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The Crystal Structure of the Weberite Na_2MgInF_7

Armen Caramanian, Jean-Paul Souron, Patrick Gredin, and Ariel de Kozak[1]

Laboratoire de Cristallochimie du Solide, Université Pierre-et-Marie-Curie, 4 place Jussieu, case courrier 176, 75252 Paris Cedex 05, France

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The fluoride Na_2MgInF_7 is orthorhombic: $a = 10.435(1)$ Å, $b = 7.345(1)$ Å, $c = 7.553(1)$ Å, $Z = 4$. Its crystal structure was solved in the space group *Pnma* (No. 62), from X-ray single crystal data using 1879 unique reflections (1183 with $F_o/\sigma(F_o) > 4$). The three-dimensional network is built up from tilted chains of trans corner-sharing $[MgF_6]$ octahedra running along the shortest axis of the cell. These chains are linked together through four corners of $[InF_6]$ octahedra. The sodium ions are 8 and 7 coordinated to fluorine. The $[NaF_8]$ polyhedron can be described as a distorted cube, whereas the $[NaF_7]$ polyhedron is a pentagonal bipyramid. Despite a different space group, the crystal structure of Na_2MgInF_7 can be easily related to the orthorhombic body-centered weberite-type structure. © 2001 Academic Press

Key Words: **weberite; Na_2MgInF_7; crystal structure.**

INTRODUCTION

The crystal structure of the mineral called "Weberite," Na_2MgAlF_7, discovered in Ivigtut (Greenland), was determined by Byström in 1944 (1) and again, using modern techniques, in 1978 (2). Both investigations led to the same body-centered orthorhombic cell: $a \approx 7.05(1)$ Å, $b \approx 9.98(2)$ Å, $c \approx 7.29(1)$ Å, but disagreed in the choice of the space group: *Imm*2 (No. 44), non-centrosymmetric for (1) and *Imma* (No. 74), centrosymmetric for (2). Nevertheless, the two structure descriptions are nearly the same. Since then many synthetic analogs were discovered by substitution of Mg and/or Al by other bivalent and/or trivalent cations (3–6) and the crystal structure of one of them: Na_2NiFeF_7 was determined precisely in 1978 (7). The authors solved the structure in the space group *Imm*2, as Byström did it for Weberite (1). However, some problems remained: a very short Na–F distance of 2.160 Å and the impossibility of refining the anisotropic displacement parameters of the later fluorine atom, showing that something had to be improved. In 1982 a paper entitled "What Is the True Space Group of Weberite?" (8) reviewed all the possible space groups, trying to answer this question and concluded that the noncentrosymmetric *Imm*2 was probably the best space group for Weberite in the absence of a proof of achirality. In the late 1980s, the crystal structure of Na_2NiFeF_7 was reexamined, concluding this time that the true space group is *Imma* despite weak reflections observed for $hk0$: $h = 2n + 1$, attributed to the Renninger effect (9). The space group *Imma* was also attributed to Na_2NiCrF_7 by the same authors (10). The problem is that a primitive space group was never considered for orthorhombic weberite until the structure determinations of Na_2CuCrF_7 (11), Na_2NiInF_7 (12), and Na_2CuInF_7 (13), because all previous reports agreed with a body-centered cell. As we had the opportunity to prepare a powder of Na_2MgInF_7 for optical studies, we observed on its X-ray diffractogram many lines of weak intensity which could not be indexed in an orthorhombic body-centered cell, but only in a primitive one. Therefore we decided to determine the crystal structure of Na_2MgInF_7, starting from a single crystal. The problems mentioned before were resolved when refining the structure in the space group *Pnma* (the cell parameters *a* and *b* are here reversed for a conventional space group, No. 62). It is valuable to mention that weberite-type fluorides crystallize also with monoclinic and trigonal symmetries and that all weberite variants were abundantly studied for several years by D. Babel's group (14–16 and references therein).

SYNTHESIS OF Na_2MgInF_7

The starting fluorides NaF and MgF_2 used in the synthesis of Na_2MgInF_7 are commercial products, while InF_3 was prepared in the laboratory by fluoridation of In_2O_3 in an anhydrous hydrogen fluoride stream at 750°C in 6 h.

The synthesis of Na_2MgInF_7 was performed in the solid state at 700°C, by annealing for 15 h a stoïchiometric mixture of the three elementary fluorides placed in a platinum crucible under inert argon atmosphere. Its powder pattern, recorded on a 17-cm vertical Philips PW 1050/25 diffractometer (copper anti-cathode), is globally similar to that

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[1] To whom correspondence should be addressed. Fax: 33 1 44 27 25 48. E-mail: adk@ccr.jussieu.fr.

