

## THE CRYSTAL STRUCTURE OF FOORDITE

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### ABSTRACT

The crystal structure of foordite,  $\text{Sn}^{2+}\text{Nb}_2\text{O}_6$ ,  $a$  17.093(3),  $b$  4.877(1),  $c$  5.558(1) Å,  $\beta$  90.85(1)°,  $V$  463.3(1) Å<sup>3</sup>, space group  $C2/c$ , has been refined to a residual  $R$  of 3.6% on 654 unique observed [ $I > 3\sigma(I)$ ] reflections (MoK $\alpha$  radiation). Foordite is isostructural with thoreaulite, and the present study represents the first correct refinement in  $C2/c$  for either mineral. Refinement confirms the above formula, and the assignment of all Sn to the divalent state, for the sample studied. The structure consists of alternations of two types of layers perpendicular to  $X$ . One type of layer consists of corner-linked  $\text{NbO}_6$  octahedra forming a flat, perforated, two-octahedron-thick sheet with closest-packed anions. The other type consists of distorted, edge-sharing  $\text{Sn}^{2+}\text{O}_8$  square antiprisms forming a flat, perforated sheet. The  $\text{Sn}^{2+}$  coordination polyhedron is severely distorted owing to the presence of a stereoactive lone-pair of electrons.

**Keywords:** foordite, thoreaulite, crystal structure, Nb-oxide mineral, divalent tin, lone-pair cation.

### SOMMAIRE

La structure cristalline de la foordite,  $\text{Sn}^{2+}\text{Nb}_2\text{O}_6$ ,  $a$  17.093(3),  $b$  4.877(1),  $c$  5.558(1) Å,  $\beta$  90.85(1)°,  $V$  463.3(1) Å<sup>3</sup>, groupe spatial  $C2/c$ , a été affinée jusqu'à un résidu  $R$  de 3.6% en utilisant 654 réflexions uniques observées [ $I > 3\sigma(I)$ ] (rayonnement MoK $\alpha$ ). La foordite est isostructurale avec la thoreaulite, et nos résultats constituent la première ébauche des deux structures dans le groupe spatial  $C2/c$ . L'affinement confirme aussi la formule ci-haut, et l'attribution de la totalité de l'étain à la forme bivalente pour l'échantillon examiné. La structure contient deux sortes de feuillettes en alternance perpendiculaire à  $X$ . Un des feuillettes est fait d'octaèdres  $\text{NbO}_6$  à coins partagés: le feuillet est plat, perforé, d'une épaisseur de deux octaèdres, et montre un empilement compact des anions. L'autre contient des antiprismes carrés difformes de  $\text{Sn}^{2+}$  à arêtes partagées, qui définissent aussi un feuillet plat et perforé. Le polyèdre de coordination du  $\text{Sn}^{2+}$  est fortement difforme à cause d'une paire stéréoactive d'électrons isolés.

(Traduit par la Rédaction)

**Mots-clés:** foordite, thoreaulite, structure cristalline, oxyde de Nb, étain bivalent, cation à paire d'électrons isolés.

### INTRODUCTION

The mineral foordite,  $\text{Sn}^{2+}\text{Nb}_2\text{O}_6$ , is isostructural with its Ta-analog thoreaulite,  $\text{Sn}^{2+}\text{Ta}_2\text{O}_6$  (Černý *et al.* 1988). Although a structure analysis has not been done previously for foordite, several analyses exist for thoreaulite.

The first structure-analyses of thoreaulite were made from photographic data (Maksimova & Ilyukhin 1967, Mumme 1970). Both studies assumed the Sn to be tetravalent, and from the 1:2 Sn:Ta ratio, a formula of  $\text{Sn}^{4+}\text{Ta}_2\text{O}_7$ ,  $Z = 4$  was assigned. This results in 28 anions per unit cell, 4 more than are present. Both studies proposed an additional site for these anions, which resulted in unreasonable stereochemistries and high  $R$  indices ( $R = 15\%$  for the model of Mumme 1970).

Maksimova *et al.* (1976) re-investigated the thoreaulite structure, this time using diffractometer data, corrected for absorption and refined by full-matrix least-squares methods. In an attempt to avoid "premature assumptions", they refined the structure in  $Cc$ . Difference-Fourier maps showed none of the additional oxygen atoms, confirming the formula as  $\text{Sn}^{2+}\text{Ta}_2\text{O}_6$ . Although refined in  $Cc$ , the structure of Maksimova *et al.* (1976) is strongly pseudocentric. However, when Maksimova *et al.* (1976) refined the same data in  $C2/c$ ,  $R$  increased from 5.9 to  $\sim 8\%$ ; hence they concluded that the acentric model is correct.

