

ON THE LUMINESCENCE OF THE CHROMATE (CrO_4^{2-}) COMPLEX

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The chromate (CrO_4^{2-}) complex is shown to luminesce in some specific host lattices. The emission is situated in the red and the quantum efficiency is low. No luminescence was observed for oxocomplexes of Re^{7+} .

1. Introduction

Complexes consisting of highly-charged transition-metal ions without d electrons surrounded by oxygen ions are well known for their luminescence. The vanadate (VO_4^{3-}) and the tungstate (WO_4^{2-}) group are representative examples. If one scans the transition-metal series from left to right, the heaviest metals for which luminescence has been observed in oxocomplexes are vanadium, molybdenum and tungsten in the first, second and third transition-metal series, respectively [1]. As far as we are aware, the literature does not contain reference to luminescence from oxocomplexes of chromium, technetium and rhenium. There is one exception, viz. a report by Freiberg and Rebane [2] on the luminescence of $\text{K}_2\text{Cr}_2\text{O}_7$ below 30 K. An assignment of the excitation and emission spectra was given by one of us [3].

The present study was started to find the borderline between complexes of this type which luminesce and those which do not. It has been noted before [1] that the absorption bands of these complexes shift to lower energy going from left to right in a given transition-metal series. This shift seems to influence the quenching temperature of the luminescence of these complexes. A requirement for efficient luminescence at higher temperatures seems to be absorption bands at high energy (or, more trivial, colourless complexes). The fact that the Stokes shift of the luminescence in these complexes is large is probably a main factor in this relation. From the luminescence point of view our results are clearly negative. The CrO_4^{2-}

complex luminesces only very weakly, whereas the oxocomplexes of rhenium did not luminesce at all. Nevertheless the results have several interesting aspects, some of which are by no means understood.

The compositions investigated were the following: Na_2CrO_4 , K_2CrO_4 , $\text{K}_2\text{Cr}_2\text{O}_7$, CaCrO_4 (note that this compound is isomorphous and practically isoelectronic with the well-known luminescent YVO_4) and KBr containing small amounts of K_2CrO_4 ; further KReO_4 and $\text{Sr}_2\text{LiReO}_6$. The latter compounds contain ReO_4^- and ReO_6^{5-} complexes, respectively. They are isomorphous and isoelectronic with the luminescent CaWO_4 and Sr_2MgWO_6 [4].

2. Experimental

Most samples were available as commercial, high-purity compounds. $\text{Sr}_2\text{LiReO}_6$ was prepared as described by Kemmler-Sack et al. [5]. KReO_4 was obtained as a single crystal by courtesy from Dr. L.G. van Uitert (Bell Laboratories). Powder samples were checked by X-ray analysis.

Samples of KBr containing a small amount of K_2CrO_4 (denoted as $\text{KBr}/\text{K}_2\text{CrO}_4$) were prepared by pressing intimate mixtures up to about 200 bar during 50 min. The K_2CrO_4 concentration was 1 mole%. Reference measurements were performed on comparable $\text{MgO}/\text{K}_2\text{CrO}_4$ mixtures.

The optical measurements were performed at liquid nitrogen and helium temperatures using a Perkin-Elmer spectrofluorimeter MPF-3 equipped with the

required cryostats. For further details see, for example, ref. [6]

3. Results

The luminescence of $K_2Cr_2O_7$ reported before [2] was confirmed in our studies. The quantum efficiency at liquid helium temperature amounts to about 10%. The decay time of the luminescence at that temperature was 800 μs

We observed only measurable CrO_4^{2-} luminescence in the case of $CaCrO_4$. Although pure K_2CrO_4 , as well as MgO/K_2CrO_4 , did not luminesce, the samples KBr/K_2CrO_4 did show emission. All emission and excitation spectra are shown in fig. 1. Diffuse reflection spectra for $CaCrO_4$ and KBr/K_2CrO_4 at room temperature are shown in fig 2. The Stokes shift is estimated to be some 6000 cm^{-1} , which is a low value in comparison with values reported for well-known luminescent complexes of this type ($10000\text{--}15000\text{ cm}^{-1}$ [1]). The quantum efficiency of the luminescence of $CaCrO_4$ at 4.2 K is about 1% and the decay time about 100 μs . The weak luminescence disappeared at about 150 K

Infrared spectroscopy showed that at least a small part of the K_2CrO_4 in KBr is present as a solid solution in the KBr lattice [7,8].

