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A Structural Study of a New Lithium Oxyfluorotungstate, LiW_3O_9F

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The structure of LiW_3O_9F was determined from 972 single crystal reflections and refined by least squares to an R factor of 0.065. It has orthorhombic symmetry with space group $Fdd2$ and parameters a = 12.716(2) Å, b = 15.230(2) Å, c = 7.288(1) Å, and Z = 8. The structure is related to the HTB structure and can be described as a complex stacking of HTB layers perpendicular to the b axis. The lithium atoms are found in the hexagonal cavities of the HTB layers.

Introduction

A number of studies have been carried out recently in our laboratory on the alkali oxyfluorotungstates (*1–4*). We now focus our attention on the pseudo-binary system $LiF–WO_3$. A preliminary study of this system was made by Schmitz-Dumont and Bruns in 1953 (*5*). However, under the operating conditions of these last authors no phases were found to exist. This study was therefore again undertaken and a new unknown phase LiW_3O_9F was prepared.

The growing interest for the crystallographic and physical properties, and in particular, for the ferroelectric properties of this type of compound (*1, 3*) led us to carry out a detailed structural study of LiW_3O_9F.

Experimental

Preparation

The starting products LiF and WO_3 of purity greater than 99.9% were first dried and then taken at different molar ratios (LiF/WO_3), mixed and ground. The mixture was introduced into gold or platinum tubes, evacuated, and then filled with dry oxygen and sealed. The syntheses were carried out at 680°C for 72 hr.

An X-ray diffraction study of the obtained products indicated a new phase appearing for the ratio LiF/WO_3 = 1/3. On either side of this ratio the phase coexisted with LiF or WO_3 depending on the ratio chosen. No homogeneity range was found.

A heat treatment at 700°C and slow cooling allowed us to obtain small colorless single crystals of rectangular form.

X-Ray Diffraction Study

The X-ray diffraction powder pattern was obtained using a Philips diffractometer with the radiation Cu$K\alpha$. The spectrum given in Table I was indexed on the basis of an orthorhombic cell and the parameters are a = 12.716(2) Å, b = 15.230(2) Å, and c = 7.288(1) Å. The Weissenberg and precession photographs gave the following sys-

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TABLE I

X-RAY DIFFRACTION POWDER SPECTRUM OF LiW_3O_9F

h	k	l	d_{obs} (Å)	d_{calc} (Å)	I/I_0
1	1	1	5.843	5.840	25
2	2	0	4.886	4.880	50
1	3	1	3.960	3.959	75
0	4	0	3.813	3.807	100
3	1	1	3.562	3.562	20
4	0	0	3.177	3.179	80
2	0	2	3.162	3.161	100
3	3	1	2.9702	2.9710	40
4	4	0	2.4389	2.4402	100
2	4	2	2.4326	2.4324	100
2	6	0	2.3581	2.3574	10
4	2	2	2.2855	2.2852	5
5	3	1	2.1701	2.1706	10
1	3	3	2.1597	2.1597	5
0	6	2	2.0827	2.0829	40
1	7	1	2.0571	2.0573	10
6	2	0	2.0408	2.0417	10
3	3	3	1.9454	1.9457	10
0	8	0	1.9046	1.9037	45
3	7	1	1.8714	1.8707	35
6	0	2	1.8318	1.8320	30
5	1	3	1.7458	1.7452	10
7	3	1	1.6648	1.6651	25
5	3	3	1.6612	1.6601	20
6	4	2	1.6516	1.6509	10
0	4	4	1.6437	1.6437	10
2	8	2	1.6313	1.6309	35
6	6	0	1.6273	1.6268	20
5	7	1	1.6127	1.6123	10
1	7	3	1.6083	1.6078	15
8	0	0	1.5900	1.5894	15
4	0	4	1.5808	1.5809	30
5	5	3	1.5215	1.5218	5
3	7	3	1.5134	1.5139	5
8	4	0	1.4665	1.4668	10
4	4	4	1.4603	1.4600	10
2	6	4	1.4417	1.4417	5
8	2	2	1.4306	1.4310	5
1	9	3	1.3805	1.3804	5
7	7	1	1.3691	1.3696	10
5	7	3	1.3667	1.3668	10
1	11	1	1.3520	1.3525	10
9	3	1	1.3377	1.3380	5
6	8	2	1.3201	1.3201	15
3	9	3	1.3201	1.3196	15
0	8	4	1.3160	1.3164	15

Note. Lattice spacings calculated using λ = 1.5405 Å and a = 12.716(2) Å, b = 15.230(2) Å, c = 7.288(1) Å.

tematic presences:

hkl: $h + k = 2n$ $h + l = 2n$ $k + l = 2n$
$0kl$: $k + l = 4n$
$h0l$: $h + l = 4n$.

