JOURNAL OF SOLID STATE CHEMISTRY 98, 144–150 (1992)

Structure and Luminescence of $Cs_2WO_2F_4$: Efficient Luminescence of Isolated $[WO_2F_4]^{-2}$ Octahedra

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Received June 20, 1991; in revised form November 13, 1991

The structure of $Cs_2WO_2F_4$ was determined and refined to an R value of 6.8%. $Cs_2WO_2F_4$ crystallizes in the trigonal space group $P\bar{3}m1$ with a = 6.275(1) Å and c = 5.035(1) Å. The Cs ions are in 12-coordination and W in an octahedral 6-coordination. The oxyfluorotungstate octahedra are isolated in this structure and exhibit efficient luminescence under both UV and X-ray excitation at room temperature. The luminescence properties of $Cs_2WO_2F_4$ are compared with those of $Cs_2WO_2Cl_4$ and $Ba_2WO_3F_4$. © 1992 Academic Press, Inc.

Introduction

In a recent paper we reported on the efficient luminescence from structurally isolated $[NbOF_5]^{-2}$ octahedral groups in a new oxyfluoroniobate, Cs_2NbOF_5, crystallizing with the Cs_2ZrF_6 structure (*1*). By replacing Nb^{5+} by W^{6+} in Cs_2NbOF_5 and maintaining charge balance via anionic charge compensation, we were able to synthesize the structurally isomorphous oxyfluorotungstate, $Cs_2WO_2F_4$.

It is the purpose of this study to investigate the structure and luminescence of the oxyfluorotungstate.

Experimental

A. Synthesis

$Cs_2WO_2F_4$ was synthesized via two different aqueous routes. By the first method 0.1 mole of WO_3 was mixed with 0.2 mole of CsF in 100 ml of 25% HF/H_2O. The solution was evaporated to dryness at 80C after which another 100 ml of acid was added. The drying/acid-addition cycle was repeated until no evidence of the sparingly soluble WO_3 was seen upon acid addition. At this point the temperature was reduced to 50°C and the solution was slowly evaporated to dryness.

The second method of preparation reacted 0.1 mole of Cs_2CO_3 with 0.1 mole of WO_3 at 700°C in an alumina crucible to form Cs_2WO_4. This oxide was dissolved in 150 ml of 25% HF/H_2O at 80°C. The solution is cooled to 50°C and then evaporated to dryness. If precipitation of WO_3 occurred, 100 ml of acid solution was added to redissolve the product and the heating cycle was repeated. $Cs_2WO_2F_4$ precipitates from solution as a white polycrystalline mass. Single crystals were grown by slow evaporation of the solution.

B. X-Ray Studies

1. Powder diffraction. Room temperature X-ray powder diffraction patterns were obtained with a Philips D500 diffractometer

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calibrated before and after each measurement with pure silicon. A nominal scan rate of 1/4° 2θ/min was employed. Refined cell dimensions were obtained using a local computer program with least-squares procedures.

2. *Single-crystal studies.* $Cs_2WO_2F_4$ tends to grow into needles with a typical size of $1 \times 1 \times 5$ mm^3. One of these was selected for structure determination. Single-crystal diffraction intensities were measured on a SIEMENS P3F four circle diffractometer with Cu$K\alpha$ radiation selected with graphite monochromator. Full matrix structure refinement was done utilizing the program SHELXTL-89 implemented on a DEC microvax computer. An empirical absorption correction was applied using eight standard reflections.

C. Optical Studies

Luminescence excitation and emission spectra were measured at room temperature using a SPEX FLUROLOG II system, yielding automatically corrected spectra. Instrumental limitations would not permit accurate excitation below 250 nm. The relative energy emitted per unit energy, ϕ, is obtained from the relative energy emitted per unit wavelength according to the procedure described by Curie and Prener (*2*).

TABLE I

XRD PATTERN OF $Cs_2WO_2F_4$

2θ	d(Å)	*hkl*
16.303	5.4558	100
17.650	5.0331	001
24.104	3.6892	101
28.451	3.1346	110
33.705	2.6570	111
37.603	2.3901	201
39.448	2.2824	102
47.847	1.8996	211
49.305	1.8467	202
50.400	1.8092	300
54.651	1.6780	003
57.407	1.6039	103
57.902	1.5913	212
58.803	1.5691	220
62.750	1.4795	113
64.454	1.4445	311
65.298	1.4278	203
71.901	1.3121	401
73.145	1.2928	312
75.454	1.2589	004
76.256	1.2476	320
77.450	1.2313	303
77.804	1.2266	104
79.048	1.2104	321
81.097	1.1849	410
82.500	1.1683	114
84.405	1.1467	223
84.801	1.1424	204
87.106	1.1180	322

Results and Discussions

A. Structure

X-ray powder diffraction patterns of the polycrystalline masses and ground crystals indicated a trigonal cell. The indexed powder pattern for $Cs_2WO_2F_4$ is reported in Table I. Refinement of the d-spacings yielded cell dimensions of $a = b = 6.275 \pm 0.001$ Å and $c = 5.035 \pm 0.001$ Å. A diligent effort was made to find reflections indicative of a larger supercell. In no case was a supercell reflection found.

