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The Luminescence of Ba_2TiO_4, a Compound with Titanate Tetrahedra

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The luminescence of Ba_2TiO_4, the only compound with TiO_4 tetrahedra, is reported and discussed. The quantum efficiency is low. The reason for this is discussed in relation to the luminescence of isoelectronic complexes. © 1995 Academic Press, Inc.

INTRODUCTION

The luminescence of compounds containing complexes consisting of a central ion with p^6d^0 electron configuration and O^{2-} ligands, is well known and has been studied extensively (1–3). Here we denote these species as d^0 complexes. Examples are $CaWO_4$, YVO_4, $MgWO_4$, and $YTaO_4$. These examples have all been used in several applications, luminescent lighting, cathode-ray tubes, and X-ray imaging (3).

Luminescence has been reported for complexes of all the early transition metal ions in such a complex, viz. Sc, Ti, V, Cr, Y, Zr, Nb, Mo, Hf, and Ta (2–5). In some cases complexes with several coordinations were found to be luminescent, e.g., NbO, NbO_4, and NbO_6 with coordinations 1, 4, and 6, respectively (2, 6, 7). It is therefore surprising that the tetrahedral TiO_4 group has hardly been studied. Kröger (1) reports on titanium-activated silicates, but his titanium concentrations are so high that it is hard to imagine that the Ti^{4+} ions are all in the Si^{4+} sites in the host lattice. His results are very qualitative and variable.

In order to fill this gap we decided to study the luminescence of Ba_2TiO_4. This is, as far as we know, the only titanate which has the Ti^{4+} ions exclusively on tetrahedral sites. Its crystal structure can be derived from that of β-K_2SO_4 (8). Further, Ba_2SiO_4 has the β-K_2SO_4 structure (8), so that by studying Ba_2SiO_4:Ti it is also possible to obtain the properties of the isolated species without changing the crystal structure.

EXPERIMENTAL

Samples were prepared by firing $BaCO_3$ and TiO_2 in the required proportions at 1200°C. They were checked by X-ray diffraction and were found to be of a single phase. In some samples a small part of Ba was replaced by Pb, in others Ti was replaced for the most part by Si. Starting materials were then $PbSO_4$ or SiO_2.

The luminescence measurements were performed by using a Spex Fluorolog spectrofluorometer equipped with double monochromators and a liquid helium cryostat. Diffuse reflection spectra were measured on a Perkin–Elmer Lambda 7 spectrometer equipped with a diffuse reflection unit.

RESULTS

None of the samples showed photoluminescence at room temperature. At liquid helium temperature we observed a very weak emission. For Ba_2TiO_4 the emission and excitation spectra at 4.2 K are given in Fig. 1. As usual for titanates, the spectral bands are broad. The emission band has its maximum at 480 nm, the corresponding excitation band peaks at 320 nm. This corresponds to the absorption edge in the diffuse reflection spectrum. These results imply that the Stokes shift is about 11,000 cm^{-1}. For $Ba_2Si_{0.99}Ti_{0.01}O_4$ the results are essentially the same.

By comparing with standard phosphors (9) we estimate the quantum efficiency of these luminescences to be 1% or even lower. Kröger (1) observed that the introduction of lead into weakly emitting $BaMoO_4$ and $BaWO_4$ improved the luminescence efficiency. The same effect occurs for $SrTiO_3$ upon replacing Sr by Pb (10). For this reason we replaced a small percent of the barium in Ba_2TiO_4 by lead. This leads to an additional absorption at longer wavelengths than the absorption edge in the

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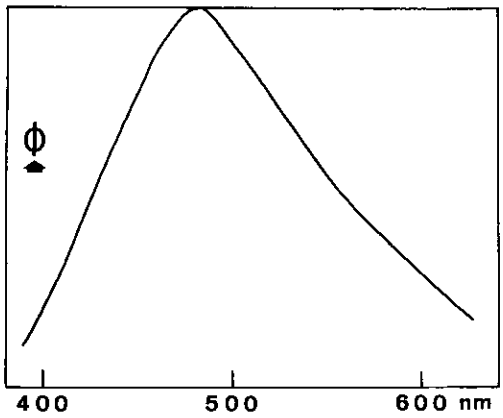

FIG. 1. Spectral energy distribution of the emission of Ba_2TiO_4 at 4.2 K. Excitation wavelength 300 nm.

diffuse reflection spectrum. Excitation into this region does not lead to luminescence, nor is the overall efficiency of the luminescence of this sample higher than that of those without lead.