These are compatible with the space group *Fdd*2. The measured density, $d_{exp} = 6.76$ g/cm^3, corresponds to eight formula units per cell ($d_{calc} = 6.79$ g/cm^3).

The single crystal intensity data were measured on a crystal with a rectangular form and dimensions 0.09 × 0.06 × 0.04 mm using an automatic diffractometer E-N CAD3 and molybdenum monochromatic radiation (λ = 0.70929 Å) up to $\theta_{max} = 40°(\theta/2\theta$ scan). Two groups of equivalent reflections were averaged (hkl and $\bar{h}kl$) and corrected for the Lorentz-polarization factor. A total of 1150 independent reflections were obtained and 972 were retained with $I > 3\sigma(I)$.

Determination and Refinement

The study of the three-dimensional Patterson synthesis allowed to determine the positions of the heavy atoms: W(1) in 8(a) and W(2) in 16(b). The positions of the anions as well as the lithium atom were found following a Fourier synthesis: X(N) (N = 1, 2, 3, 4, 5) in 16(b) and Li in 8(a). No distinction was made between oxygen and fluorine atoms. The first cycles of refinement with isotropic temperature factors led to an R factor of 0.15. At this stage a careful examination of the structure factors indicated an absorption problem at low angles. After the application of an absorption correction (μr = 2.30) the R factor was lowered to 0.12.

Several cycles of full-matrix least squares refinement with anisotropic temperature factors (*6*) gave a final reliability index of 0.065. Both the (xyz) and ($\bar{x}\bar{y}\bar{z}$) models were tested for absolute configuration. The one retained was chosen on a purely statistical basis (Hamilton's test).

The atomic scattering factors for Li^+, W^{+6}, F^-, and O^{-2} were those of McMaster

TABLE II

FINAL ATOMIC COORDINATES AND ANISOTROPIC TEMPERATURE FACTORS (× 10^4 Å^2) FOR LiW_3O_9F

Site	Atom	X	Y	Z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
8(*a*)	W(1)	0.00	0.00	0.20	076(5)	442(9)	76(7)	3(5)		
16(*b*)	W(2)	0.01010(7)	0.26754(1)	0.2297(1)	106(3)	206(3)	111(4)	14(3)	−12(3)	−13(3)
8(*a*)	Li	0.00	0.00	0.8012(20)	15[b]	10	47			
16(*b*)	*X*(1)[a]	0.2863(12)	−0.0016(14)	0.2238(26)	109(62)	238(67)	27(47)	68(53)	−2(52)	16(62)
16(*b*)	*X*(2)	0.0029(15)	0.1255(8)	0.2209(52)	157(79)	21(41)	127(65)	32(60)	91(95)	−20(63)
16(*b*)	*X*(3)	0.1019(15)	−0.0011(17)	0.4091(27)	105(67)	289(135)	112(73)	00(68)	−68(58)	−59(79)
16(*b*)	*X*(4)	0.1420(14)	0.2498(15)	0.2852(27)	71(59)	200(114)	131(73)	−11(59)	−8(53)	−50(71)
16(*b*)	*X*(5)	−0.0024(24)	0.3841(13)	0.2302(53)	342(87)	181(87)	237(136)	−255(92)	−137(134)	235(139)

[a] The symbol *X* represents here the atoms O and F.

[b] The Li atom was refined only isotropically and the U_{ii} values correspond to the B_{iso}.

Note. The temperature factor expression is $\exp[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + hka^*b^*U_{12} + hla^*c^*U_{13} + klb^*c^*U_{23})]$.

