THE LUMINESCENCE OF MAGNESIUM TUNGSTATE DIHYDRATE, $MgWO_4 \cdot 2H_2O$

G. Blasse, G.J. Dirksen, M. Hazenkamp and J.R. Günter*

Physical Laboratory, University of Utrecht
P.O. Box 80.000, 3508 TA Utrecht, The Netherlands

*Institute for Inorganic Chemistry, University of Zürich
Winterthurerstrasse 190, CH-8057 Zürich, Switzerland

ABSTRACT

The luminescence of $MgWO_4 \cdot 2H_2O$ contains two emission bands, one due to the tungstate tetrahedron, and another one related to the hydrate group. The former is compared with the tungstate luminescence of anhydrous $MGWO_4$.

MATERIALS INDEX: tungstates, magnesium

## Introduction

The wolframite modification of $MgWO_4$ is known to be an efficient luminescent material (1). The optical transitions involved occur in the tungstate group and are of the charge-transfer type (2). Recently, Günter and Dubler (3) have reported the crystal structure of the dihydrate of $MgWO_4$ ($MgWO_4 \cdot 2H_2O$). The latter structure contains tungstate tetrahedra, whereas the wolframite modification has tungstate octahedra which form zig-zag chains by edge sharing. In view of this structural difference, it seemed interesting to investigate the luminescence properties of the dihydrate and to compare them with those of the $MgWO_4$ wolframite phase. In fact, they turn out to be different.

## Experimental

Samples of the dihydrate were prepared as described before (3). Anhydrous $MgWO_4$ was prepared by a solid-state reaction following ref. 1.
An anhydrous $MgWO_4$ sample was obtained by firing the dihydrate at 500°C. This transforms into wolframite by firing above 650°C, but below 1200°C. These observations were described in (3). Samples were checked by X-ray powder diffraction. The optical instrumentation has been described previously (4).

## Results

The $MgWO_4 \cdot 2H_2O$ samples show a luminescence of a complicated nature. Figure 1 gives a survey of the spectral data. At room temperature we observe
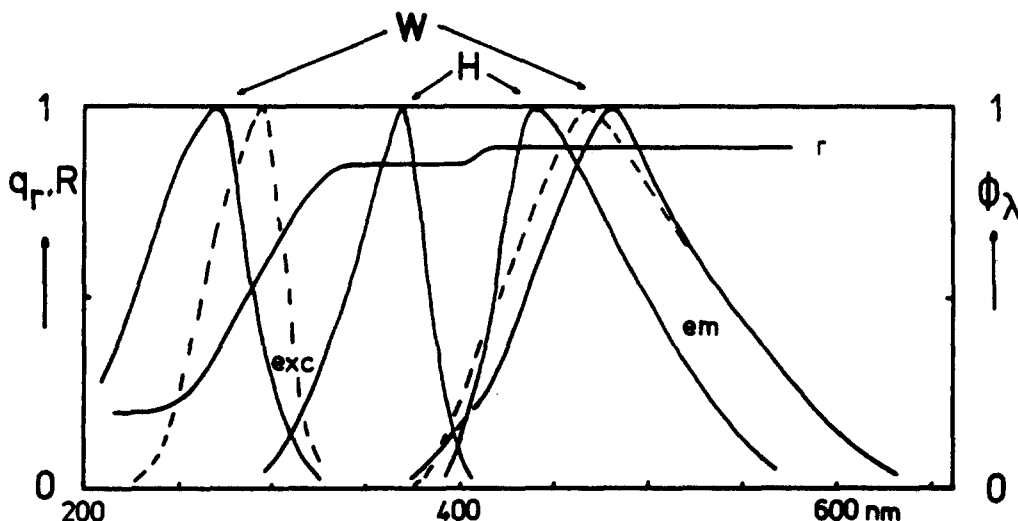
FIG. 1

Luminescence spectra of wolframite $MgWO_4$ (broken lines) and $MgWO_4 \cdot 2H_2O$ (solid lines) at 4.2 K.  r gives the diffuse reflection spectrum of $MgWO_4 \cdot 2H_2O$.  H indicates the emission and excitation spectra of the H luminescence, and W the emission and excitation spectra of the W luminescence of $MgWO_4 \cdot 2H_2O$.  $q_r$ gives the relative quantum output and $\phi_\lambda$ the spectral radiant power per constant wavelength interval, both in arbitrary units.  R gives the reflection.

only a blue emission with an emission band maximum at 440 nm.  The Stokes shift is small:  the corresponding excitation maximum is at 370 nm.  This emission will be designated as H luminescence.  Note also in Fig. 1 that the absorption strength in the area of H luminescence excitation is weak.  The transition is either forbidden, or the center concentration is small.  Since the H luminescence disappears upon dehydration, its origin should be related to the presence of the water molecules.

