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SHORT COMMUNICATION

$Ba_2WO_3F_4$, A NEW FLUOROTUNGSTATE WITH HIGH LUMINESCENCE EFFICIENCY

G. BLASSE, H.C.G. VERHAAR and M.J.J. LAMMERS

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

G. WINGEFELD and R. HOPPE

Institut für Anorganische und Analytische Chemie, Justus-Liebig Universität, D-6300 Giessen, FRG

P. DE MAAYER

Agfa-Gevaert N.V., B-2510 Mortsel, Belgium

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$Ba_2WO_3F_4$ is an efficient luminescent material under UV and X-ray excitation. The luminescence properties show a similarity with those of the tungstates, especially $MgWO_4$.

1. Introduction

The luminescence of tungstates is well known since a long time and was reviewed by one of us [1]. Up until now only oxytungstates have been reported as luminescent materials. New fluorotungstates were obtained recently by one of us [2]. Among these is $Ba_2WO_3F_4$. Since bariumtungstates show only weak luminescence, even down to liquid helium temperature [3,4], we were surprised to find that $Ba_2WO_3F_4$ is an efficient phosphor. Its properties are described in this short communication.

2. Experimental

Samples were prepared as described in ref. [2]. The performance of the optical measurements has been described before [5].

3. Results and discussion

$Ba_2WO_3F_4$ shows an efficient blue–green emission under UV and X-ray excitation at room temperature and below. Fig. 1 shows the emission spectrum

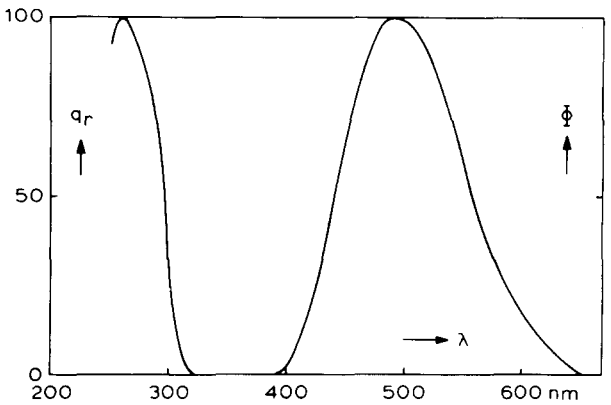

Fig. 1. Emission and excitation spectra of the luminescence of $Ba_2WO_3F_4$ at LHeT. Φ gives the radiant power per constant wavelength interval in arbitrary units; q_r gives the relative quantum output.

at LHeT under photoexcitation. The corresponding excitation spectrum is in the same figure. Especially at LHeT we noted a slight dependence of the emission maximum on the excitation wavelength: for example 485 nm for 260 nm excitation and 505 nm for 305 nm excitation. At room temperature all spectra shift slightly (5–10 nm) to longer wavelength. The emission spectrum under X-ray excitation is the same as under photoexcitation (at room temperature). The quantum efficiency for photoexcitation at 300 K was found to be about 75% by comparison with standard phosphors.

These spectra are characteristic of the luminescence of the tungstate group [1]. After excitation a strong lattice relaxation occurs resulting in a broad emission band with a large Stokes shift. The spectra of $Ba_2WO_3F_4$ are very similar to those of $MgWO_4$, when position, halfwidth and quenching temperature are compared. In fact there is also a structural analogy. The crystal structure of $MgWO_4$ contains tungstate chains by edge-sharing of tungstate octahedra. In this way every W^{6+} ion is coordinated by four O^{2-} ions which coordinate two W^{6+} ions and two O^{2-} ions which coordinate only one W^{6+} ion. Since the chains are zigzag, the latter O^{2-} ions are in a cis-position. In $Ba_2WO_3F_4$ there are linear chains of WO_4F_2 octahedra [6]. These octahedra share corners via O^{2-} ions. Further, there are two F^- ions and two O^{2-} ions, both in cis-position, which coordinate only one W^{6+} ion. The emitting state is in both compounds located in the "WO_2(cis)-group", because this group contains the less-stabilized anion orbitals [1]. Charge transfer from F^- to W^{6+} is at much higher energy than from O^{2-} [7]. The O^{2-} ions which coordinate two W^{6+} ions are more stabilized than those which coordinate only one W^{6+} ion.

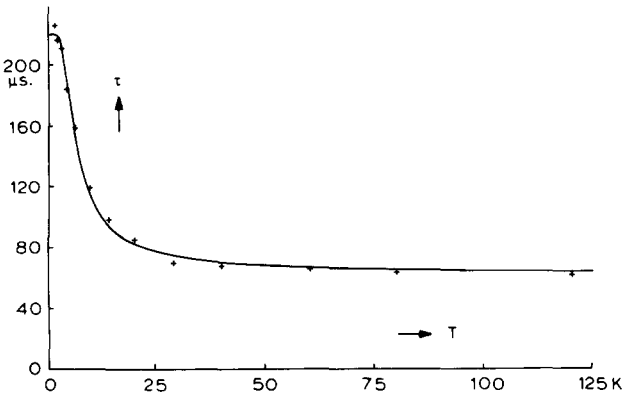

Fig. 2. Decay times of the luminescence of $Ba_2WO_3F_4$ as a function of temperature. The drawn curve was obtained with the three-level parameters given in the text.

The slight dependence of the emission spectra on excitation wavelength suggests a small amount of disorder between the O^{2-} and F^- ions which coordinate the W^{6+} ion.

Finally fig. 2 shows decay times of the emission of $Ba_2WO_3F_4$ as a function of temperature. All decay curves appeared to be exponential. The temperature dependence can be described with a three-level scheme with levels $0 < 1 < 2$ with ΔE_{21} the energy difference between levels 2 and 1, and p_{ij} the transition probability between levels i and j [8]. From the experimental data we found $\Delta E_{21} = 10\ cm^{-1}$, $p_{10} = 4.5 \times 10^3\ s^{-1}$ and $p_{20} = 3 \times 10^4\ s^{-1}$. This behavior is also typical of tungstate emission. Level 0 is the singlet ground state and levels 1 and 2 belong to the lowest excited triplet state [1]. The spin-selection rule is relaxed by strong spin–orbit coupling. One of the levels, viz. 1, acts as a shallow optical trap. The splitting ΔE_{21} is due to spin–orbit interaction.

In conclusion we have found a new type of tungstate with high luminescence efficiency. The investigations are continued.

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