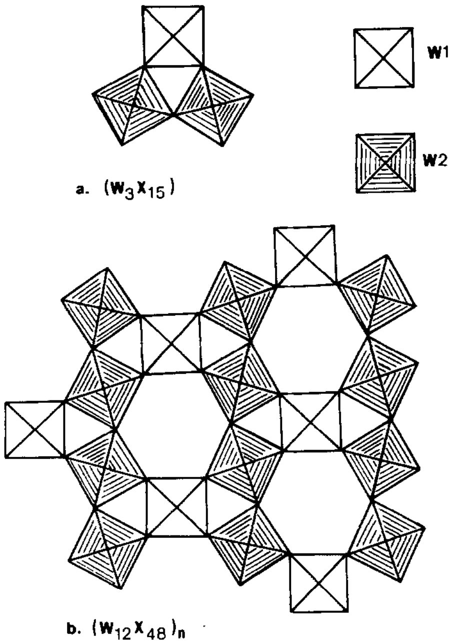

FIG. 1. (a) The basic building block W_3X_{15} of the HTB layer. (b) Infinite layers $(W_{12}X_{48})_n$ of the HTB type.

et al. (*7*), and anomalous dispersion factors those of Dauben and Templeton (*8*). A weighted mean $f_0(O/F = 9/1)$ was used for the anion scattering factor. The function $\Sigma w(|F_o| - |F_c|)^2$ was minimized, where F_o and F_c are the observed and calculated structure factors and *w* the weight taken as one for all reflections. The final atomic coordinates and anisotropic temperature factors are given in Table II. The interatomic distances are shown in Table III. A table giving the F_o and F_c values can be obtained from NAPS.[1]

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[1] See NAPS document No. 04131 for 7 pages of supplementary material. Order from ASIS/NAPS, Microfiche Publications, P.O. Box 3513, Grand Central Station, New York, NY 10163. Remit in advance $4.00 for microfiche copy or for photocopy, $7.75 up to 20 pages plus $.30 for each additional page. All orders must be prepaid. Institutions and organizations may order by purchase order. However, there is a billing and handling charge for this service of $15. Foreign orders add $4.50 for postage and handling, for the first 20 pages, and $1.00 for additional 10 pages of material. Remit $1.50 for postage of any microfiche orders.

TABLE III

INTERATOMIC DISTANCES (IN Å) FOR LiW_3O_9F

2 × W(1)-X(2)	1.92(2)	W(2)-X(1)	1.82(2)
2 × W(1)-X(3)	2.00(2)	W(2)-X(1)	1.97(2)
		W(2)-X(2)	2.17(2)
		W(2)-X(3)	1.85(2)
		W(2)-X(4)	1.99(2)
⟨W(1)-X⟩	= 1.91	W(2)-X(5)	1.78(2)
2 × X(2)-X(3)	2.68(3)	⟨W(2)-X⟩	= 1.93
2 × X(2)-X(3)	2.69(3)	X(1)-X(2)	2.67(3)
2 × X(2)-X(4)	2.70(3)	X(1)-X(2)	2.67(3)
2 × X(2)-X(4)	2.73(3)	X(1)-X(3)	2.71(3)
X(3)-X(3)	2.59(4)	X(1)-X(3)	2.70(3)
		X(1)-X(4)	2.64(2)
2 × X(3)-X(4)	2.73(3)	X(1)-X(4)	2.65(2)
X(4)-X(4)	2.75(4)	X(1)-X(5)	2.76(3)
⟨X-X⟩	2.70	X(1)-X(5)	2.79(3)
2 × Li-X(4)	2.19(3)	X(2)-X(3)	2.75(3)
2 × Li-X(5)	1.84(3)	X(2)-X(4)	2.63(3)
		X(3)-X(5)	2.79(3)
		X(4)-X(5)	2.78(3)
		⟨X-X⟩	2.71
W(1)-W(2)	4.082(1)	W(1)-Li	4.38(2)
W(1)-W(2)	4.929(1)	W(1)-Li	2.91(2)
W(1)-W(2)	3.679(1)	W(2)-Li	3.56(2)
W(1)-W(2)	3.686(1)	W(2)-Li	3.58(2)
W(2)-W(2)	3.692(2)	W(2)-Li	3.86(2)
W(2)-W(2)	4.913(2)		

