

THE LUMINESCENCE OF COMPOUNDS WITH  $\text{Bi}_2\text{O}_2^{2+}$  LAYERS

G. Blasse and G.J. Dirksen  
Physics Laboratory, University of Utrecht  
P.O. Box 80.000, 3508 TA Utrecht  
The Netherlands

and

C. Greaves and S.K. Blower  
Dept. of Chemistry, University of Birmingham  
Birmingham B15 2TT, UK

(Received July 28, 1988; Communicated by W.B. White)

**ABSTRACT** The luminescence of the compounds  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  is reported and compared with that of  $\text{BiOCl}$ . Differences are related to changes in the axial neighbours of the  $\text{Bi}^{3+}$  ion.

**MATERIALS INDEX:** bismuth, carbonates

Introduction

The crystal structure of  $\text{BiOCl}$  is a well-known type of layer structure consisting of  $\text{Bi}_2\text{O}_2^{2+}$  layers and double  $\text{Cl}^-$  layers (1). The luminescence of  $\text{Bi}^{3+}$  in  $\text{BiOCl}$  and the isomorphous host lattices  $\text{LnOCl}$  ( $\text{Ln} = \text{La}, \text{Gd}, \text{Y}$ ) has been investigated some years ago (2). This reference reviews also the literature on this subject.

It is well known that many other bismuth (and lanthanide) compounds have crystal structures which also contain  $\text{Bi}_2\text{O}_2$  ( $\text{Ln}_2\text{O}_2$ ) layers (3). A recent powder neutron diffraction study of  $\text{Bi}_2\text{O}_2\text{CO}_3$  (4) confirmed the presence of  $\text{Bi}_2\text{O}_2^{2+}$  and  $\text{CO}_3^{2-}$  layers. In the structurally related compound  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  the layer sequence is now  $\text{Bi}_2\text{O}_2^{2+} - \text{CO}_3^{2-} - \text{Ca}^{2+} - \text{CO}_3^{2-} - \text{Bi}_2\text{O}_2^{2+}$  (5). As a matter of fact the high- $T_c$  superconductor  $\text{Bi}_2\text{Sr}_{3-x}\text{Ca}_x\text{Cu}_2\text{O}_{8+y}$  is also closely related to this family of bismuth compounds (6,7).

It seemed interesting to investigate the luminescence of  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  and to compare the results with those of  $\text{BiOCl}$ . In view of the very similar  $\text{Bi}_2\text{O}_2$  layers in these compounds, we expected that the luminescence would also be very similar. It turned out, however, that there are marked differences.

### Experimental

$\text{Bi}_2\text{O}_2\text{CO}_3$  was prepared and crystallographically investigated as described before (4).  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  was prepared by hydrothermal treatment of an intimate mixture of  $\text{CaCO}_3$  and  $\text{Bi}_2\text{O}_2\text{CO}_3$  in a PTFE-lined pressure vessel: 300 bar,  $220^\circ\text{C}$ , 72h in  $\text{Na}_2\text{CO}_3$  solution. No impurity phases were detectable using powder X-ray diffraction. The performance of the optical measurements was described elsewhere (2).

### Results

The compounds  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  both show a weak luminescence at 4.2 K. The spectra are similar to those of  $\text{BiOCl}$  as far as band shapes are concerned. In Table I we compare their luminescence characteristics with those of  $\text{BiOCl}$  and  $\text{LaOCl-Bi(2)}$ , and of  $\text{LiBi}_3\text{O}_4\text{Cl}_2$  (8).

The diffuse reflection spectra of the compounds  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  show steep optical absorption edges, which have tails extending into the visible area (fig. 1).

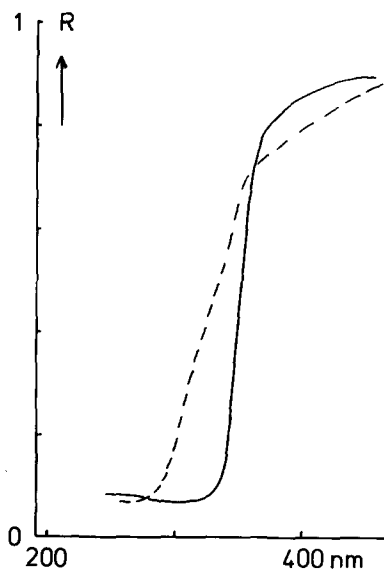


FIG. 1

Diffuse reflection spectra at room temperature of  $\text{Bi}_2\text{O}_2\text{CO}_3$  (drawn line) and  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  (broken line).

