JOURNAL OF SOLID STATE CHEMISTRY **67**, 21–25 (1987)

Structure and Luminescence of K_2TaF_7 and K_2NbF_7

C. C. TORARDI AND L. H. BRIXNER

E. I. du Pont de Nemours and Co., Central Research and Development Department, Experimental Station, Wilmington, Delaware 19898*

AND G. BLASSE

Physics Laboratory, State University, 3508 TA Utrecht, The Netherlands

Received March 28, 1986; in revised form June 11, 1986

The crystal structure of K_2TaF_7 has been refined using single-crystal X-ray diffraction data. It is monoclinic with lattice parameters $a = 5.8559(6)$, $b = 12.708(1)$, and $c = 8.5125(9)$ Å and $\beta = 90.17°$ in the space group $P2_1/c$. The structure is composed of TaF_7 units that are interconnected by potassium ions. TaF_7 polyhedra may be described as monocapped trigonal prisms with the capping atom located on one of the rectangular faces. Potassium atoms are 9-coördinated and may be viewed as distorted monocapped square prisms. The previously unreported luminescence properties of K_2TaF_7 and K_2NbF_7 are reported and discussed. In addition to the intrinsic emission, impurity luminescence due to OH^- and Eu^{2+} were observed.

Introduction

Both K_2TaF_7 and K_2NbF_7 are important precursors in the commercial manufacture of high-purity Ta and Nb metal and are produced by Cabot Corporation. The first structural study of these compounds was carried out by Hoard (*1*) and later the structure of K_2NbF_7 was confirmed via neutron diffraction by Brown and Walker (*2*). Blaumanis and Coyle (*3*) did some additional high-temperature X-ray diffraction work and found that at least two additional structural modifications exist. No information exists in the literature concerning the luminescence of these compounds. For this reason, it appeared worthwhile to reexamine the structure of K_2TaF_7 and correlate our luminescence findings with that information.

Experimental

Crystals of K_2TaF_7 and K_2NbF_7 were obtained from Cabot Corporation. According to the manufacturer, they contained up to 200 ppm of oxygen. Infrared spectra showed this oxygen to be present as OH^-, either substitutionally on the F sites or as surface water. The intensity of the band at $\sim$3500 cm^{-1} was greater in K_2NbF_7 than in K_2TaF_7. The crystals were not given any other treatment prior to use for the structural work and luminescence studies.

Single-crystal X-ray structure determination. A crystal of K_2TaF_7 with dimensions

---

* Contribution No. 4084.

0022-4596/87 $3.00

TABLE I

POSITIONAL[a] AND ANISOTROPIC THERMAL[b] PARAMETERS FOR THE ATOMS OF K_2TaF_7

Atom	x	y	z		
Ta	0.27303(3)	0.87107(1)	0.22258(2)		
K1	0.23778(17)	0.55972(7)	0.18279(12)		
K2	0.76421(16)	0.71566(8)	0.44409(12)		
F1	0.0444(5)	0.7578(2)	0.1989(3)		
F2	0.4566(5)	0.7430(2)	0.2118(4)		
F3	0.0431(5)	0.8922(2)	0.3872(3)		
F4	0.4606(5)	0.8895(2)	0.4108(3)		
F5	0.2149(6)	0.0210(2)	0.2152(4)		
F6	0.1886(7)	0.8774(3)	0.0048(4)		
F7	0.5590(5)	0.9211(2)	0.1318(3)		
B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
0.94(1)	0.99(1)	0.85(1)	0.00(0)	0.01(0)	−0.05(0)
2.08(4)	1.35(3)	1.84(4)	−0.11(2)	0.10(3)	0.14(2)
1.46(3)	2.48(3)	1.55(3)	0.07(3)	−0.05(3)	0.50(3)
1.57(10)	1.74(9)	2.00(11)	−0.31(8)	−0.01(8)	−0.12(8)
1.59(10)	1.62(9)	3.02(13)	0.25(7)	−0.47(10)	−0.49(8)
1.70(11)	2.30(10)	1.93(11)	0.24(8)	0.51(9)	−0.15(9)
1.75(11)	3.15(11)	1.62(10)	0.21(9)	−0.33(9)	−0.48(9)
4.1(2)	1.5(1)	4.2(2)	0.8(1)	2.0(1)	0.9(1)
4.8(2)	4.9(2)	1.9(1)	−2.9(1)	−1.2(1)	1.1(1)
1.80(11)	2.47(11)	2.13(11)	−0.47(8)	0.83(9)	−0.02(9)

[a] Space group $P2_1/c$.