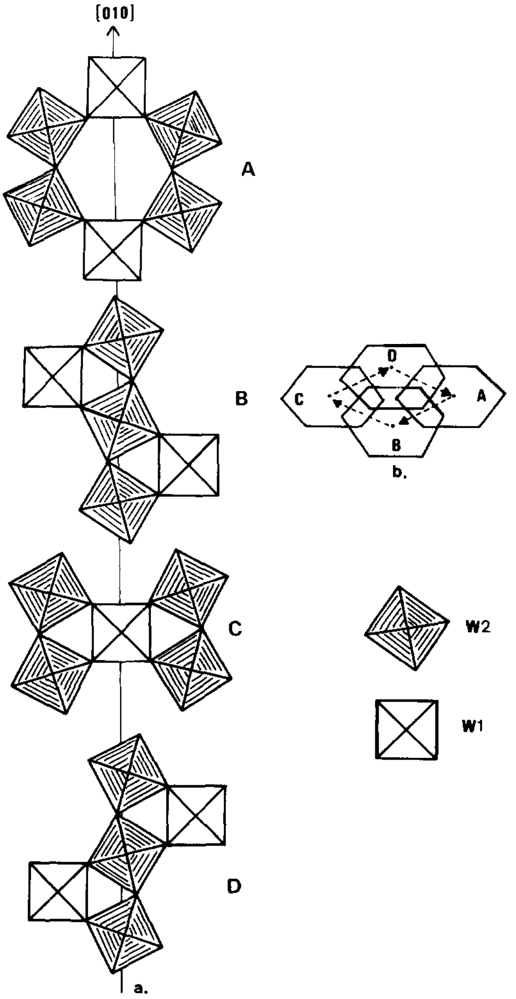

FIG. 2. (a) Stacking of the HTB layers along the [010] direction in the LiW_3O_9F structure. (b) Displacement of these layers with respect to each other in the (010) plane. Layers projected along [010].

Description of the Structure and Discussion

The structure is a three-dimensional framework lattice made up of two kinds of WX_6 octahedra, $W(1)X_6$ and $W(2)X_6$ (X = O, F). It can be described using the basic building block W_3X_{15} (Fig. 1a) formed by three octahedra sharing corners. These units are put together to give infinite HTB layers in the (010) plane with formula $(W_{12}X_{48})_n$ (Fig. 1b). These layers share common corners with each other to give a three-dimensional lattice $W_{12}X_{40}$ (W_3X_{10}) in which the lithium atoms are inserted leading to the overall formula AW_3X_{10}. The stacking of the HTB (hexagonal tungsten bronze) layers is rather complex and shows a repeat sequence of four layers ABCD. Figure 2a represents the arrangement of these layers with respect to one another along a common axis (b axis). The specific orientation of three of these layers with respect to the fourth one seems to follow the three principal directions of the hexagonal cavity. Their resulting displacement is shown in Fig. 2b and can be represented by a vector $\mathbf{T} = \frac{1}{4}(\mathbf{a} + \mathbf{b} + \mathbf{c})$. This displacement gives rise to a certain number of structural consequences:

The W(2)X_6 octahedra share only five of their six corners, leaving one free. The free corners are always directed towards the hexagonal cavities of the HTB layers where the lithium atoms are situated. We have then units of formula (W_3X_{10}) made up by string of three octahedra (W(2)X_6–W(1)X_6–W(2)X_6) along the *b* axis, on each end of which there are lithium atoms (Fig. 3).

The structure also presents alternating planes of W(1)X_6 and W(2)X_6 octahedra tied to each other by common corners, parallel to the (110) or ($\bar{1}\bar{1}0$) plane. In the W(1)X_6 planes the octahedra are completely isolated whereas in the W(2)X_6 planes they form isolated chains running along the [001] direction.

The hexagonal cavities of the HTB layers communicate with one another in the [110] and [$\bar{1}\bar{1}0$] directions forming intersecting tunnels of complex cross sections.

The lithium atoms are found in the hexagonal cavities of the HTB layers. It has the same *y* coordinate as the anions *X*(1), *X*(3), and *X*(4) forming the hexagon, but is displaced in the HTB plane towards the *X*(4) anion (see Fig. 4). This displacement is obviously necessary to assure normal bonding distances for the lithium atom, the center of the hexagon at a distance of 2.60 Å being too long for a Li–*X* bond.

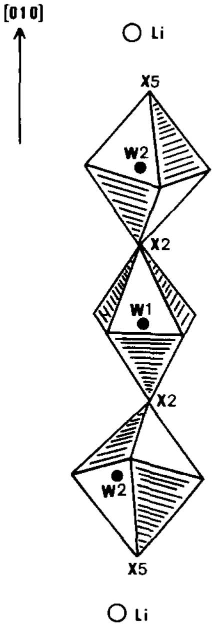

FIG. 3. String of three octahedra (belonging to layers B, C, and D) along the [010] direction.

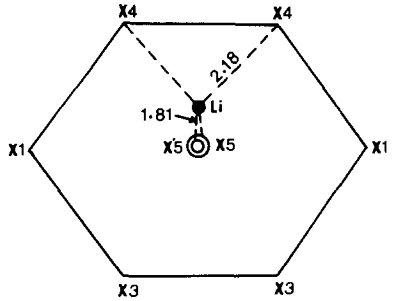

FIG. 4. Position of the lithium atom in the hexagonal cavity of a HTB layer.