### Discussion

This paragraph treats the two questions which immediately arise, viz.

why is the emission intensity of the compounds Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and CaBi<sub>2</sub>O<sub>2</sub>(CO<sub>3</sub>)<sub>2</sub> so low, and why is there such a large variation in the spectral properties of these bismuth compounds in spite of the common Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layer in their structures.

Table I

Luminescence characteristics of some compounds with Bi<sub>2</sub>O<sub>2</sub><sup>2+</sup> layers.  
All values in 10<sup>3</sup> cm<sup>-1</sup>.

Composition	Maximum excitation band	Maximum emission band	Stokes shift	Reference
LaOCl-Bi <sup>3+</sup>	37	28	9	2
CaBi <sub>2</sub> O <sub>2</sub> (CO <sub>3</sub> ) <sub>2</sub>	36	22	14	this work
BiOCl	32	24	8	2
		21		
Bi <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	30	22	8	this work
		18		
LiBi <sub>3</sub> O <sub>4</sub> Cl <sub>2</sub>	28.5	19	9.5	8

The problem of the low emission intensity is probably trivial. Diffraction methods show that the crystallites are of good quality. However, optical excitation will not reach the bulk of the crystals, since the oscillator strength of the optical transitions of the Bi<sup>3+</sup> ion is very high. Since these ions are present in high concentration, the exciting radiation will only penetrate the surface layer. This layer may be full of defect centres of an unknown nature. It seems only obvious to assume that they act, at least partly, as quenching centres of the luminescence (9). Their presence explains also why the diffuse reflection spectra contain such a long tail into the visible. Excitation into these tails does not yield any luminescence at all. However, the emission bands observed show a large spectral overlap with these tails which makes energy transfer from the emitting to the quenching centres a process with a potentially high rate. The luminescence of BiOCl at 4.2 K is also not intense and quenches rapidly at increasing temperature (2). The lower-energy emission band of BiOCl as well as of Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> may be due to Bi<sup>3+</sup> ions in a disturbed coordination.

The difference in the spectral position of the emission and excitation (absorption) bands is of a more intrinsic nature. In view of the structural analogy between the bismuth compounds of table I, this difference is unexpected. We discuss the spectral variation in a way which is similar to that which was used to explain the different luminescent properties of bismuth compounds in general (10).

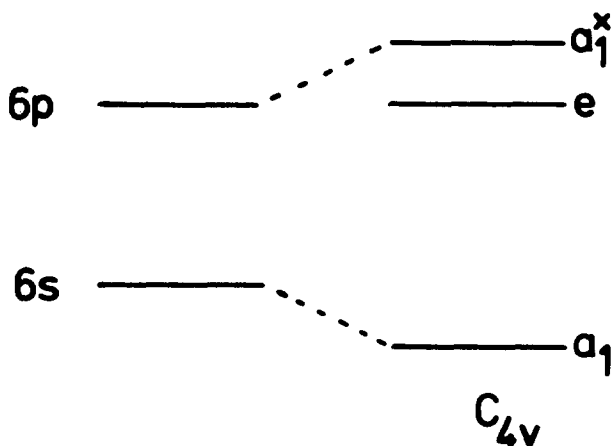


FIG. 2

Energy level scheme for  $\text{Bi}^{3+}$  in compounds with a  $\text{Bi}_2\text{O}_2^{2+}$  layer (schematic). The representations given refer to  $C_{4v}$  site symmetry. See also text.

To this purpose we consider the simple energy level diagram of fig. 2. The 6s and 6p orbital wave functions of the free  $\text{Bi}^{3+}$  ion will be mixed by the tetragonal field on the  $\text{Bi}^{3+}$  site of the compounds under investigation. As a consequence the  $a_1$  orbital, which is filled, is stabilized and the  $a_1^*$  (mainly  $p_z$ ) orbital is destabilized. The e ( $p_x, p_y$ ) orbital is not influenced.

This model predicts:

- a. the stronger the 6s and 6p orbital mixing is, the higher the position of the first absorption band (i.e.  $a_1 \rightarrow e$ ).
- b. the stronger the orbital mixing is, the larger the relaxation in the excited state will be, and the larger the Stokes shift of the emission will be. This is due to the fact that the mixing leads to a charge distribution which is concentrated along the z axis ( $p_z$ ) in the ground state, but in the x,y plane ( $p_x, p_y$ ) in the excited state.

In the case of  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$ ,  $\text{BiOCl}$ ,  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{LiBi}_3\text{O}_4\text{Cl}_2$  the  $\text{Bi}^{3+}$  coordination is very similar apart from the ion on the tetragonal axis. In these four compounds this ion will be  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{Bi}^{3+}$  and  $\text{Bi}^{3+}$ , respectively. In  $\text{LiBi}_3\text{O}_4\text{Cl}_2$  there are layers  $(\text{Li}_{0.5}\text{Bi}_{1.5}\text{O}_2)^+$  separated by single  $\text{Cl}^-$  layers. At first sight the sequence of these ions does not make much sense.