[b] $\exp[-0.25(B_{11}h^2a^{*2} \cdots +2(B_{12}hka^*b^* \ldots))]$.

$0.167 \times 0.250 \times 0.333$ mm^3 was placed on an Enraf-Nonius CAD4 X-ray diffractometer equipped with a monochromatic Mo$K\alpha$ radiation source. From settings of 25 reflections, the lattice parameters of the monoclinic cell were refined to $a = 5.8559(6)$, $b = 12.708(1)$, $c = 8.5125(9)$ Å, and $\beta = 90.17(1)°$. For $Z = 4$, the calculated density is 4.11 g · cm^{-3}.

A total of 4102 reflections were collected by the 2θ-ω mode from $2° \leq \theta \leq 30°$ in the $\pm h$, $\pm k$, l octants. The data were merged to yield 1548 independent reflections with $I \geq 3\sigma(I)$ in $2/m$ symmetry. Polarization and Lorentz corrections were made, and after a full isotropic least-squares structural refinement, an absorption correction (DIFABS) (*4*) was applied (μ = 185.4 cm^{-1}).

An examination of the data revealed systematic absences compatible with space group $P2_1/c$ as previously observed by Hoard (*1*). The positional parameters of K_2NbF_7, reported by Brown (*2*), were used as the initial values for the present refinement. Full-matrix least-squares refinement for all positional and anisotropic thermal parameters including terms for anomalous dispersion and for anisotropic extinction converged with $R = 0.020$ and $R_w = 0.022$ where $R_w = \{\Sigma w(|F_O| - |F_C|)^2/\Sigma w|F_O|^2\}^{1/2}$ with w proportional to $1/\}\sigma^2(I) + (0.02I)^2\}$. The largest peak in a final difference Fourier was 0.83 e/Å^3 near the tantalum atom.

The data were also averaged in monoclinic 2 symmetry and refinements of the mirror-image structures in the space group $P2_1$ gave essentially identical R factors. Data were later collected in the $\pm h$, k, $\pm l$ octants (to $2\theta = 55°$) and averaged in monoclinic m symmetry. Refinements for the enantiomeric structures in the space group Pc also gave identical residuals indicating that the structure is truly centrosymmetric.

Optical measurements. Details for the performance of these measurements have been given before (*5*).

Results and Discussion

Structural Description

Positional and thermal parameters for K_2TaF_7 are given in Table I. Important interatomic distances are listed in Table II.

The structure of K_2TaF_7 is composed of TaF_7 units that are interconnected by potassium ions. Figure 1 shows a TaF_7 polyhedron which may be described as a monocapped trigonal prism with the capping atom located on one of the rectangular faces. These TaF_7^{2-} ions are distorted from having true mm (C_{2v}) symmetry, and possess the symmetry of the point group C_1. Ta–F bond lengths vary from 1.918 to 1.975 Å with the average value of 1.95 Å being slightly lower than the sum of ionic radii, 1.99 Å (*6*). Each TaF_7 unit shares eight edges and two corners equally with the two independent potassium ions. Fluorine at-

TABLE II

IMPORTANT INTERATOMIC DISTANCES (Å) IN K_2TaF_7

Ta–F1	1.976(2)	K1–F5	2.834(4)
Ta–F2	1.952(3)	K1–F6	2.871(4)
Ta–F3	1.965(3)	K1–F7	2.646(3)
Ta–F4	1.954(3)	K2–F1	2.737(3)
Ta–F5	1.937(3)	K2–F1′	2.712(3)
Ta–F6	1.919(3)	K2–F2	2.956(4)
Ta–F7	1.953(3)	K2–F2′	2.693(3)
K1–F1	2.763(3)	K2–F3	2.818(3)
K1–F2	2.670(3)	K2–F4	2.850(3)
K1–F3	2.826(3)	K2–F5	2.824(3)
K1–F3′	2.754(3)	K2–F6	2.798(4)
K1–F4	2.738(3)	K2–F7	2.651(3)
K1–F4′	2.905(3)		