No luminescence was observed for $KReO_4$ and Sr_2LiReO_6 , not even at 4.2 K. The respective optical

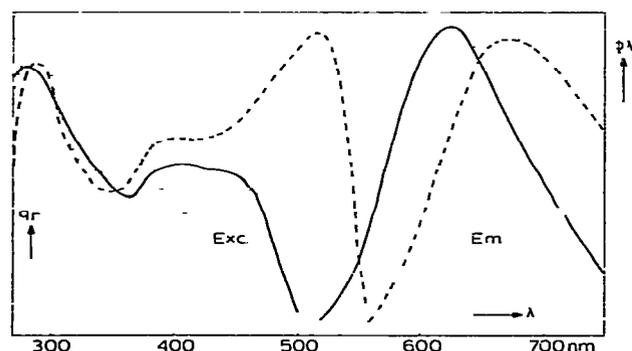


Fig. 1. Excitation (left) and emission (right) spectra of the CrO_4^{2-} luminescence at 4.2 K. q_r gives the relative quantum output. Φ_λ gives the radiant power per constant wavelength interval in arbitrary units. Full line: $CaCrO_4$; broken line: $K_2Cr_2O_7$; dotted line: KBr/K_2CrO_4

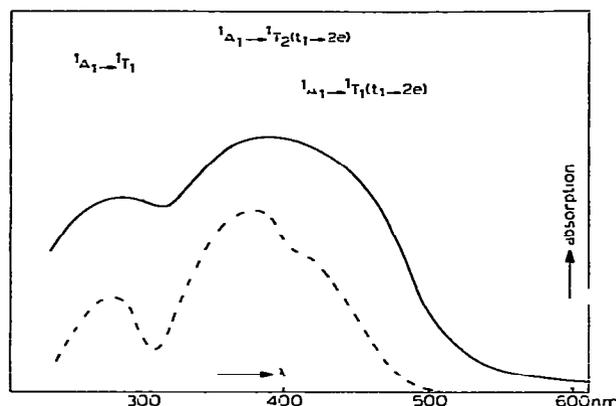


Fig. 2. Diffuse reflection spectra at room temperature. Full line: $CaCrO_4$, dotted line: KBr/K_2CrO_4 , broken line with dots: MgO/K_2CrO_4

absorption edges of these compounds are 280 and 450 nm.

4. Discussion

Ziegler et al [9] calculated an energy level scheme for the CrO_4^{2-} complex. This has been used successfully to explain the luminescence properties of closed-shell transition-metal oxocomplexes [1,3,6]. The excited state $t_1^5 e^1$ yields four energy levels, viz. $^1T_2 \gg ^1T_1 \gg ^3T_2 > ^3T_1$. Luminescence occurs from the lower triplet level 3T_1 .

From the measured decay times and quantum efficiencies the radiant decay time is estimated to be 10 ms. This is well in line with the spin- and orbital-forbidden character of the emission transition ($^3T_1 \rightarrow ^1A_1$). Such long decay times have also been observed for the VO_4^{3-} group [6].

The excitation spectrum corresponds to the well-known absorption spectrum of the CrO_4^{2-} complex [10]. The lower bands are due to the transitions $^1A_1 \rightarrow ^1T_1$ and 1T_2 . The former transition becomes allowed by the less-than-cubic symmetry of the chromate tetrahedron in $CaCrO_4$ and KBr/K_2CrO_4 . In the latter case we were even able to resolve the vibrational structure of the $^1A_1 \rightarrow ^1T_2$ transition reported before [10].