In order to ascertain the absolute structure a single crystal was selected for diffraction intensity measurement. A full sphere of reflection intensities were collected with $3° < 2\theta < 55°$. Reflection intensities were empirically corrected for absorption using ψ scans of eight strong reflections. Systematic reflections were consistent with the trigonal space group $P\bar{3}m1$ (No. 164) and subsequent determination were performed using this symmetry. As the structure evolved it was found that there was only one position which contained both fluorine and oxygen. The stoichiometry then required that the site occupancy factor for oxygen be fixed at $\frac{1}{2}$ of that of the fluorine and that both their

TABLE II

DATA COLLECTION AND STRUCTURE REFINEMENT

System used	Siemens SHELXTL PLUS (VMS)
Radiation	Mo$K\alpha$ ($\lambda = 0.71073$ Å)
2θ range	3.5 to 55.0°
Scan type	$2\theta - \theta$
Reflections collected	1642
Independent reflections	179 ($R = 11.3\%$) after correction
Observed reflections	177 ($F > 2.5\sigma(F)$)
Solution	Direct methods
Refinement method	Full-matrix least-squares
Quantity minimized	$\Sigma w(F_o - F_c)^2$
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0010F^2$
Number of parameters refined	12
Final R indices (obs. data)	$R = 6.83\%$, $R_w = 7.89\%$
R Indices (all data)	$R = 6.84\%$, $R_w = 7.92\%$
Goodness-of-fit	1.32
Data-to-parameter ratio	14.8 : 1

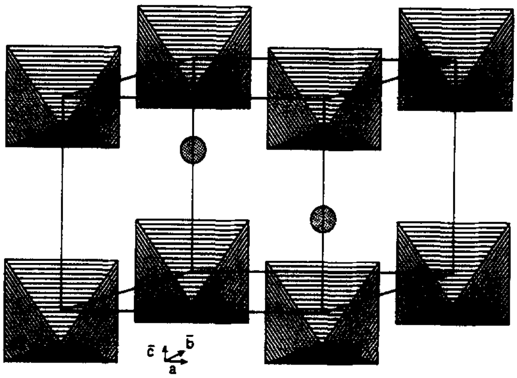

FIG. 2. The structure of $Cs_2WO_2F_4$ showing the W-polyhedra.

position and thermal parameters be equal. With the anion structure parameters thus defined, it was possible to obtain a structure refinement with structure factor residuals of $R = 0.0683$ and $R_w = 0.0789$. The collection details and structure refinement are given in Table II.

The structure of $Cs_2WO_2F_4$ is presented in Fig. 1, and as a W-polyhedra projection in Fig. 2. It is identical to that of archtypical $(NH_4)_2SiF_6$, and contains isolated $[WO_2F_4]^{-2}$ octahedra oriented with their 3-fold axes along the trigonal c-axis. Symmetrically dispersed on the second set of 3-fold axes between the octahedra are distorted CsF_{12} dodecahedra.

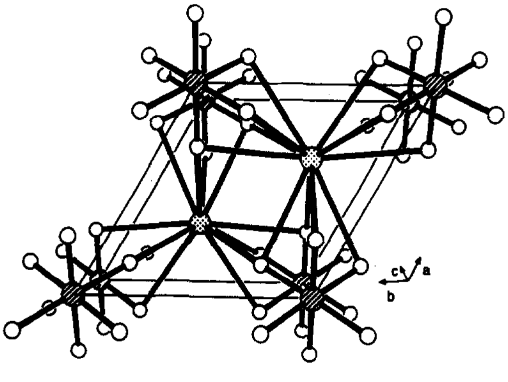

FIG. 1. Ball-Stick projection of the $Cs_2WO_2F_4$ structure.