DISCUSSION

Although the luminescence intensity is disappointing, the results are interesting for several reasons.

First, we note that the titanate tetrahedra in Ba_2TiO_4 are not only isolated from each other in the crystal–chemical sense (i.e., they do not share oxygen ions), but also electronically, since the optical spectra are the same for Ba_2TiO_4 and Ba_2SiO_4: Ti. The same has been observed for $CaWO_4$ and $CaSO_4$: W, but not for YVO_4 and YPO_4: V, where a spectral shift of about 5,000 cm^{-1} is observed in the excitation spectra (11). Obviously the presence of two large Ba^{2+} ions per titanate tetrahedron in Ba_2TiO_4 is enough to isolate the tetrahedra electronically.

Second, we note that the first absorption band of the TiO_4 group in Ba_2TiO_4 is at relatively low energy (~31,000 cm^{-1}). For the isolated TiO group it is at about 35,000 cm^{-1} (7), for the TiO_6 octahedron in Mg_2SnO_4 it is at 40,000 cm^{-1} (12), and in La_2MgSnO_6 it is at 38,000 cm^{-1} (13). This is different from the situation for the complexes containing Nb^{5+} or W^{6+} (2). The low-energy position in the case of Ba_2TiO_4 is obviously due to the presence of many large ions (Ba^{2+}) in this oxidic lattice. As a result the potential on the oxygen ions will be low, so that charge transfer from oxygen to titanium is expected at relatively low energy (14). It becomes clear that this is an important effect from the much higher absorption position of the VO_4 tetrahedron in YPO_4 (~37,000 cm^{-1}, Ref. 11), whereas it is expected at lower energy due to the formal 5+ charge of vanadium.

Third, we wonder why the luminescence efficiency in Ba_2TiO_4 is so low, even at 4.2 K. In view of the results for Ba_2SiO_4: Ti, concentration quenching can be excluded. It has to be realized that the luminescence of these d^0 complexes is not well understood at all. It has been suggested long ago that it is possible to describe their luminescence properties with a simple single-configurational coordinate diagram (15). However, the structure of the relaxed excited state is more complicated than that, as has been shown especially by the work of Van der Waals' group on tetrahedral complexes (16). Nevertheless there cannot be much doubt that the conditions for efficient luminescence from d^0 complexes are those which follow from the configurational coordinate diagram and which have a rather general validity (3, 15), viz.

–the emitting state should be at high energy

–the surroundings of the luminescent complex should be "stiff", i.e., there should be no large and/or low-charged metal ions present.

The Ba_2TiO_4 case does not satisfy these conditions: the Ba^{2+} ions are very large, and the emitting state is at relatively low energy. In Table 1 we have gathered some data to illustrate this further for other tetrahedral d^0 complexes. It is clear that large surroundings cations with low charge have a detrimental influence on the luminescence efficiency. The single configurational coordinate diagram predicts simultaneously a larger Stokes shift (3), and the data suggest that this is the case. It is not clear why $CaWO_4$ shows its excitation maximum at lower energy than $BaWO_4$ and Na_2WO_4. Simple rules (see above) predict the reverse. This also shows that, although a condition for efficient luminescence is a high-energy position of the emitting level, this is not sufficient in itself. However, how essential this high-energy position is becomes clear from the fact that the yellow chromate ion (CrO_4^{2-}) luminesces only weakly at 4.2 K, and the purple permanganate ion (MnO_4^-) does not luminesce at all (19).

For the octahedral complexes the situation is similar (20), but often obscured by other effects due to interaction between the complexes (energy band broadening, see Refs. (21, 22)).