### EXPERIMENTAL

The sample used in this study is type foordite from the Lutsiro pegmatite, Rwanda, and was obtained from the Université Catholique de Louvain, number P1284 (THF-5 of Černý *et al.* 1988). Subsequent to intensity-data collection, the crystal was chemically analyzed by electron microprobe under the operating conditions given in Černý *et al.* (1988). The resulting formula is given in Table 1.

An equant cleavage-fragment was mounted on a Nicolet R3m automated four-circle diffractometer, and 25 intense reflections were centered using

TABLE 1. MISCELLANEOUS INFORMATION: FOORDITE

a	17.093(3) Å	Crystal size (mm)	0.12x0.14x0.15
b	4.877(1)	Rad/Mono	MoK $\alpha$ /graphite
c	5.558(1)	Total  F <sub>o</sub>	673
$\beta$	90.85(1)°	F <sub>o</sub>   > 3 $\sigma$	654
V	463.3(1) Å <sup>3</sup>	Final R(obs), wR(obs)	3.6, 3.6%
		$\mu$ (cm <sup>-1</sup> )	283
Space group	C2/c		
Unit cell contents:	(Sn <sup>2+</sup> <sub>2</sub> , <sub>50</sub> Pb <sub>0.50</sub> ) <sub>Z4</sub> .00(Nb <sub>5.59</sub> Ta <sub>2.41</sub> ) <sub>Z8</sub> .00O <sub>24</sub>		
R =	$\Sigma ( F_o  -  F_c ) / \Sigma  F_o $		
wR =	$\Sigma w( F_o  -  F_c )^2 / \Sigma w F_o ^2$		

graphite-monochromated MoK $\alpha$  X radiation. Least-squares refinement of the setting angles gave the unit-cell parameters of Table 1, and the orientation matrix used for data collection. Intensity data were collected over 2 asymmetric units to a maximum  $\sin \theta/\lambda$  of 0.7035, according to the experimental method of Ercit *et al.* (1986). An empirical absorption-correction ( $\psi$ -scan),  $L$ - $p$  and background corrections were made, and equivalent reflections were merged to give 673 unique data (merging  $R = 4.9\%$ ), of which 654 were considered observed [ $I > 3\sigma(I)$ ].

### STRUCTURE SOLUTION AND REFINEMENT

The SHELXTL package of programs was used in all computations. Scattering curves for neutral atoms, together with anomalous dispersion corrections, were taken from Cromer & Mann (1968) and Cromer & Liberman (1970), respectively.  $R$  indices are of the form given in Table 1.

The mean value of  $|E^2 - 1|$  is 0.959, which favors  $C2/c$  as the space group for foordite. Using the coordinates for the thoreaulite structure in  $Cc$  (Maksimova *et al.* 1976) as a basis, starting parameters for foordite in  $C2/c$  were calculated. In all stages of the refinement, the mean-scattering curves for the cation sites were constrained to conform with the results of the microprobe analysis (Table 1). Refinement of an isotropic model gave  $R$  5.5%,  $wR$  6.5%. Conversion to anisotropic temperature-factors reduced  $R$  to 4.9%,  $wR$  to 6.1%. High  $\Delta/\sigma$  values for several high-intensity, low-angle diffraction-maxima suggested an extinction problem. An isotropic primary extinction-correction was applied, resulting in final indices of  $R$  3.6%,  $wR$  3.6%.

At this stage, a refinement in  $Cc$  was attempted to assess the validity of the model of Maksimova *et al.* (1976). The final model had anisotropically vibrating cations, but isotropically vibrating anions because most anions had nonpositive definite sets of temperature parameters when modeled as vibrating anisotropically. Addition of an isotropic, primary extinction-correction resulted in  $R$  3.2,  $wR$  3.4%. This model is extremely pseudocentric: in terms of positional parameters, the mean absolute deviation from a centric model is only 2.8  $\sigma$ . This finding con-

TABLE 2. POSITIONAL PARAMETERS FOR FOORDITE

Site	x	y	z	U <sub>equiv</sub> *
Sn	0	0.24046(11)	1/4	2.28(2)
Nb	0.33007(2)	0.25807(7)	0.32770(7)	1.42(2)
0(1)	0.4269(2)	0.4201(10)	0.4013(8)	1.95(11)
0(2)	0.3574(2)	0.0419(10)	0.0692(8)	1.93(11)
0(3)	0.2192(2)	0.0632(9)	0.3527(7)	1.60(10)