Along the c-axis between the tungsten octahedra are octahedral voids such that the structure cannot be regarded totally as space-filling metal polyhedra. This is more apparent when the structure is considered as a derivative of the hexagonal $BaNiO_3$ structure which is space-filling and contains face-sharing chains of octahedra along the c-axis with Ba in between them. If alternate Ni atoms along the chain are removed the $(NH_4)_2SiF_6$ structure is produced. The individual metal environments are shown in Figs. 3 and 4; the interconnection of the Cs polyhedra is shown in Fig. 4.

The W atoms (Fig. 2) are not precisely in the highly symmetric O_h arrangement but are in D_{3d} local symmetry. All six W–(O, F) bond distances are 1.891 Å. The slight distortion of the octahedra occurs via a compression along the c-axis. Similarly, the Cs polyhedra distortion results when the Cs is moved out of the basal plane of the dodecahedron which contains six anions. The atomic positions and thermal parameters are given in Table III. The resulting Cs–(O, F) and the corresponding W–(O, F) bond distances and bond angles are reported in Table IV.

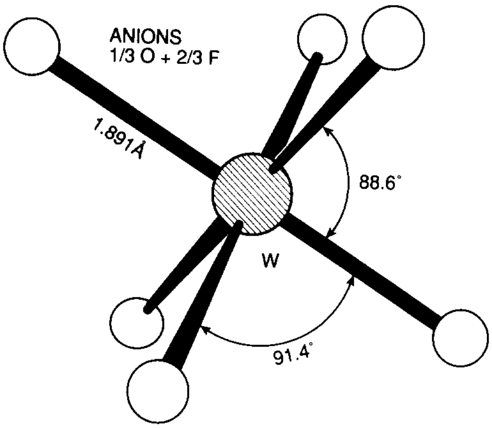

FIG. 3. W coordination in $Cs_2WO_2F_4$.

B. Luminescence of $Cs_2WO_2F_4$

At room temperature, $Cs_2WO_2F_4$ fluoresces bright yellow under both short UV and X-ray excitation. Room-temperature UV excitation and emission spectrum are exhibited in Fig. 5. The emission consists of a broad band with maximum at ~16,600 cm^{-1}. Because of the large width of this band it is not easy to accurately determine the emission maximum. The corresponding excitation band exhibits a maximum at ~37,700 cm^{-1}. The Stokes shift of emission amounts to roughly 21,000 cm^{-1}, a large value. To the best of our knowledge, for an octahedral tungstate group, this is the largest Stokes shift ever observed. Tetrahedrally coordinated tungstate groups, on the other hand, are known to exhibit Stokes shift value of up to 20,000 cm^{-1} (*3*). The single-crystal structural data of $Cs_2WO_2F_4$, however, clearly indicates the presence of six coordinated, slightly distorted oxyfluorotungstate octahedra.

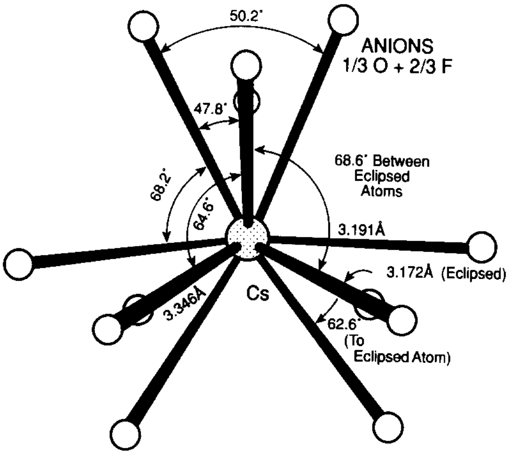

FIG. 4. Cs coordination in $Cs_2WO_2F_4$.

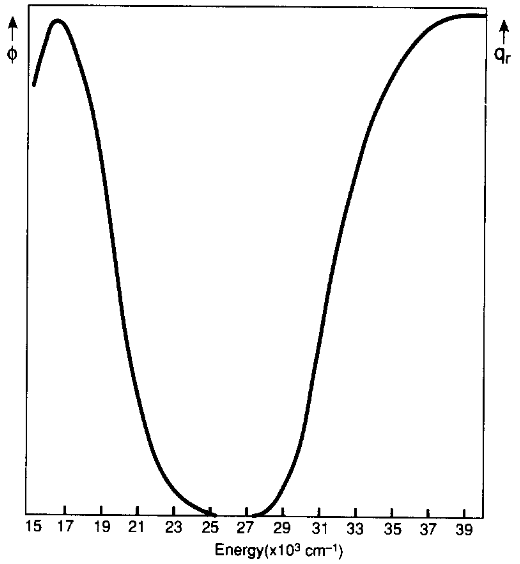

FIG. 5. Excitation (right hand side) and emission (left hand side) of $Cs_2WO_2F_4$. ϕ gives the relative energy emitted per unit energy and q_r the relative quantum output in arbitrary units.

