ELSEVIER

Journal of Alloys and Compounds 224 (1995) 342–344

Journal of ALLOYS AND COMPOUNDS

The luminescence of MoO_3 and WO_3: a comparison

G. Blasse, M. Wiegel

Debye Institute, Utrecht University, Postbox 80 000, 3508 TA Utrecht, Netherlands

Received 20 December 1994; in final form 28 January 1995

Abstract

The luminescence spectra of MoO_3 and WO_3 at 4.2 K are reported. They are very different. The optical absorption edge of MoO_3 is at much higher energy than that of WO_3. The Stokes shift of the MoO_3 emission is about twice that of WO_3. The differences are discussed in terms of the different crystal structures.

Keywords: Luminescence; Stokes shift; Van der Waals gap; Crystal structure

1. Introduction

The luminescence of molybdates and tungstates have been studied a long time [1–3]. Several of these compounds ($MgWO_4$, $CaWO_4$, $CdWO_4$ [3]) show efficient luminescence and are, or have been, applied as luminescent material in several devices. The optical transitions in the molybdate and tungstate groups are of the so-called charge-transfer type and show up in the spectra as very broad bands. According to expectation the first molybdate absorption band is always at lower energy than the corresponding tungstate band.

As far as we are aware, the literature does not contain any report on possible luminescence of MoO_3 or WO_3. Only for the latter is there a report on the luminescence of ill-defined layers [4]. Since the metal-ion polyhedra are strongly coupled in these trioxides, there is reason to expect that they do not luminesce at all [3].

Usually MoO_3 is reported to be colorless, whereas WO_3 is said to be yellow, see for example Ref. [5]. This is an exceptional case, because the colors suggest that the absorption edge of MoO_3 is at higher energy than that of WO_3. This was another reason to investigate these oxides further. It turns out that their optical properties are very different indeed and that the differences can be explained by the different crystal structures.

2. Experimental

The MoO_3 was obtained from Philips Research (Eindhoven) by courtesy of Dr. M. Ouwerkerk; it has been prepared by heating high purity ammonium paramolybdate. The color of the powder is white and X-ray powder diffraction showed it to be the stable α modification of MoO_3. The WO_3 sample was prepared by drying high purity WO_3 (Merck). X-ray powder diffraction showed it to be single phase WO_3.

The optical measurements were performed using a Spex Fluorolog spectrofluorometer equipped with an Oxford helium flow-cryostat and a Perkin–Elmer Lambda 7 spectrometer.

3. Results

Both trioxides show a weak photoluminescence below 100 K. Fig. 1 shows the diffuse reflection spectra of

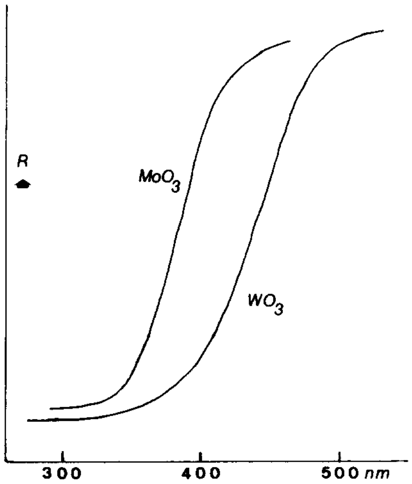

Fig. 1. Diffuse reflection spectra of MoO_3 and WO_3 at 300 K.

0925-8388/95/$09.50 © 1995 Elsevier Science S.A. All rights reserved
SSDI 0925-8388(95)01569-8

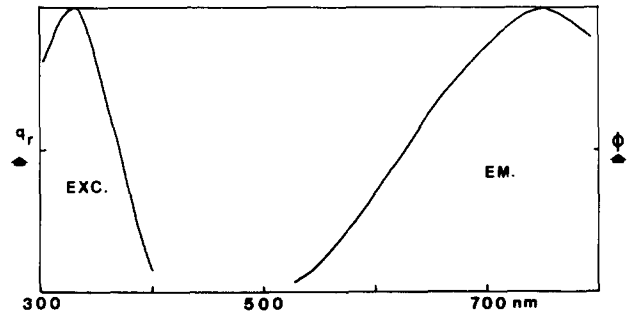

Fig. 2. Emission and excitation spectra of the luminescence of MoO_3 at 4.2 K. The parameter Φ gives the spectral power per constant wavelength interval in arbitrary units, whereas q_r gives the relative quantum output.