Below 200 K another luminescence occurs, here designated as W luminescence.  Its emission band has a maximum at 480 nm, the corresponding excitation band at 270 nm.  This excitation band coincides with the strong absorption band in the diffuse reflection spectrum (Fig. 1).  The Stokes shift is large, viz. 17.000 $cm^{-1}$.  This luminescence is ascribed to the tungstate group in $MgWO_4 \cdot 2H_2O$.  The two emission bands can be recorded separately by selective excitation (e.g., 360 and 260 nm).  The excitation spectra below 200 K consist always of a mixture of the two excitation bands, because the emission bands overlap strongly.  There was no clear evidence for energy transfer between the two luminescent centres.

The dihydrate was dehydrated at 500°C which leads to a topotactical formation of the metastable high-temperature modification of $MgWO_4$ (3).  Its structure is unknown.  This sample did not show luminescence at room temperature.  Actually Kröger (1) reports the same for high-temperature $MgWO_4$ (called by him $\alpha-MgWO_4$).  At low temperatures we observed the same luminescence charac-

teristics for the metastable modification as Kröger reported for the high-temperature modification.  These are not discussed here any further, because the crystal structure is unknown.

At higher temperatures the metastable modification transforms into the wolframite modification (3). This sample, and the one made directly via solid-state reaction, show the very efficient $MgWO_4$ luminescence reported long ago (1).  In order to facilitate the comparison, the emission and excitation spectrum of this luminescence is also given in Fig. 1.  It resembles the W luminescence, but the Stokes shift is smaller.  Table I summarizes some of the experimental results.

TABLE I

Some data on the luminescence of several magnesium tungstates
and other tungstates with tetrahedral tungstate groups.

| Composition | | Excitation maximum (nm) | Emission maximum (nm) | Stokes shift $(10^{-3} \ cm^{-1})$ | Ref. |
|---|---|---|---|---|---|
| $MgWO_4 \cdot 2H_2O$ | H | 370 | 440 | 5.0 | * |
| | W | 270 | 480 | 17.0 | * |
| $MgWO_4$ (wolframite) | | 295 | 470 | 13.5 | * |
| $MgWO_4$ (high temp.) | | ~275 | 420 | 12.5 | 1 |
| $SrWO_4$ | intr. | 245 | 460 | 19.5 | 8 |
| | extr. | ~260 | 530 | 20.0 | 8 |
| $GdWO_4Cl$ | | 275 | 485 | 16.0 | 9 |

*This work

## Discussion

### The H luminescence of $MgWo_4 \cdot 2H_2O$

In view of the small value of the Stokes shift of the H luminescence and its disappearance upon dehydration, it is obvious that it is related to the water molecules, and not to the tungstate group.  The crystal structure of $MgWO_4 \cdot 2H_2O$ is built up from $MgO_4(H_2O)$ octahedra and $WO_4$ tetrahedra (3), i.e., the water molecules are coordinated to the magnesium ions.  A very similar structure has been reported for $ZnMoO_4 \cdot 2H_2O$ (5).  There it is proposed that hydrogen bridges are formed with the oxygen ion of the molybdate group that is coordinated to molybdenum only.  It seems likely that a similar situation occurs in $MgWO_42H_2O$.

The blue H luminescence has been observed in many other systems containing more or less water.  Some examples are listed in (6).  Recently, McGlynn et al. (7) have reconsidered all the assignments made before and concluded that they are not convincing.  Their own proposal, viz. an exciplex of a hydrogen atom with water, $[(H_2O)_n H \cdot]^*$, is tentative.

The hydrogen positions in this crystal structure not being known, and the nature of the emission being under discussion, we refrain here from further discussion.

