spectral shift of the Sb^{3+} emission (fig. 1), the overlap is expected to depend on temperature. At room temperature the Sb^{3+} emission overlaps the ${}^6\text{A}_1 \rightarrow {}^4\text{E}, {}^4\text{A}_1$ Mn^{2+} absorption transition. This contribution vanishes at LHeT. However, the overlap with the ${}^6\text{A}_1 \rightarrow {}^4\text{T}_1$ transition increases, so that the total spectral overlap does not change too much. This results in a practically temperature-independent transfer rate.

Finally, we consider the red-shift of the emission of both luminescent centres if the temperature is decreased. That of the Mn^{2+} emission is relatively small and can be related to a stronger crystal field on the Mn^{2+} ion at lower temperatures due to the shorter interatomic distances. It is well known that a larger crystal-field splitting of the excited ${}^4\text{G}$ state decreases the transition energy ${}^4\text{T}_1({}^4\text{G}) \rightarrow {}^6\text{A}_1$.

The red-shift of the Sb^{3+} emission is unexpectedly large however. In view of the $5s^2$ electron configuration, the emission transition will be ${}^3\text{P}_{1,0} \rightarrow {}^1\text{S}_0$. It is hard to explain the large Stokes shift and the red-shift by considering the free-ion transitions. For the iso-electronic $6s^2$ case (Pb^{2+} , Bi^{3+}) it has recently been shown that a large Stokes shift of the emission is due to an off-centre position of the s^2 ion [11]. An off-centre position of Sb^{3+} on the Ca(II) site is not very surprising, because (a) the Sb^{3+} ion ($r = 0.76 \text{ \AA}$) is smaller than the Ca^{2+} ion ($r = 1.00 \text{ \AA}$) (ionic radii for six coordination according to ref. [12]), and (b) the Sb^{3+} ion (with positive effective charge: $\text{Sb}_{\text{Ca}}^{3+}$) and the O^{2-} ion (with negative effective charge: O_{F}^{2-}) will attract each other. The energy-level diagram becomes complicated in such a situation [11]. The red-shift suggests that the Sb^{3+} ion is situated more off-centre at LHeT than at RT which is well conceivable. The strong red-shift is not to be expected for an A_X type emission [13] as suggested previously [14]. In conclusion, we ascribe the large Stokes shift of the Sb^{3+} emission in halophosphates to an off-centre position of the Sb^{3+} ion following the extensive experimental evidence described elsewhere [11].

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