\* U<sub>equiv</sub> = U<sub>equiv</sub> × 10<sup>2</sup> (Å<sup>2</sup>)

TABLE 3. ANISOTROPIC TEMPERATURE-FACTOR COEFFICIENTS FOR FOORDITE

Site	U <sub>11</sub> *	U <sub>22</sub>	U <sub>33</sub>	U <sub>12</sub>	U <sub>13</sub>	U <sub>23</sub>
Sn	197(4)	235(4)	251(4)	0	13(2)	0
Nb	130(3)	144(3)	150(3)	1(1)	-8(1)	-1(1)
0(1)	138(17)	197(20)	250(22)	-22(15)	-20(15)	5(16)
0(2)	171(17)	197(20)	212(19)	13(16)	3(15)	-22(17)
0(3)	152(17)	160(19)	168(18)	-12(15)	1(14)	-19(15)

\* U<sub>ij</sub> = U<sub>ij</sub> × 10<sup>4</sup>

TABLE 4. INTERATOMIC DISTANCES (Å) AND ANGLES (°) IN FOORDITE

Sn Polyhedron		Nb Polyhedron	
Sn-0(1)a,c	2.177(5) x2	Nb-0(1)b	1.874(4)
-0(1)b,d	2.420(4) x2	-0(2)b	1.848(5)
-0(2)a,c	3.006(6) x2	-0(2)c	2.035(5)
-0(2)b,d	3.216(6) x2	-0(3)a	2.128(4)
<Sn-O>	2.705	-0(3)b	2.160(4)
		-0(3)c	1.975(4)
		<Nb-O>	2.003
0(1)a,c-0(1)b,d	2.82, 75.6 x2	0(1)b-0(2)b	2.86, 100.2
0(1)a	-0(1)c	-0(2)c	2.72, 88.0
0(1)a,b-0(1)d,c	2.89, 77.6 x2	-0(3)b	2.86, 90.2
0(1)a,c-0(2)d,b	3.03, 65.1 x2	-0(3)c	2.93, 99.3
0(1)b,d-0(2)c,a	2.72, 58.9 x2	0(2)b-0(2)c	2.81, 92.5
0(1)b,d-0(2)d,b	4.12, 93.0 x2	-0(3)a	2.86, 91.8
0(1)a,c-0(2)b,d	4.96, 105.7 x2	-0(3)b	2.90, 98.4
0(2)a	-0(2)c	0(2)c-0(3)a	2.69, 80.3
0(2)a,b-0(2)d,c	2.72, 53.5 x2	-0(3)b	2.72, 80.6
<O-O>	3.42	0(3)a-0(3)b	2.66, 76.6
<O-Sn-O>	79.3	-0(3)c	2.90, 89.8
		0(3)b-0(3)c	2.85, 86.9
		<O-O>	2.81
		<O-Nb-O>	89.6

$\sigma$  for O-O separations is 0.01, for angles is 0.2

sidered with the insignificantly different values of  $wR$  of the centric and acentric models (Abrahams 1974) indicates that there is no reason to reject a centric model. It is impossible to assess why Maksimova *et al.* (1976) obtained the opposite result as they did not cite estimated values of  $\sigma$  for any of the structural parameters of their models, and gave no structural details about their centric model.

Final positional parameters (centric model) are given in Table 2, anisotropic temperature-factor coefficients in Table 3, bond lengths, polyhedral edge-lengths and angles in Table 4, and empirical bond-valences in Table 5. Observed and calculated structure-factors are available from the Depository of Unpublished Data, CISTI, National Research Council of Canada, Ottawa, Ontario K1A 0S2.