The emission consists of a structureless band. It should be realized, however, that due to the low lumi-

nescence intensity. The optical conditions were not optimal to find vibrational structure. The Stokes shift is large enough to prevent energy migration at low temperatures [11]. It seems hard, therefore, to ascribe the luminescence to any other species than the CrO_4^{2-} complex.

These results, together with the absence of any rhenate emission, show that the transition between presence and absence of luminescence in complexes of the type under discussion lies between V and Cr, Mo and probably Tc, and W and Re in the first, second and third transition-metal series, respectively.

We are left with some intriguing questions, however. As remarked in ref [1] and confirmed in this study, the value of the quenching temperature of efficient luminescence of the oxocomplexes bears no relation to the Stokes shift. This is in contradiction with simple conclusions from a configurational-coordinate model [1]. It should be realized, however, that the Stokes shift obtained from the spectral data does not only contain the offset of the excited state relative to the ground state, but also the energy difference between the singlet and triplet levels concerned. This is because excitation is into the singlets, but emission from the triplet 3T_1 . This energy difference is not necessarily constant within the group of complexes under study, which makes further interpretation not feasible, if not impossible.

Further, one may wonder what is the reason that luminescence of the oxocomplexes is only observed for the lighter transition metals. The present results confirm an earlier suggestion [1], viz. that the probability of radiationless processes increases considerably if the excited state parabola in the configuration diagram is lowered. At the moment it does not seem possible to present a more quantitative picture.

Note, finally, that the influence of the host lattice

on radiationless processes can be explained as suggested earlier for the other oxocomplexes [1,12]. Large, monovalent ions (Na^+ , K^+) are not favourable for efficient luminescence. The Ca^{2+} ions, together with the zircon structure, are more successful in counteracting the expansion of the CrO_4^{2-} complex upon excitation. This runs parallel with a similar observation for the isoelectronic VO_3^{3-} group in this crystal structure. The observation that K_2CrO_4 does not luminesce, whereas the solid solution $\text{KBr}/\text{K}_2\text{CrO}_4$ does (and the mixture $\text{MgO}/\text{K}_2\text{CrO}_4$ does not) shows again the influence of the surroundings of the CrO_4^{2-} complex on the radiationless processes. Probably the CrO_4^{2-} complex on a substitutional Br^- site in KBr is so compressed in the ground state that not much extra space is available for the excited state [12].

References

- [1] G. Blasse, *Struct. Bonding*, to be published
- [2] A. Freiberg and L. A. Rebanc, *J. Luminescence* 18/19 (1979) 702.
- [3] G. Blasse, *Chem. Phys. Letters* 63 (1979) 441.
- [4] A. B. van Oosterhout, *J. Chem. Phys.* 67 (1977) 2412.
- [5] S. Kemmler-Sack, I. Roos, W. R. Cyrus and A. Gadani, *Z. Anorg. Allg. Chem.* 453 (1979) 153.
- [6] H. Rondé and G. Blasse, *J. Inorg. Nucl. Chem.* 40 (1978) 215.
- [7] S. C. Jain, A. V. R. Warriar and S. K. Agrawal, *Chem. Phys. Letters* 14 (1972) 211.
- [8] P. J. Miller, G. L. Cessac and R. K. Khanna, *Spectrochim. Acta* 27 (1971) 2019.
- [9] T. Ziegler, A. Rauk and E. J. Baerends, *Chem. Phys.* 16 (1976) 209.
- [10] L. W. Johnson and S. P. McGlynn, *Chem. Phys. Letters* 7 (1970) 618.
- [11] R. C. Powell and G. Blasse, *Struct. Bonding*, to be published
- [12] G. Blasse, *J. Chem. Phys.* 51 (1969) 3529.