

Luminescence of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$

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The compound $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ with statistically distributed $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ complexes shows a weak, red emission at low temperatures. This emission is discussed in relation to similar luminescent compounds.

1. Introduction

The luminescence of complex ions like vanadate, niobate and tungstate is well known and has been studied intensively [1]. We have shown that edge- or face-sharing octahedra of this type are luminescent species with high quenching temperatures [2, 3]. Examples are $\text{Mg}_4\text{Nb}_2\text{O}_9$ and $\text{Ba}_3\text{SrNb}_2\text{O}_9$ with $\text{Nb}_2\text{O}_9^{8-}$ anions and $\text{Ba}_3\text{W}_2\text{O}_9$ with $\text{W}_2\text{O}_9^{6-}$ anions. These anions consist of face-sharing niobate and tungstate octahedra, respectively.

Since the vanadate group is strongly luminescent in some lattices [1], we were interested in coupled vanadate octahedra. However, the V^{5+} ion occurs usually in oxides in tetrahedral coordination and a species $\text{V}_2\text{O}_9^{8-}$ has not been reported, as far as we are aware. Recently Mattes and Förster [4] reported the crystal structure of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ which appeared to be of the $\text{Cs}_3\text{Fe}_2\text{F}_9$ type and thus to contain face-sharing bioctahedral $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ anions. Since the F^- ion is isoelectronic with O^{2-} , it seemed interesting to investigate the possible luminescence of this complex anion. The results are described in this paper.

2. Experimental

Samples of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ were prepared from 40% HF solutions as described by Pausewang and Dehnicke [5]. They were checked by X-ray powder diffraction. Luminescence measurements were performed at liquid helium temperatures (LHeT) on an MPF-3 spectrofluorimeter (Perkin Elmer) equipped with an Oxford flow cryostat. Further details are described in ref. [6].

3. Results

The compound $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ was obtained as small, light-yellow crystals. They show a very weak red luminescence under long wavelength ultraviolet excitation at temperatures below 100 K. Even at

LHeT the luminescence efficiency is low. By comparison with standard phosphors the quantum efficiency of the luminescence was estimated to be about 10%. Fig. 1 shows the emission spectrum of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ at LHeT. It consists of a broad band with a maximum at about 13.200 cm^{-1} . The longer wavelength part of the emission band is outside the range of the spectrofluorimeter. Note that the visual weakness of the emission is not only due to the low quantum efficiency, but also to the fact that the greater part of the emission is situated outside the eye sensitivity curve.

The excitation spectrum of this emission starts at about 21.000 cm^{-1} , has a flat maximum between 25.000 and 28.000 cm^{-1} and falls off slowly for higher excitation energies. Fig. 2 shows the reflection spectrum of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ at 300 K. If one corrects for the well-known thermal shift of the vanadate group,

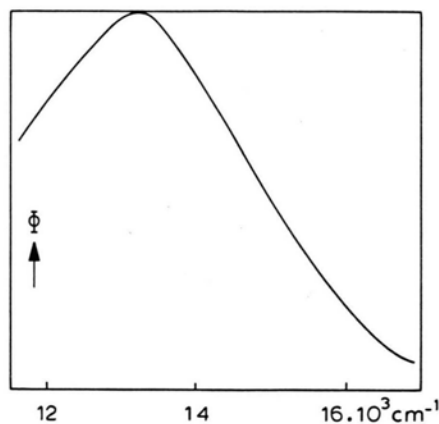


Fig. 1. Spectral energy distribution of the emission of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ at LHeT. Excitation is by 380 nm. Φ denotes the spectral radiant power per constant energy interval in arbitrary units.

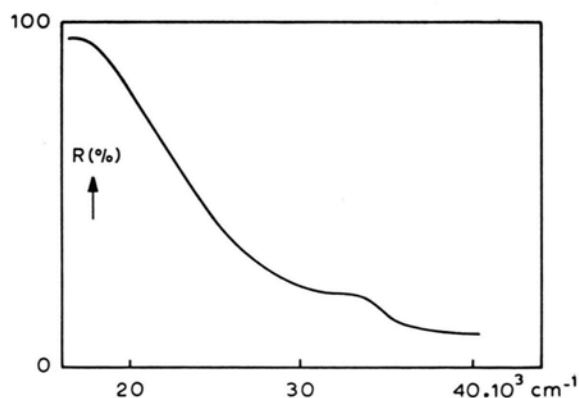


Fig. 2. Diffuse reflection spectrum of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ at room temperature.

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this spectrum corresponds reasonably with the excitation spectrum as far as the lower energy part is concerned.

The Stokes shift of the emission is estimated from these data to be about 12.000 cm^{-1} . We were not able to perform decay time measurements in view of the low emission intensity. Because the quantum efficiency is low, the value of the decay times would have been of comparative value only.

4. Discussion

Optical absorption

Efficiently luminescent vanadate groups have optical absorption above some 28.000 cm^{-1} (ref. [6]). The optical absorption of the $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ complex starts at relatively low energy (see Fig. 2). We note two facts in the reflection spectrum, *viz.* (i) there seem to be two absorption regions, *viz.* from 20.000 to 33.000 cm^{-1} and a more intense one starting at about 34.000 cm^{-1} . (ii) The absorption bands are extremely broad.

The two regions may be ascribed to singlet-triplet and singlet-singlet transitions, respectively [1, 6]. The broadness of the bands can only partly be intrinsic (compare excitation spectra in ref. [6]). Mattes and Förster [4] have shown that the composition of the close-packed Cs-O-F layers is near the average composition $\text{CsO}_{4/3}\text{F}_{5/3}$ and that the vanadium atoms are seeking favourable positions between the layers. This causes a statistical distribution of the vanadium atoms over the octahedral sites, which all have an occupancy factor of $2/3$. We assume that this statistical distribution contributes also to the broadness of the absorption band.

From the infrared spectrum of $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ it follows that the $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ complex does not

contain oxygen bridge bonds. There are only terminal V-O bonds [4]. Since the optical absorption bands of the vanadate group are due to charge-transfer transitions [1, 6] and fluorine is more negative than oxygen, the lower-energy absorption (as well as the emission) must be ascribed to vanadium-oxygen charge transfer. Since the oxygen ion in $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ is poorly charge compensated, these transitions are in fact expected at low energy [7]. This means also that the $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ ions cannot be compared with the luminescent species $\text{Nb}_2\text{O}_9^{8-}$ and $\text{W}_2\text{O}_9^{6-}$, because the luminescence processes are restricted to the terminal bonds only.

Luminescence

The Stokes shift of the emission is of the same order of magnitude as observed usually for vanadate emission [1, 6]. Note that the emission maximum is situated at about half of the excitation maximum. According to Dexter *et al.* [8] this corresponds to a situation where the quantum efficiency q can be very low, even at low temperatures, since the system can tunnel from the excited state to the electronic ground state without thermal activation. We assume that this is exactly the case here, so that $\text{Cs}_3\text{V}_2\text{O}_4\text{F}_5$ forms a border case between luminescent and non-luminescent vanadates. A similar situation for the molybdate octahedron has been reported by us before, *viz.* for $\text{K}_2\text{MoO}_3(\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (ref. [9]).

In conclusion the complex anion $[\text{V}_2\text{O}_4\text{F}_5]^{3-}$ does not show efficient luminescence due to a large Stokes shift of the emission relative to the lowest absorption level, which is situated at relatively low energy. This situation makes nonradiative return to the ground state without thermal activation favourable [10].

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