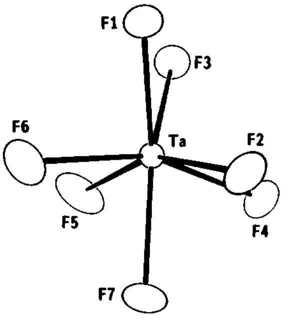

FIG. 1. The TaF_7 polyhedron.

oms F1, F2, F3, and F4 are each tetrahedrally coordinated to one tantalum and three potassium ions. The average value of the bond angles for these fluorine atoms is 109.3 ± 1°. Atoms F5, F6, and F7 have roughly trigonal planar geometry with the sum of the Ta–F–K1, Ta–F–K2, and K1–F–K2 bond angles being 351.6, 359.8, and 352.3°, respectively.

An interesting feature of this structure emerges when only the Ta, K, and F5, F6, and F7 ions are viewed. Chains consisting of Ta–F–K–F–Ta connections are oriented parallel to the a axis. Individual chains are then linked to other chains by the tetrahedrally coordinated fluorine ions.

Both of the crystallography unique potassium ions are nine-coordinated, and may be viewed as distorted monocapped square prisms. Figure 2 shows the fluorine atom arrangement around K1 and K2. Each KF_9 polyhedron shares nine edges and three corners with tantalum and other potassium ions. In addition, K1 and K2 share a common face via atoms F1, F5, and F6 and are separated by 4.075 Å. K1–F bond distances range from 2.646 to 2.908 Å, and K2–F bond lengths vary from 2.651 to 2.957 Å. The average potassium–fluorine bond distance for K1 and K2 is the same, 2.78 Å, and agrees quite well with the value reported for K_2NbF_7 (*2*).

Luminescence of K_2TaF_7 and K_2NbF_7

The compound K_2TaF_7 has its absorption edge, as derived from diffuse reflectance spectra, at about 230 nm. Only with difficulty it is possible to excite into this area,

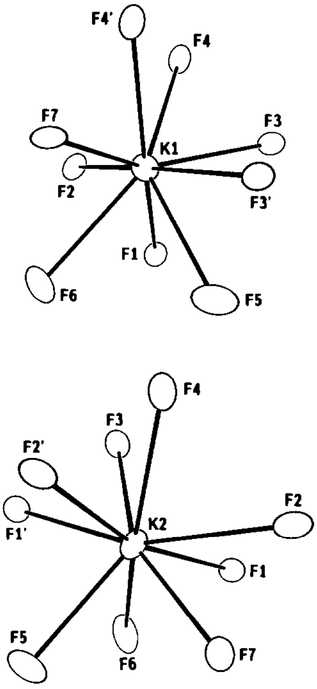

FIG. 2. The two KF_9 polyhedra.

since the spectrometer is equipped with a Xenon lamp. Upon 230-nm excitation a broad emission band is observed with a maximum at 350 nm. The Stokes shift is, therefore, about 16,000 cm^{-1}. At 300 K, the emission intensity has dropped to 50% of the value at 4.2 K. The emission spectrum was measured with relatively large slit widths due to the low excitation intensity.

These luminescence characteristics are very similar to those observed for oxidic tantalates (*7*). The transitions involved are of the charge-transfer type. For fluorine ligands these are expected at higher energy than for oxygen ligands. However, these transitions shift to lower energy for higher coordination number (seven in the present compounds). Obviously both effects compensate each other in K_2TaF_7. Energy transfer is clearly impossible in view of the large Stokes shift.