Finally the question arises whether the tetrahedral TiO_4 group can luminesce efficiently at all. In connection with the samples under study, it is interesting to note that Kröger (1) reports efficient blue luminescence for $BaSiO_3$: Ti under short wavelength ultraviolet excitation. In the crystal structure there are corner-sharing silicate chains, so that each SiO_4 tetrahedron will have two Si–O distances ending on bridging oxygens and two ending on terminal oxygens (distances 1.66 and 1.59 Å, respectively, Ref. (23)). It was shown before that these terminal oxygens tend to improve the luminescence considerably. In $MgWO_4$, $Ba_2WO_3F_4$, and $Ba_2MoO_3F_4$ (24, and references cited) a similar configuration is found and yields efficient luminescence. The same structural situation occurs in $Li_2Si_2O_5$ and $Na_2Si_2O_5$ (25), host lattices in which the Ti^{4+}

TABLE 1
Some Data on the Luminescence of Tetrahedral d^0 Complexes

Composition	Luminescent complex	Excitation maximum (10^3 cm^{-1})	Emission maximum (10^3 cm^{-1})	Stokes shift (10^3 cm^{-1})	Luminescence efficiency (300 K)	Ref.
$Y(P,V)O_4$	VO_4^{3-}	37	24	13	High	(11)
$Sr_3\{(P,V)O_4\}_2$	VO_4^{3-}	36	24	12	Low	(11)
Li_3VO_4	VO_4^{3-}	34	18	16	0[a]	([b])
$CaWO_4$	WO_4^{2-}	40	24	16	High	(1)
$BaWO_4$	WO_4^{2-}	42	22	20	0[c]	(1, 17)
Na_2WO_4	WO_4^{2-}	41	20,5	~20	0[c]	(18)
$CaMoO_4$	MoO_4^{2-}	34	18,5	15,5	Medium	(1)
$BaMoO_4$	MoO_4^{2-}	35,5	—	—	0	(1)

[a] At 40 K the luminescence intensity has dropped to 50%.
[b] M. Wiegel and G. Blasse, unpublished results.
[c] Weak luminescence at 4.2 K.

ion on silicon sites has also been reported to show an efficient luminescence (1). Actually, the Ti–O group (sometimes called titanyl group) is the most extreme example of this situation, now with one terminal oxygen ion. It often shows a very intense luminescence (7, 26).

In order to check Kröger's information (1), we also prepared and investigated the composition $BaSi_{0.99}Ti_{0.01}O_3$. It shows a luminescence of reasonable efficiency. The emission band has its maximum at 490 nm, the corresponding excitation band is at about 250 nm, which yields a very large Stokes shift, i.e., close to 20,000 cm^{-1}. This confirms that asymmetric coordination of the d^0 ion improves the luminescence efficiency and increases the value of the Stokes shift, the titanyl group being the most extreme example.

Also Zn_2SiO_4:Ti yields efficient luminescence from a tetrahedral titanate group. The emission peaks at about 390 nm (1). Unfortunately this system is not suitable for further analysis, since the host lattice absorbs at energies below the titanate absorption band. Nevertheless the emission maximum increased by a Stokes shift of about 10×10^3 cm^{-1} would bring the corresponding absorption band at a position comparable to that of the VO_4^{3-} group in YPO_4 (see Table 1), so that this system seems to follow the conditions formulated above.

It is clear that the introduction of lead into Ba_2TiO_4 does not improve the low luminescence efficiency. We ascribe this to the fact that the additional absorption in the reflection spectrum is situated around 350 nm, which is too low a value to expect efficient luminescence. In $BaWO_4$ the Pb^{2+} ion induces an extra absorption region at about 260 nm, and the efficiency of the luminescence is drastically increased (1).

In conclusion, the conditions for efficient luminescence from tetrahedral d^0 complexes are a high-energy position of the emitting level and highly charged metal ions around the complex. However, when the tetrahedra in the host lattice are no longer isolated from each other, i.e., when they share oxygen ions, efficient luminescence seems to be possible. This situation may easily occur for tetravalent central metal ions, but for penta- and hexavalent ions it is more exceptional.

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