

NOTE

Photoluminescence of $Ba_3W_2O_9$: Confirmation of a Structural Principle

The crystal structure of $Ba_3W_2O_9$ contains isolated $W_2O_8^{6-}$ groups. These are reported to luminesce efficiently. This shows that clusters of tungstate octahedra emit more efficiently than the isolated species.

Introduction

The crystal structure of $Ba_3W_2O_9$ has recently been described by Poepfelmeier *et al.* (1). It has the same structure as $Cs_3Ti_2Cl_9$; i.e., two-thirds of the octahedral sites between the hexagonal close-packed BaO_3 layers are filled by tungsten. In this way isolated $W_2O_8^{6-}$ groups are formed consisting of two tungstate octahedra sharing a face. This is quite exceptional in the crystal chemistry of the tungstates.

For this reason it seemed interesting to investigate the possible luminescence of $Ba_3W_2O_9$. In this laboratory we have performed extensive investigations on tungstate luminescence (see, e.g., (2)). The luminescence properties of $Ba_3W_2O_9$ proved to be very different from those of other tungstates in the system $BaO-WO_3$. The reasons for this are discussed below.

Experimental

Samples were prepared as described in Ref. (1). They were checked by X-ray analysis using $CuK\alpha$ radiation. Optical measurements were performed as described previously (3). The apparatus is a Perkin-Elmer spectrofluorimeter MPF 3 equipped with a helium cryostat. Diffuse reflection spectra were measured at room temperature on a Perkin-Elmer spectrometer EPS-3T.

Results

The compound $Ba_3W_2O_9$ shows a strong blue photoluminescence upon short-wavelength ultraviolet excitation below 150 K. The emission spectrum consists of the usual, broad-band emission found for many tungstates (4). The maximum of this band is situated at about 460 nm at 5 K. At 80 K it tends to shift to a wavelength longer by a few nanometers. The main excitation band peaks at about 280 nm at 5 K with also a tendency to shift a few nanometers to longer wavelengths at 80 K. This is well in line with the diffuse reflection spectrum which indicates an optical absorption edge at 285 nm at 300 K.

The reflection spectrum shows in addition a tail in the region 310-325 nm. A different luminescence can be excited in this tail. Due to the broad-band character of the emissions involved it is very hard, however, to separate this emission from the blue emission which is observed upon 280-nm excitation. At 5 K the blue emission always dominates, but upon tail excitation it shows clearly a long-wavelength tail. At 80 K it is possible to observe this emission separately; it consists of a broad band with a maximum at about 560 nm. The excitation spectrum of the long-wavelength part of the emission (say 600 nm) shows an excitation band which coincides with the tail in the reflection spectrum.

The infrared spectrum of our samples (KBr pellets) are similar to those by Poepelmeier *et al.* (1); the absorption bands are even somewhat sharper. Further we tried to activate $\text{Ba}_3\text{W}_2\text{O}_9$ with lead and uranium. Lead was unsuccessful because it was not incorporated under the experimental conditions applied. Uranium entered the $\text{Ba}_3\text{W}_2\text{O}_9$ lattice only for a very small amount. The luminescence spectra indicate that it is mainly present in second phases, viz., $\text{Ba}_2\text{WO}_5\text{-U}$ (5) and $\text{Ba}_3\text{WO}_6\text{-U}$ (6). These were not detected by X-ray analysis. The uranium emission in $\text{Ba}_3\text{W}_2\text{O}_9$ is situated in the red spectral region (maximum at 640 nm).

Discussion

1. Structural Aspects

One of us has drawn attention to the fact that especially niobates, but also electronically similar compounds like tantalates and tungstates, tend to show clustering of the niobate, tantalate, and tungstate octahedra (7). Striking examples are Li_3NbO_4 and $\text{Mg}_4\text{Nb}_2\text{O}_9$. The former compound has an ordered rock salt structure containing tetrameric units of niobate octahedra. The latter compound has an ordered $\alpha\text{-Al}_2\text{O}_3$ structure containing $\text{Nb}_2\text{O}_9^{8-}$ groups. These consist of two face-sharing niobate octahedra and are isoelectronic with the $\text{W}_2\text{O}_9^{6-}$ group in $\text{Ba}_3\text{W}_2\text{O}_9$ if we neglect some inner shells.

Compounds of this type containing clusters of octahedra with highly charged noble gas ions proved to show exceptional optical properties. Usually they show efficient luminescence (8, 9) and high vibrational stretching frequencies (10). For the tungstates there is one example, viz., Li_4WO_5 (11). It has been suggested that the crystal structure contains edge-sharing pairs of tungstate octahedra. It luminesces efficiently.

These considerations led us to the idea that $\text{Ba}_3\text{W}_2\text{O}_9$ might luminesce efficiently in view of its crystal structure containing face-sharing tungstate octahedra. Also $\text{Mg}_4\text{Nb}_2\text{O}_9$ containing a similar group shows efficient luminescence (8, 9). We show below that the similarity with $\text{Mg}_4\text{Nb}_2\text{O}_9$ goes even further. How exceptional luminescence from $\text{Ba}_3\text{W}_2\text{O}_9$ becomes clear from a consideration of the luminescence of other barium tungstates. The scheelite BaWO_4 with isolated WO_4^{2-} tetrahedra shows only inefficient luminescence at low temperatures (4, 12). The ordered perovskite Ba_3WO_6 with isolated tungstate octahedra does not luminesce efficiently either (13). The absence of efficient luminescence has been ascribed to the nature of the Ba^{2+} ions which surround the tungstate groups. These ions are large and will not counteract the expansion of the tungstate group upon excitation. As a consequence the offset of the excited-state parabola in the configurational coordinate diagram is large, resulting in a low thermal quenching temperature of the luminescence and a relatively high probability of radiationless transitions. The analogous calcium compounds (CaWO_4 and Ca_3WO_6) are in fact efficient luminescent materials. The high efficiency of the luminescence of $\text{Ba}_3\text{W}_2\text{O}_9$ confirms that condensation of octahedral tungstate (niobate) octahedra will result in tungstate luminescence with high efficiency. The harmful influence of barium is still noticeable from the value of the quenching temperature of the $\text{Ba}_3\text{W}_2\text{O}_9$ luminescence. For a barium compound it is a high value, but considerably higher values are known for other compounds (4). Finally we note that Ba_2WO_5 , the structure of which is unknown, did not show efficient luminescence.

2. Luminescence

The optical transitions in the tungstate group responsible for the luminescence are

of the charge-transfer type. Since their exact nature is not even known for the simple tetrahedral and octahedral group (2) we refrain from further discussion. The additional optical absorption in the region 310–325 nm and the corresponding emission around 560 nm will not be due to intrinsic $W_2O_9^{2-}$ groups in the crystal structure of $Ba_3W_2O_9$. Additional absorption and emission has been observed in many tungstates and is usually ascribed to tungstate groups near defects (see, e.g., Ref. (12)). Similar phenomena have been observed for $Mg_4Nb_2O_9$ by Macke (9). He ascribed this additional emission to partial disorder of the Mg^{2+} and Nb^{5+} ions on the ordered cation sites. Such a disorder, or the possibility of stacking faults in the BaO_3 layer sequence, may explain why we observe the additional absorption and emission bands.

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G. BLASSE
G. J. DIRKSEN

*Solid State Chemistry Department
Physical Laboratory, State University
P.O. Box 80.000, 3508 TA Utrecht
The Netherlands
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