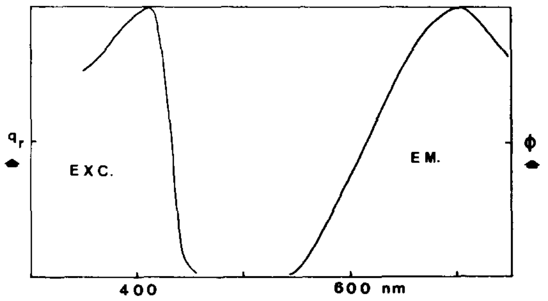

Fig. 3. Emission and excitation spectra of the luminescence of WO_3 at 4.2 K.

the two oxides at room temperature. It is clear that the optical absorption starts at lower energies (longer wavelengths) in the case of WO_3.

Fig. 2 shows the emission and excitation spectra of the luminescence of MoO_3 at 4.2 K. The excitation spectrum follows the reflection spectrum. The emission spectrum shows a maximum at about 750 nm. In view of the decreasing sensitivity of the photomultiplier in this spectral region, the real value may even be at slightly longer wavelengths. The Stokes shift of this emission is estimated to be some 16 000 cm^{-1}. At 60 K the luminescence intensity has decreased to 50% of the value at 4.2 K.

Fig. 3 shows the same data for WO_3. The emission band shows a maximum at about 700 nm, whereas the corresponding excitation maximum is at 410 nm. This yields a much smaller Stokes shift than for MoO_3, i.e. about 10 000 cm^{-1}. The temperature at which the luminescence intensity has decreased to 50% is 65 K.

4. Discussion

It has recently been argued by Mestl et al. [6] that there are two ways to interpret the complicated crystal structure of MoO_3. One is to consider MoO_6 octahedra as the building units which are interconnected in one direction by common edges and corners forming zigzag rows which are linked together by corner sharing in a perpendicular direction. The so-formed layers are stacked upon each other without having ions in common (van der Waals gap). An alternative description is based on MoO_5 polyhedra. However, a later structure analysis allows another description [7]. MoO_3 layers are separated by a van der Waals gap of about 700 pm. Each Mo^{6+} ion has four neighbors at distances ranging from 167 to 195 pm. The other two completing the octahedron are at 225 and 233 pm. In all descriptions the Mo–O bond pointing to the van der Waals gap is the shortest one, as is to be expected, since the oxygen involved has only one molybdenum neighbor. The tetrahedra are connected by sharing two oxygen corners to form chains. The angle Mo–O–Mo is about 140°.

The latter structure description seems to be the more suitable one to understand the relatively high energy position of the absorption edge. It is reasonable to assume that the bonds with the shorter Mo–O distances play the more important role. The 140° angle prevents favorable wavefunction overlap, so that the tetrahedra remain more or less electronically isolated. In fact the absorption edge of MoO_3 is at only some 5000 cm^{-1} lower energy than in $CaMoO_4$ with isolated and regular tetrahedra [1]. For comparison, the value of this difference is about 16 000 cm^{-1} for WO_3 and $CaWO_4$.

The low energy position of the absorption edge of WO_3 is ascribed to energy band broadening which is not unexpected in a perovskite-like crystal structure with corner sharing tungstate octahedra [3]. The exceptional difference between the optical absorption of MoO_3 and WO_3 is, therefore, ascribed to the difference in crystal structure. In MoO_3 the molybdate polyhedra remain electronically isolated, whereas the tungstate polyhedra do not.

With this in mind, we turn now to the emission. The emission band of MoO_3 shows a Stokes shift of about 16 000 cm^{-1}. This is actually a characteristic value for the Stokes shift of the tetrahedral molybdate group luminescence [1–3]. That of the octahedral molybdate group luminescence is considerably smaller, i.e. about 8000 cm^{-1} [8]. This confirms the description of MoO_3 as consisting of molybdate tetrahedra.

The low efficiency and quenching temperature of this molybdate emission is undoubtedly due to the energy position of the first excitation band, which lies lower than for $CaMoO_4$, in which compound thermal quenching of the luminescence starts at 200 K [1]. Lowering of the energy levels leads to a drastic increase of the role of radiationless transitions [3].