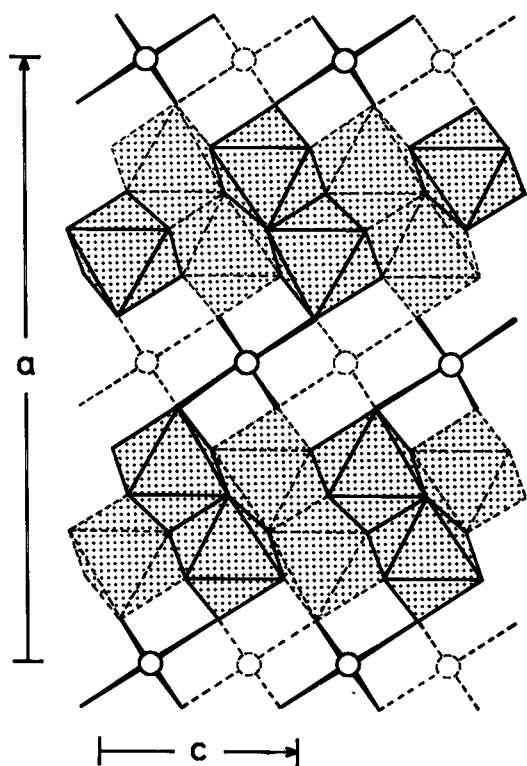


FIG. 1. The foordite structure, as projected down  $Y$ . Nb polyhedra are shaded, and  $\text{Sn}^{2+}$  polyhedra are given as balls and spokes to emphasize the sheeted, closest-packing plus gap structure of the anions. For simplicity, only the four shortest bonds of each  $\text{Sn}^{2+}$  polyhedron are shown. Solid lines represent polyhedra, atoms and bonds at one level along  $Y$ ; dashed lines represent these structural features at adjacent levels.

#### DESCRIPTION OF THE STRUCTURE

Despite significant errors in their drafting of the thoreaulite structure, Graham & Thornber (1974) correctly described the anion packing of the thoreaulite-foordite structure as interrupted closest-packing; that is, the anion packing consists of isolated sheets of hexagonally closest-packed oxygen atoms, each separated from adjacent sheets by a 3.7-Å gap. The sheets are perpendicular to  $X$ , but the closest-packing within these sheets is perpendicular to  $Y$  (Fig. 1).

In the closest-packed sheets, Nb (and Ta) atoms occupy 50% of the octahedral interstices. The  $\text{NbO}_6$  octahedra are linked by corners to form a flat, two-octahedron-thick, perforated sheet (Fig. 2a). The gap between adjacent closest-packed sheets has  $\text{Sn}^{2+}$  cations occupying [8]-coordinated, square antiprismatic voids. These  $\text{SnO}_8$  polyhedra are linked

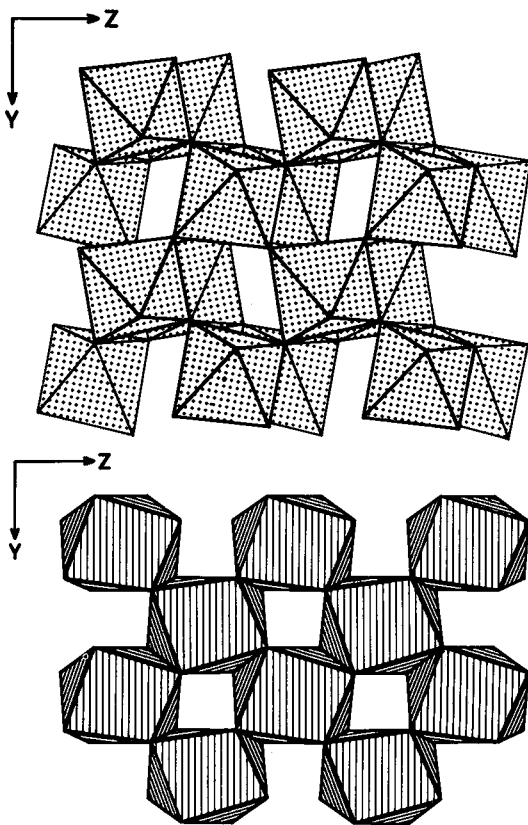


FIG. 2. The layers of the foordite structure. Top: the Nb-layer; bottom: the  $\text{Sn}^{2+}$  layer. The full coordination of the  $\text{Sn}^{2+}$  polyhedra is shown.

via edges to form a flat, perforated sheet of single polyhedron thickness (Fig. 2b).