The lithium atom is further bonded to the unshared anion *X*(5) of the W(2) octahedron of the HTB layers above and below the hexagon plane, at a distance of 1.84 Å, thus forming a distorted tetrahedron (Fig. 5a).

A compound with the same stoichiometry, UNb_3O_{10}, has been reported previously (*9, 10*). It has orthorhombic symmetry with space group *Fddd* and a = 7.38 Å, b = 12.78 Å, c = 15.96 Å. Both UNb_3O_{10} and LiW_3O_9F have similar octahedral skeleton structures related to the HTB type. The metric relationship to the HTB is

$$a_{\mathrm{Li}} \approx b_{\mathrm{U}} \approx a_{\mathrm{HTB}}\sqrt{3},\ b_{\mathrm{Li}} \approx c_{\mathrm{U}} \approx 2c_{\mathrm{HTB}},\ c_{\mathrm{Li}} \approx a_{\mathrm{U}} \approx a_{\mathrm{HTB}}.$$

The major difference between the two structures is the coordination of the Li atom by comparison to the U atom, both of which occupy similar positions in the two structures. In UNb_3O_{10} the U atom is found in the center of the hexagon and has hexagonal bipyramidal coordination. The Li atom in LiW_3O_9F is displaced towards one side of the hexagon and is only bonded to two of the hexagon atoms, thus forming a dis-

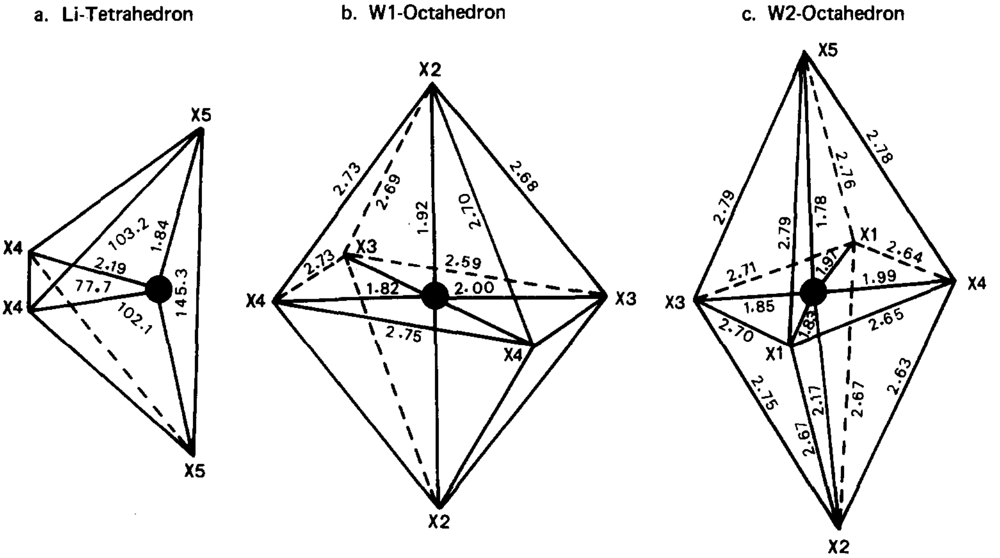

FIG. 5. Coordination polyhedra for (a) lithium, (b) W(1), and (c) W(2) atoms.

torted tetrahedron with two other anions above and below the hexagon plane.

As can be seen in Table III and in Figs. 5b and c, the W(1)–X distances vary from 1.92 to 2.00 Å ($\langle W(1)–X \rangle$ = 1.91 Å) while those for W(2)–X are in the range of 1.78 to 2.17 Å ($\langle W(2)–X \rangle$ = 1.93 Å). The X–X distances in the W(1) and W(2) octahedra vary, respectively, from 2.59 to 2.75 Å and from 2.63 to 2.79 Å. The distances are comparable to distances found in a great number of HTB derivative structures.

Although all thermal parameters are within normal limits, the value of U_{22} for W(1) is rather high and the value of U_{22} of X(2) is lower by comparison to the other anion U_{22} values. This is surely the results of correlation between the U_{22}(W1) and U_{22}(X2) tensors.

The SHG test proved to be positive with a value of about 20 times that of quartz.

Physical studies on this new material are in progress.

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