It should be remarked that there are also other ways possible to describe this luminescence. For example, $K_2MoO_2F_4 \cdot H_2O$ shows an emission band with a maximum at 680 nm and an excitation band at about 330 nm [9]. This luminescence is due to the MoO_2 group, but is very similar to that of MoO_3. Large Stokes shifts have also been observed for the luminescence of

Table 1
Some data on the luminescence of perovskite-like compounds with an octahedrally coordinated d^0-ion; all values for 4.2 K

Compound	Excitation maximum (nm)	Emission maximum (nm)	Stokes shift (10^3 cm^{-1})	[a] T_q (K)	Reference
$SrTiO_3$	380	500	7	35	[12]
$BaTiO_3$	340	490	9	45	[10]
$KNbO_3$	335	530	11	35	[13]
$KTaO_3$	330	490	10	35	[13]
NbO_2F	370	500	8	–	[14]
TaO_2F	365	500	8.5	–	[14]
WO_3	410	700	10	65	This work

[a] Quenching temperature as defined in the text.

$M(d^0)$–O groups with short bonding distances like titanyl [10]. Therefore, it cannot be excluded that there are even less than four oxygens of the molybdate polyhedron in MoO_3 involved in the luminescence process. Ab-initio calculations for the case of isoelectronic vanadate have confirmed this view [11].

The luminescence of WO_3 is of a different nature, as is already clear from the much smaller Stokes shift. In Table 1 we have compiled some data on the luminescence of perovskite-like compounds containing octahedra with a central ion with d^0 configuration. Given the nature of the d^0-ion octahedron, the absorption edges (approximately equal to excitation maxima) are all at relatively low energy [1–3]. The similarity between isostructural and isoelectronic NbO_2F, TaO_2F and WO_3 is striking. The emission is usually ascribed to a self-trapped exciton on the d^0-ion octahedron [3,12,13]. At higher temperatures the exciton becomes mobile and migrates to quenching centers. In MoO_3 this is not possible due to the large Stokes shift of the emission. The structural difference between MoO_3 and WO_3 has a striking consequence for their luminescences, which are also different: that of MoO_3 corresponds to a more localized situation than that of WO_3.

Finally we note that the spectral data for WO_3 show a certain similarity to those of the $[W_{10}O_{32}]^{4-}$ complex in which corner sharing of tungstate octahedra also occurs. The complex emits with an emission maximum at 660 nm, but the Stokes shift of this emission is 25% larger than in the case of WO_3 [15].

References

[1] F.A. Kröger, *Some Aspects of the Luminescence of Solids*, Elsevier, Amsterdam, 1948.

[2] G. Blasse, *Struct. Bonding, 42* (1980) 1.

[3] G. Blasse and B.C. Grabmaier, *Luminescent Materials*, Springer, Berlin, 1994.

[4] C. Paracchini and G. Schianchi, *Phys. Status Solidi A:, 72* (1982) K129.

[5] *Handbook of Chemistry and Physics*, Chemical Rubber, Cleveland, OH, USA.

[6] G. Mestl, P. Ruiz, B. Delmon and H. Knözinger, *J. Phys. Chem., 98* (1994) 11269.

[7] L. Kihlborg, *Ark. Kemi, 21* (1963) 357.

[8] M. Wiegel and G. Blasse, *J. Sol. State Chem., 99* (1992) 388.

[9] M.F. Hazenkamp, E.H. Voogt and G. Blasse, *J. Sol. State Chem., 101* (1992) 26.

[10] B. Bouma and G. Blasse, *J,. Phys. Chem. Sol., 56* (1995) 261.

[11] M.F. Hazenkamp, F.B. van Duijneveldt and G. Blasse, *Chem. Phys., 169* (1993) 55.

[12] L.G.J. de Haart, A.J. de Vries and G. Blasse, *J. Sol. State Chem., 59* (1985) 291.

[13] M. Wiegel, M.H.J. Emond, E.R. Stobbe and G. Blasse, *J. Phys. Chem. Sol., 55* (1994) 773.

[14] G. Blasse, G.J. Dirksen, M.P. Crosnier-Lopez and J.L. Fourquet, *Sol. State Commun., 90* (1994) 595.

[15] T. Yamase and M. Sugeta, *J. Chem. Soc. Dalton Trans.*, (1993) 759.