The  $\text{Sn}^{2+}$  polyhedron deserves further comment. Although described here as a distorted square antiprism, previous studies have assigned [4]-coordination to the  $\text{Sn}^{2+}$  site, with  $\text{Sn}^{2+}$  occupying the apex of a square pyramid with a base of O atoms. These four O atoms are at a mean distance of 2.30 Å from the  $\text{Sn}^{2+}$  atom; however, there are an additional 4 O atoms on the opposite side of the  $\text{Sn}^{2+}$  atom at distances of  $2 \times 3.006$  and  $2 \times 3.216$  Å from the  $\text{Sn}^{2+}$  atom. Both the discrepancy in the distances of the two sets of O atoms from the  $\text{Sn}^{2+}$  site and the local geometry of these anions about that site had led previous investigators to suggest that the  $\text{Sn}^{2+}$  is only [4]-coordinated; however, the bond-valence sum to the  $\text{Sn}^{2+}$  site for the [8]-coordinated model is clearly superior to the sum for the [4]-coordinated model (Table 5). The  $\text{Sn}^{2+}$  polyhedron (Fig. 3) has (1) longer mean bond-lengths, (2) wider mean O-O separations, and (3) longer interbond angles on the  $+Y$  side, *cf.*  $-Y$  side, of the polyhe-

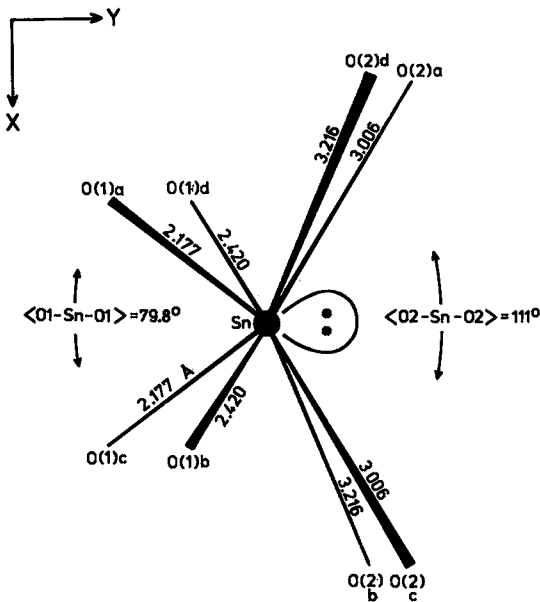


FIG. 3. The  $\text{Sn}^{2+}$  polyhedron. Comparison of the coordination by O(2) with that by O(1) shows the former to have (1) longer mean bond-lengths (3.11 vs. 2.30 Å), (2) wider mean O-O separations (4.12 vs. 2.89 Å), (3) larger interbond angles (111 vs. 79.8°). All points are consistent with the location of a lone pair of electrons between O(2) a, b, c, d.

dron. These points, considered with the displacement of the  $\text{Sn}^{2+}$  atom from the center of the polyhedron by 0.05 Å in the + Y direction, are consistent with the location of a stereoactive lone-pair of electrons directed along + Y toward the two faces bound by the O(2) atoms. Although very few structural data exist for  $\text{Sn}^{2+}$  in solid-state oxide compounds, this sort of asymmetric environment seems typical of  $\text{Sn}^{2+}$  with a stereoactive lone-pair of electrons (Galy

TABLE 5. EMPIRICAL BOND-VALENCE TABLE FOR FOORDITE

	Sn*	Nb*	$\Sigma_4$	$\Sigma_8$
O(1)	0.51 <sup>x2</sup> , 0.31 <sup>x2</sup>	1.12	1.94	1.94
O(2)	0.12 <sup>x2</sup> , 0.09 <sup>x2</sup>	1.20, 0.74	1.94	2.14
O(3)		0.59, 0.54, 0.86	1.99	1.99
$\Sigma_4$	1.65	5.05		
$\Sigma_8$	2.05	5.05		

$$\text{Sn}^* = 0.92(\text{Sn}) + 0.08(\text{Pb}), \quad \text{Nb}^* = 0.70(\text{Nb}) + 0.30(\text{Ta})$$

$\Sigma_4$ ,  $\Sigma_8$ : bond-valence sums assuming [4]- and [8]-coordinated Sn.

Bond valences in v.u., calculated from the curves of Brown (1981) and Ercit (1986).

*et al.* 1975, Jeitschko & Sleight 1972, Mathew *et al.* 1977).

## CONCLUSIONS

The foordite formula has been confirmed to be  $\text{Sn}^{2+}\text{Nb}_2\text{O}_6$ , both on the basis of the numbers of atoms and on the bond-valence sum to Sn (2.05 v.u.). Although Maksimova *et al.* (1976) have suggested the space group *Cc* for thoreaulite, this was not confirmed in the current study. Given the lack of significant anisotropy in atom positions of the *Cc* model, the incomplete reporting of structural data in Maksimova *et al.* (1976), the insignificant differences in *R* indices of the centric and acentric models in the current study, and the superior *R* indices of the current study, we conclude that the correct space-group for members of the foordite-thoreaulite series is *C2/c*.

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