It is perhaps most appropriate to compare the luminescence of $Cs_2WO_2F_4$ with that reported by Blasse *et al.* for $Cs_2WO_2Cl_4$ (*4*). The former compound crystallizes in the closely related K_2PtCl_6 structural type with isolated $[WO_2Cl_4]^{-2}$ octahedra (*5*). This is shown in Table V. Note that the Stokes shift of $Cs_2WO_2Cl_4$ is also large, viz., 15,000 cm^{-1}. The large Stokes shift in both the compounds may be attributed to the presence of large Cs^+ ions on the A-site and the presence of B-site vacancy when the structure is viewed as being perovskite de-

TABLE III

ATOMIC COORDINATES ($\times 10^4$), EQUIVALENT ISOTROPIC DISPLACEMENT COEFFICIENTS ($Å^2 \times 10^3$),[a] AND CRYSTAL DATA

	X	Y	Z	$U_{(eq)}$	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
W	0	0	0	32(1)	32(11)	32(1)	33(1)	16(1)	0	0
Cs	6667	3333	6891(3)	27(1)	28(1)	38(1)	26(1)	14(1)	0	0
F	8564(5)	1436(5)	2113(10)	32(2)	33(2)	33(2)	29(3)	16(2)	5(1)	−5(1)
O	8564(5)	1436(5)	2113(10)	32(2)	33(2)	33(2)	28(3)	26(2)	5(1)	−5(1)

Empirical formula	$Cs_2WO_2F_4$
Color; habit	White needles
Crystal size (mm)	0.1 × 0.1 × 0.5
Space group	Trigonal, $P\bar{3}m1$ (No. 164)
Unit cell dimensions	$a = 6.275(1)$ Å, $c = 5.035(1)$ Å
Volume	171.7(6) $Å^3$
Z	1

[a] Equivalent isotropic U is defined as one-third of the trace of the orthogonalized U_{ij} tensor. O and F are fixed on the same site with equivalent U_{ij}. The site occupancy factor is fixed at $\frac{1}{3} \times 0.5$ for O and $\frac{2}{3} \times 0.5$ for F. The anisotropic displacement exponent takes the form

$$-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*U_{12}).$$

rived. Upon excitation, the oxyhalotungstate octahedra are unhindered in expansion so that a large Stokes shift results (*4*). The large Stokes shift of emission and the presence of structurally isolated $[WO_2X_4]^{-2}$ groups, suggest that after excitation and relaxation to the equilibrium position of the excited state, the excitation energy is strongly localized at that particular site, accompanied by a large lattice relaxation. In literature such a situation is usually referred to as a self-trapped state.

The major difference between the optical properties of the two oxyhalotungstates is

TABLE IV

INTERATOMIC DISTANCES AND BOND ANGLES IN $Cs_2WO_2F_4$

Bond distances		
W–(O, F)	6	1.891(5) Å
Cs–(O, F)	3	3.172(8) Å
	3	3.346(8) Å
	6	3.191(8) Å
Bond angles		
(O, F)–W–(O, F)	88.6(2)	
	91.4(2)	
(O, F)–Cs–(O, F)	68.6	
	64.6	
	68.2	
	50.2	
	47.8	
	62.6	

TABLE V

COMPARISON OF THE LUMINESCENCE PROPERTIES OF $Cs_2WO_2F_4$ AND $Cs_2WO_2Cl_4$

	$Cs_2WO_2F_4$[a]	$Cs_2WO_2Cl_4$[b]
Excitation max. ($\times 10^3$ cm^{-1})	~37.7	31.3
Emission max. ($\times 10^3$ cm^{-1})	~16.6	16.6
Stokes shift ($\times 10^3$ cm^{-1})	~21.1	15.0
Quenching temp.	High (>300 K)	Low

[a] Room temperature data.
[b] Results for $T = 4.2$ K from Ref. (*3*).