The H luminescence of $MgWO_4 \cdot 2H_2O$

There cannot be any doubt that the W luminescence is due to the tungstate tetrahedron of $MgWO_4 \cdot 2H_2O$. This tetrahedron has three types of oxygens at the corners, viz. O(4) with W-O 1.827Å, belonging also to two magnesium octahedra which are edge shared; O(1) with W-O 1.760 Å and O(2) with W-O 1.746 Å, each belonging also to one magnesium oxtahedron, O(3) with W-O 1.759 Å which does not belong to any other polyhedron (3). If O(3) would be terminal, the W-O distance is expecetd to be shorter. This favours the hydrogen bonding suggested above.

The position of the absorption and excitation bands of the tungstate tetrahedron is at relatively low energy compared with other $WO_4^{2-}$ tetrahedra. Table I compares with $SrWO_4$, where not only the oxygen-deficient $WO_3$ group (8). The comparison shows the large Stokes shift for the $WO_4^{2-}$ tetrahedron, which is characteristic for this coordination (2). The lower-energy position in the case of $MgWO_4 \cdot 2H_2O$ may be due to the unsaturated character of the O(3) ion, but this is hard to evaluate since the hydrogen positions are not known. For the luminescence of $GdWO_4Cl$ which also has $WO_4$ tetrahedra, very similar spectral data have been observed (see Table I, ref. 9). This tetrahedron is more or less comparable with the one in $MgWO_4 \cdot 2H_2O$, since 2 oxygens are oversaturated (1W and 2Gd neighbours) and 2 oxygens are undersaturated (1W and 1Gd neighbours) (10). Also the distances are comparable, viz. 1.80 Å and 1.76 Å, respectively.

Efficient $WO_4^{2-}$ luminescence at room temperature has been observed for $CaWO_4$ which has a Stokes shift of 1600 $cm^{-1}$ (1). The low quenching temperature of the $SrWO_4$ emission is due to the larger Stokes shift, that of $MgWO_4 \cdot 2H_2O$ to the lower energy position (11). There are no indications that the high-frequency OH vibrations lead to a marked lowering of the quenching temperature. This is not too surprising since the water molecules coordinate the $Mg^{2+}$ ions, and not the $W^{6+}$ ions (3). The luminescence of $GdWO_4Cl$, with comparable spectral positions, has a quenching temperature which is also comparable to that of $MgWO_4 \cdot 2H_2O$, viz. 200 K (9).

The luminescence of the dehydrated samples

It is satisfying to find a similar luminescence for the metastable high-temoperature form as observed previously for the high-temperature form. Also their X-ray powder diffraction data are similar (3).

This metastable phase transforms above 650°C to wolframite $MgWO_4$, which shows luminescence properties similar to those reported before (1). The Stokes shift has decreased relative to $MgWO_4 \cdot 2H_2O$ (see Table I), and consequently the quenching temperature has increased considerably. The fact that the small Stokes shift of (metastable) high-temperature $MgWO_4$ does not yield efficient room-temperature luminescence points to delocalisation of the excited state (12).

In conclusion, we have described the luminescence of the dihydrate of $MgWO_4$ and of the dehydrated modifications. Our fundamental knowledge about this luminescence is still so restricted that only qualitative comparisons can be made.

References

1.    F.A. Kröger, Some Aspects of the Luminescence of Solids, Elseviers Publ. Co., Amsterdam (1948).

2.  G. Blasse, Structure and Bonding 42, 1 (1980).

3.  J.R. Günter and E. Dubler, J. Solid State Chem. 65, 118 (1986).

4.  A. Wolfert, E.W.J.L. Oomen and G. Blasse, J. Solid State Chem. 59, 280 (1985).

5.  J.Y. le Marouille, O. Bars and D. Grandjean, Acta Cryst. B36, 2558 (1980).

6.  S.O. Cholakh and G. Blasse, J. Solid State Chem. 46, 139 (1983).

7.  T.L. Mathers, R.V. Nauman and S.P. McGlynn, Chem. Phys. Lett. 126, 408 (1986).

8.  G. Blasse and W.J. Schipper, Phys. Stat. Sol(a) 25, K163 (1974).

9.  G. Blasse and L.H. Brixner, J. Solid State Chem. 47, 368 (1983).

10. L.H. Brixner, H.Y. Chen and C.M. Foris, Mat. Res. Bull. 12, 1545 (1982).

11. K.C. Bleijenber and G. Blasse, J. Solid State Chem. 28, 303 (1979).

12. G. Blasse, J. Solid State Chem., in press.