Since K_2TaF_7 is transparent for $\lambda > 250$ nm, every impurity, which absorbs in this area, may show up in the emission spectrum. We noticed in emission at about 361 nm a double sharp line followed by a vibronic feature at 290 cm^{-1}. Its excitation spectrum consists of broad bands at 290, 280, and 260 nm. We tentatively ascribe this to a Eu^{2+} impurity. The excitation bands correspond to $4f^7 \rightarrow 4f^65d$ transitions, the emission lines to the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transition. It is well known that in fluorides the line emission prevails (*8*). The double character of the line is due to the fact that there are two different K^+ sites in the structure of K_2TaF_7. The Eu^{2+} ion will occupy both of these. The vibronic feature is due to coupling with a Ta–F deformation mode. A similar phenomenon has been observed also for Gd^{3+} (*9*).

The Raman spectrum of K_2TaF_7 shows peaks at 645 cm^{-1} (Ta–F stretching) and 395 and 280 cm^{-1} (Ta–F bending).

Further we note an emission band at 450 nm, which can be excited by wavelengths in between 280 and 250 nm. This is probably due to a niobium impurity in the tantalate (see below).

Finally, there is a rather sharp band peaking at 390 nm. Its excitation spectrum is very complicated. It consists essentially of a weak band between 350 and 310 nm and a stronger one between 310 and 270 nm. These bands carry a vibrational structure. We ascribe this emission to triplet state emission of the OH^- group. This is based upon the analogy between our spectra and those reported in the literature for solid hydroxides, hydroxide solutions and OH^- in alkali halide crystals (*10, 11*). It was also observed for $La_3TaO_4Cl_6$ upon slow hydrolysis (*12*). The thermal quenching of this emission occurs between 200 and 300 K in agreement with the literature (*11*). The vibrational structure in the excitation spectrum has not been reported before. Unfortunately, we were not able to make a satisfying assignment. However, it appears that, next to coupling with other vibrations, there is coupling with a ~2500 cm^{-1} vibration. This is then ascribed tentatively to the stretching vibration of the OH^- group in the excited state.

The results to be reported below for K_2NbF_7 seem to indicate that the OH^- groups are on the surface, i.e., they are due to hydrolysis at the atmosphere.

The luminescence of K_2NbF_7 is similar, but the spectra are at longer wavelengths. The emission band has a maximum at 450 nm. It shows vibrational structure if measured under high resolving power (*13*). There is a clear progression in 290 cm^{-1} which indicates a strong distortion of the luminescent state of the NbF_7^{2-} complex. For further details, the reader is referred to Ref. (*13*).

The excitation maximum is at 260 nm, so that the Stokes shift is about 16,000 cm^{-1}. At about 300 K the emission is quenched. Apart from the vibrational structure, these luminescence properties are similar to those of K_2TaF_7 and oxidic niobates (*7*).

In addition we observed the Eu^{2+} line emission mentioned above and the 390 nm OH^- emission for excitation with 290 nm. Since this wavelength is also absorbed by the NbF_7^{2-} complex, we assume that OH^- is mainly present on the surface.

Acknowledgment

The authors are indebted to Mr. G. J. Dirksen for the performance of the optical measurements.

References

1. J. L. Hoard, *J. Am. Chem. Soc.* **61,** 1252 (1939).
2. G. M. Brown and L. A. Walker, *Acta Crystallogr.* **29,** 220 (1966).
3. R. Blaumanis and Francis T. Coyle, ACS Southwest Reg. Meeting, December 1966.
4. N. Walker, and D. Stuart, *Acta Crystallogr. Sect. A* **39,** 158 (1983).
5. C. W. M. Timmermans and G. Blasse, *J. Solid State Chem.* **52,** 222 (1984).
6. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
7. G. Blasse, *Structure and Bonding* **42,** 1 (1980).
8. G. Blasse, *Phys. Status Solidi (B)* **55,** K131 (1973).
9. Hao Zhiran and G. Blasse, *Mat. Chem. Phys.* **12,** 257 (1985).
10. P. B. Merkel and W. H. Hamill, *J. Chem. Phys.* **55,** 2174 (1971).
11. H. J. Maria and S. P. McGlynn, *J. Chem. Phys.* **52,** 3402 (1970).
12. M. J. J. Lammers, J. Severin, G. Blasse, L. H. Brixner, and C. C. Torardi, *J. Solid State Chem.* in press.
13. G. Blasse and L. H. Brixner, *J. Luminescence,* **35,** 179 (1986).