In our simple model these ions act as charges which polarize the  $\text{Bi}^{3+}$  charge density. It is immediately clear that the  $\text{Ca}^{2+}$  ion with its positive charge will polarize the  $\text{Bi}^{3+}$  ion strongly, i.e. it induces a strong 6s-6p mixing. In agreement with the model,  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_3$  shows the highest absorption transition and the largest Stokes shift (see table I). The  $\text{Cl}^-$  ion with its large radius and negative charge cannot be expected to have such an influence. In fact  $\text{BiOCl}$  has its absorption transition at lower energy and the value of the Stokes shift is smaller.

In  $\text{Bi}_2\text{O}_2\text{CO}_3$  and  $\text{LiBi}_3\text{O}_4\text{Cl}_2$  the neighbouring ion on the z axis is the  $\text{Bi}^{3+}$  ion, i.e. there is a Bi-Bi pair along the axis. Such a situation is well known in the literature on  $s^2$  ions (11). Charge density is built up in the overlap area, i.e. the  $s^2$  ions direct their lone pair of electrons to each other. In our model, where the  $\text{Ca}^{2+}$  and  $\text{Cl}^-$  ions are considered to be polarizing charges with a certain dimension, one of the  $\text{Bi}^{3+}$  ions should be considered as a polarizing ion which directs its negative charge to the other  $\text{Bi}^{3+}$  ion. In view of this it is not surprising to find values for this case which are not so different from those of  $\text{BiOCl}$ . Although the model is certainly an oversimplification, it explains elegantly why the spectral data for  $\text{CaBi}_2\text{O}_2(\text{CO}_3)_2$  and  $\text{Bi}_2\text{O}_2\text{CO}_3$  are so different.

In the  $\text{Bi}_2\text{O}_2^{2+}$  layers the  $\text{Bi}^{3+}$  ions will have a certain interaction with each other via the intervening  $\text{O}^{2-}$  ions. These interactions, in which the  $p_x$ ,  $p_y$  orbitals will play a dominant role, will be the same for all the bismuth compounds under investigation. In  $\text{LaOCl-Bi}^{3+}$ , however, the  $\text{Bi}^{3+}$  ions are dilute so that such an interaction is not possible. As a consequence, the transition energies move some 4-5000  $\text{cm}^{-1}$  to higher energy (table I). In the simple model of fig. 2 this can be visualized by assuming that in the bismuth compounds the e level has broadened into a band which reduces the energy of the  $a_1$ -e transition. In  $\text{LaOCl-Bi}^{3+}$  this broadening does not occur and the transition is at higher energy.

In conclusion, the simple model proposed before to explain the luminescence properties of bismuth compounds (10) is also able to explain the spectral differences between a series of structurally related compounds. Since quantitative calculations on  $\text{Bi}^{3+}$  are not so easy to perform because of the high number of electrons and the strong spin-orbit coupling, this is a satisfying result.

#### References

- 1) R.W.G. Wyckoff, Crystal Structures Vol. I, J.B. Wiley and Sons, New York (1963).
- 2) A. Wolfert and G. Blasse, Mat. Res. Bull. 19, 67 (1984)
- 3) P. Caro, C.R. Ac. Sci. Paris C, 282, 992 (1966); J. Less-Common Metals 16, 367 (1968)
- 4) C. Greaves and S.K. Blower, Mat. Res. Bull., in press

- 5) A. Lagercrantz and L.G. Sillen, Arkiv Kemi Mineral. Geol. 25A, 1 (1948)
- 6) M.A. Subramanian, C.C. Torardi, J.C. Calabrese, J. Gopalakrishnan, K.J. Morrissey, T.R. Askew, R.B. Flippen, U. Chowdhry and A.W. Sleight, Science 239, 1015 (1988)
- 7) A.K. Cheetham, A.M. Chippendale and S.J. Hibble, Nature 333, 21 (1988)
- 8) G.J. Dirksen and G. Blasse, Z. Anorg. Allg. Chem. 432, 211 (1977)
- 9) G. Blasse, E.W.J.L. Oomen and J. Liebertz, Phys. Stat. Sol. (b) 137, K77 (1986)
- 10) C.W.M. Timmermans and G. Blasse, J. Solid State Chem. 52, 222 (1984)
- 11) C.W.M. Timmermans and G. Blasse, Phys. Stat. Sol. (b) 118, 353 (1983)