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LETTERS TO THE EDITOR

Vibrational Structure in the Luminescence of the $[TiOF_5]^{3-}$ Octahedron

G. BLASSE AND G. J. DIRKSEN

Debye Research Institute, University of Utrecht, P.O. Box 80.000,
3508 TA Utrecht, The Netherlands

AND G. J. PAUSEWANG AND R. SCHMIDT

Institut für Anorganische Chemie, Universität Tübingen, Auf der
Morgenstelle 18, 7400 Tübingen 1, Federal Republic of Germany

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Vibrational structure in the emission of the $[TiOF_5]^{3-}$ octahedron in the elpasolite $K_2NaTiOF_5$ is reported. The vibrational mode involved indicates the way in which the excited state is distorted.

Introduction

Recently we have reported the luminescence of α-$Ba_3Ti_2O_2F_{10}$ which originates from the $[TiOF_5]^{3-}$ octahedron in this compound (*1*). This luminescence consists of a green emission band with a maximum at 525 nm; its excitation band has a maximum at 290 nm and its quenching temperature is at about 175 K. In order to confirm this assignment we investigated the luminescence of $K_2NaTiOF_5$. This compound has elpasolite structure (*2*). The crystal structure contains isolated $[TiOF_5]^{3-}$ octahedra without a correlation between these octahedra. This was confirmed by the infrared spectrum (*3*).

For the elpasolite we observed essentially the same luminescence as for α-$Ba_3Ti_2O_2F_{10}$. Surprisingly enough, the elpasolite emission band shows vibrational structure. As far as we are aware, no vibrational structure has ever been observed for the titanate luminescence, which has been studied for decades (*4*, *5*). This prompted this letter devoted to the vibrational structure in the $K_2NaTiOF_5$ emission.

Experimental

The sample was prepared as described in Ref. (*2*). The optical measurements were performed as described in Ref. (*1*). Next to the Perkin–Elmer MPF-3 spectrofluorometer, a Spex fluorolog spectrometer was used in order to verify the spectral details.

Results

At 4.2 K the compound $K_2NaTiOF_5$ shows an intense photoluminescence. The emission maximum is at 550 nm, the excitation maximum is at 300 nm. There is a slight shift to longer wavelength compared to the

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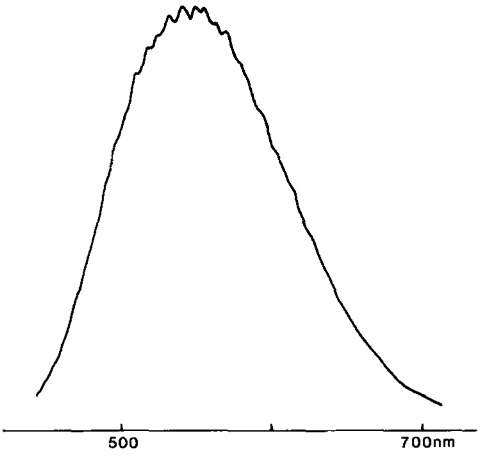

FIG. 1. The emission spectrum of $K_2NaTiOF_5$ at 4.2 K. Excitation wavelength 290 nm. Note the weak vibrational structure (see also Table I).

luminescence spectra of α-$Ba_3Ti_2O_2F_{10}$. The thermal quenching temperature of the elpasolite luminescence is at about room temperature, which is higher than for the barium compound.

This result confirms that the emission is due to the same luminescent center in these two compounds, viz. the [$TiOF_5$[$^{3-}$ octahedron. The small differences are probably due to the fact that in elpasolite the octahedra are isolated from each other, whereas in α-$Ba_3Ti_2O_2F_{10}$ they are connected (*6*).

The really surprising result, however, is the observation of vibrational structure in the emission band of $K_2NaTiOF_5$ at 4.2 K (Fig. 1; Table I). There are a number of equally spaced lines just observable on the broad emission band. They were observed on two different spectrofluorometers (see above) in order to exclude experimental accidents. The structure becomes less pronounced at higher temperatures and at about 75 K it has disappeared. Table I gives an analysis of this structure. The vibrational mode involved is 290 cm^{-1}. In considering this table it should be realized that due to restrictions of the instruments, but especially to the weakness of the individual vibronic lines relative to the total band intensity, the accuracy of the line position is not better than ± 10 cm^{-1}. The 290 cm^{-1} frequency is known from the infrared spectrum (*3*). It has been assigned to the $\gamma(TiF_4)$ mode of A_1 symmetry in the $[TiOF_5]^{3-}$ octahedron with C_{4v} symmetery, i.e., a movement of the central Ti(IV) ion relative to the horizontal F_4 plane (see Fig. 2).