the high energy position of the excitation band of $Cs_2WO_2F_4$ when compared with $Cs_2WO_2Cl_4$ (Table V). The excitation maximum of the former compound is situated at ~7000 cm^{-1} higher energy. This can be explained as follows. The excitation transition for d^0 ion complexes is usually attributed to a ligand to metal charge transfer. In view of the high electronegativity of the F^- ions, charge transfer from F^- to W^{6+} is predicted at much higher energy than from O^{-2} to W^{6+} within the $[WO_2F_4]^{-2}$ octahedra. By optical electronegativity argument, the energy position of the charge transfer transition (CTT), (σ) can be estimated by making use of Jorgensen relationship (*6*);

$$\sigma = [\chi_{\mathrm{opt}}(X) - \chi_{\mathrm{opt}}(M^{n+})] \times 30kK,$$

where $\chi_{\mathrm{opt}}(x)$ is the optical electronegativity of the ligand and $\chi_{\mathrm{opt}}(M^{n+})$ that of the metal cation in a particular oxidation state. For the ligands involved we have $\chi_{\mathrm{opt}}(\mathrm{O}) = 3.2$, $\chi_{\mathrm{opt}}(\mathrm{F}) = 3.9$, and $\chi_{\mathrm{opt}}(\mathrm{Cl}) = 3.0$. The value of $\chi_{\mathrm{opt}}(W^{6+}) = 1.95$ is taken from Ref. (*7*).

Using Eq. (1) and the optical electronegativity values of the ligands involved places the O^{-2}–W^{6+} CTT at 37,500 cm^{-1} in good agreement with the experimentally estimated value of 37,700 cm^{-1}. The corresponding F^-–W^{6+} CTT is estimated at much higher energy, viz., 58,500 cm^{-1}. We conclude that the observed excitation band should be associated with CTT within W–O bonds in the $[WO_2F_4]^{-2}$ octahedra. The situation is similar to that observed in the elpasolite $K_2NaTiOF_5$ (*8*) and in Cs_2NbOF_5 (*1*).

For $Cs_2WO_2Cl_4$, the Cl^-–W^{6+} is calculated to be 31,500 cm^{-1}. The experimentally determined value of 31,250 cm^{-1} may seem in good agreement, but the situation may be more complicated due to the proximity of electronegativities of the O^{-2}/Cl^- couple when compared with the O^{-2}/F^- couple. Nevertheless, the low energy position of the excitation band in $Cs_2WO_2Cl_4$ can be attributed to the presence of less electronegative Cl^- ligands around the central W^{6+} ion within the $[WO_2Cl_4]^{-2}$ octahedra.

The influence of the energy position of the first absorption band on the efficiency of luminescence is dramatic. While $Cs_2WO_2Cl_4$ is reported to emit weakly even at 4.2 K (*3*), $Cs_2WO_2F_4$ is an efficient luminescent material at room temperature and the luminescence persists up to 250°C. We attribute this to the high energy position of the absorption band in the oxyfluorotungstate, which in spite of the enormous Stokes shift (~2.5 eV) yields efficient luminescence. Note that the higher energy position of the absorption band yields higher quenching temperature of luminescence for many closed-shell transition metal ions as expected from the simple configuration coordinate model (*9*).

Furthermore, there are examples in the literature where despite a larger Stokes shift of emission (≥2.5 eV), efficient luminescence is observed from an optically active center at ambient temperatures. Examples include $PbAl_2O_4$, $PbGa_2O_4$, $Bi_2Al_4O_9$ (*10*), and $PbHSO_4$ (*11, 12*). The Stokes shift varies from 2.2 eV for $Bi_2Al_4O_9$ to 2.9 eV for $PbHSO_4$. In all cases, however, the excitation bands are at high energies (>4.5 eV).

Since the F^- to W^{6+} CTT is expected at very high energies (see above), the emitting state in the $[WO_2F_4]^{-2}$ octahedral complexes must be localized within the "WO_2-groups." In the literature there is one example of emission from such a group, viz., in the oxyflurotungstate $Ba_2WO_3F_4$ (*13*). In this material containing nominal $WO_4F_2^{-4}$ octahedra, Blasse *et al.* have assigned the luminescence to the "*cis*-WO_2 groups." However, the excitation and emission maximum in $Ba_2WO_4F_2$ are at 302 and 475 nm, respectively, yielding 12,060 cm^{-1} as the Stokes shift of emission (*13*). This is much smaller than that observed for the isolated $[WO_2X_4]^{-2}$ octahedral complexes in the $Cs_2WO_2(F, Cl)_4$ materials.

Conclusion

The high energy position of the excitation band in $Cs_2WO_2F_4$ exists due to the presence of the highly electronegative F^- ions, so that CTT are mainly localized in the W–O bonds. Furthermore, the $[WO_2F_4]^{-2}$ polyhedra are also electronically isolated from each other, hindering the correlation effects which would lead to a broad oxygen valence band and a broad tungsten conduction band and thus to lower energy absorptions.

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