Discussion

The luminescence of highly charged ions with "d^0" configuration (for example, Ti(IV), V(V), W(VI)) is well known and has been studied for decades (*4, 5*). The optical transitions involved are of the charge-transfer type. The spectra consist always of

TABLE I

VIBRATIONAL STRUCTURE IN THE EMISSION BAND OF $K_2NaTiOF_5$ AT 4.2 K

Position vibronic line (cm^{-1})	Difference (cm^{-1})
20.510	
	320
20.190	
	290
19.900	
	290
19.610	
	290
19.320	
	270
19.050	
	280
18.770	
	270
18.500	
	300
18.200	
	300
17.900	
	300
17.600	
Average	290

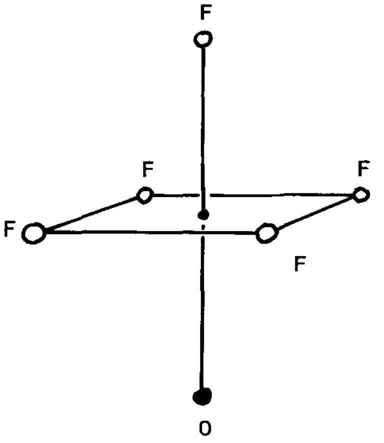

FIG. 2. The $[TiOF_5]^{3-}$ octahedron in $K_2NaTiOF_5$. In the $\gamma(TiF_4)$ vibrational mode the central Ti(IV) ion (small filled circle) moves along the vertical axis relative to the square of the four fluorine ions.

broad bands with large Stokes shift and without any vibrational structure. There are a very few exceptions to the latter fact. These are the ill-defined SiO_2–V(V) (*7*), and the well-defined $K_2Cr_2O_7$ (*8*) and K_2NbF_7 (*9*). The latter two are of special interest, because the vibrational mode involved is also a bending vibration ($K_2Cr_2O_7$, 361 cm^{-1}; K_2NbF_7, 290 cm^{-1}). The emission patterns of K_2NbF_7 and $K_2NaTiOF_5$ at 4.2 K are very similar.

The usual absence of vibrational structure in this type of emission bands prevents analysis of the electron–lattice coupling. Recently convincing evidence for the occurrence of a Jahn–Teller distortion in the excited state of VO_4^{3-} and MoO_4^{2-} complexes has been given by Van der Waals and co-workers using resonance techniques (*10–12*). The presence of vibrational structure makes it possible to obtain directly information on this deformation. Since the vibronic line with the highest intensity is estimated to be the 15th member of the progression, the coupling of the excited state with the $\gamma(TiF_4)$ mode is very strong. At first sight this is surprising. In view of the high electronegativity of fluorine, the charge–transfer transition involved in the luminescence of the $[TiOF_5]^{3-}$ octahedron will be localized in the Ti–O bond. Nevertheless there is a strong coupling with the $\gamma(TiF_4)$ vibrational mode.

This, however, can be explained as follows. Excitation of the Ti–O bond will result in an increase of the Ti–O distance, i.e., the Ti(IV) ion will move relative to the plane of the four F(–I) ions. In this way there will be a strong coupling between the Ti–O charge–transfer state and the $\gamma(TiF_4)$ vibrational mode. It cannot be excluded that there is also vibrational structure due to coupling with the Ti–O stretching vibration. However, the frequency of this mode is about thrice that of the $\gamma(MeF_4)$ vibrational mode; i.e., it may easily escape observation because of coincidence of the two progressions.

In textbooks it is usually assumed that the vibrational mode which plays the dominant role in the configurational coordinate diagram is the totally symmetric stretching mode (*13, 14*). In recent years it has been found that also Jahn–Teller active modes can play a dominant role. This has been reviewed by one of us (*14*). The case of $K_2NaTiOF_5$ shows coupling with still another type of vibrational mode, which becomes only clear by the presence of two types of ligands, viz. fluorine and oxygen.

In conclusion, the elpasolite $K_2NaTiOF_5$ shows luminescence below room temperature with a vibrational structure in the emission band which shows directly the strong coupling between the Ti–O charge–transfer state and the $\gamma(TiF_4)$ vibrational mode.

References

1. G. BLASSE, G. J. DIRKSEN, G. PAUSEWANG, AND R. SCHMIDT, *Eur. J. Solid State Inorg. Chem.*, in press.

2. G. PAUSEWANG AND W. RÜDORFF, *Z. Anorg. Allg. Chem.* **364**, 69 (1969).

3. K. DEHNICKE, G. PAUSEWANG, AND W. RÜDORFF, *Z. Anorg. Allg. Chem.* **366**, 64 (1969).

4. F. A. Kröger, "Some Aspects of the Luminescence of Solids," Elsevier, Amsterdam (1948).

5. G. Blasse, *Struct. Bond.* **42,** 1 (1980).

6. R. Schmidt and G. Pausewang, *Z. Anorg. Allg. Chem.* **575,** 197 (1989).

7. H. Ronde and G. Blasse, *J. Inorg. Nucl. Chem.* **40,** 215 (1978).

8. A. Freiberg and L. Rebane, J. Lumin. **18/19,** 702 (1979).

9. G. Blasse and L. H. Brixner, J. Lumin. **35,** 179 (1986).

10. W. Barendswaard, J. van Tol, and J. H. van der Waals, *Chem. Phys. Lett.* **121,** 361 (1985).

11. W. Barendswaard, J. van Tol, R. J. Weber, and J. H. van der Waals, *Mol. Phys.* **67,** 651 (1989).

12. W. Barendswaard and J. H. van der Waals, *Mol. Phys.* **59,** 337 (1986).

13. B. Henderson and G.F. Imbusch, "Optical Spectroscopy of Inorganic Solids", Oxford Univ. Press (Clarendon), London/New York (1989).

14. G. Blasse, *Prog. Solid State Chem.* **18,** 79 (1988).