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TABLE 1
X-ray Powder Pattern of Na_2MgInF_7

d_{meas}(Å)	d_{calc}(Å)	h	k	l	I/I_0 (peak height)	d_{meas}(Å)	d_{calc}(Å)	h	k	l	I/I_0 (peak height)
6.110	6.118	1	0	1	4	1.836	1.836	0	4	0	14
5.260	5.266	0	1	1	100	1.775	1.775	2	0	4	3
5.215	5.217	2	0	0	36	1.759	1.759	4	1	3	10
4.290	4.293	2	0	1	1	1.737	1.737	4	3	1	12
4.252	4.254	2	1	0	3	1.732	1.732	2	4	0	4
3.776	3.777	0	0	2	14	1.693	1.692	6	1	0	2
3.705	3.706	2	1	1	76	1.679	1.679	0	2	4	7
3.670	3.672	0	2	0	14	1.663	1.664	2	3	3	4
3.197	3.197	1	1	2	1	1.651	1.651	6	1	1	8
3.151	3.149	1	2	1	3	1.614	1.614	4	3	2	2
3.057	3.059	2	0	2	96	1.599	1.599	2	2	4	25
3.003	3.003	2	2	0	66	1.580	1.580	6	0	2	11
2.632	2.633	0	2	2	12	1.574	1.574	2	4	2	20
2.608	2.609	4	0	0	9	1.544	1.544	6	1	2	2
2.459	2.458	4	1	0	1	1.530	1.530	4	0	4	7
2.446	2.447	1	0	3	5	1.502	1.502	4	4	0	3
2.395	2.395	3	2	1	12	1.480	1.480	0	1	5	2
2.382	2.382	0	1	3	15	1.456	1.456	4	3	3	6
2.349	2.350	2	2	2	19	1.451	1.451	6	2	2	4
2.337	2.338	4	1	1	10	1.442	1.442	0	5	1	3
2.268	2.268	2	0	3	1	1.424	1.424	2	1	5	4
2.216	2.216	2	3	0	2	1.412	1.412	4	2	4	1
2.166	2.167	2	1	3	10	1.405	1.405	6	1	3	2
2.146	2.146	4	0	2	2	1.394	1.394	6	3	1	4
2.126	2.127	4	2	0	29	1.390	1.390	2	5	1	4
2.060	2.060	4	1	2	5	1.385	1.385	1	2	5	1
2.039	2.039	3	0	3	8	1.365	1.365	3	4	3	1
2.015	2.016	1	3	2	2	1.359	1.359	7	2	1	1
1.888	1.888	0	0	4	13	1.316	1.316	0	4	4	5
1.853	1.853	4	2	2	61						

given by Chassaing (3), reported on PDF 22-0894, and indexed in a body-centered orthorhombic cell. Nevertheless, many weak lines (one was also observed by (3) for $d = 4.27$ Å) could not be indexed with a body-centered condition: (hkl): $h + k + l = 2n$. Therefore a primitive cell had to be considered for indexing the powder pattern (Table 1).

Singles crystals of Na_2MgInF_7 were obtained after melting at 860°C the fluoride, followed by a slow cooling. Weissenberg and Buerger X-ray photographs of one of these single crystals confirmed the orthorhombic symmetry and the reflections conditions: hkl, no condition; $hk0$, $h = 2n$; and $0kl$, $k + l = 2n$ are in agreement with two space groups: *Pnma* (No. 62) and $Pn2_1a$ (No. 33). The measured cell parameters are given in Table 2.

STRUCTURE DETERMINATION

One single crystal of Na_2MgInF_7 was mounted on an Enraf-Nonius CAD4 four-circle diffractometer. A total of 2053 intensities were measured and the conditions of the data collection are gathered in Table 2. The data were corrected for Lorentz and polarization effects and a method based on psi-scans was used for the absorption correction. The scattering factors and anomalous dispersion corrections were taken from the "International Tables for X-ray

TABLE 2
Crystal Data, Data Collection, and Refinement Characteristics

Formula: Na_2MgInF_7
Symmetry: Orthorhombic Space group: Pnma (No. 62)
Cell parameters: $a = 10.435(1)$ Å, $b = 7.345(1)$ Å, $c = 7.553(1)$ Å
Volume: 578.9(1) Å^3 Formula weight: 318.1 g mol^{-1} $Z = 4$
Density (calculated): 3.65 g cm^{-3}
Radiation: Mo$K\alpha$ ($\lambda = 0.71069$ Å) F (0 0 0) = 584
Linear absorption coefficient: 4.4 mm^{-1}
Crystal size: 0.2 × 0.2 × 0.2 mm^{-3} (parallelepiped shape) Colorless
Theta range for data collection: 3 to 40°
Index range: $0 \leq h \leq 18$; $0 \leq k \leq 13$; $0 \leq \ell \leq 13$; 2053 reflections collected, 1879 unique, 1183 with $F_o/\sigma(F_o) > 4$
Refinement method: full-matrix least-squares on F^2; 62 Refined parameters
Weighting scheme: $w = 1/[\sigma^2(F_o^2) + (0.0479 \times P^2) + 0 \times P]$, where $P = [\mathrm{Max}\ (F_o^2, 0) + 2 \times F_c^2]/3$
Extinction coefficient: $x = 0.020(1)$
Electron density in Fourier difference map: Max. height: 1.64 e$^-$ Å^{-3}
Min. height: − 3.30 e$^-$ Å^{-3}
Reliability factors: Goodness-of-fit on F^2 = 1.008
Final R indices ($F_o/\sigma(F_o) > 4$) $R_1 = 0.034$ w$R_2 = 0.096$
R indices (all data) $R_1 = 0.062$ w$R_2 = 0.106$

TABLE 3
Atomic coordinates ($\times 10^4$) and Anisotropic Displacement Parameters in Å^2 ($\times 10^3$) (with e.s.d. in Parentheses) for Na_2MgInF_7

Atom Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}	U_{eq}
Na(1)	0	0	0	31	22	54	3	−5	7	36
4*a*				(1)	(1)	(2)	(1)	(1)	(1)	(1)
Na(2)	2680	$\frac{1}{4}$	2372	35	21	18	0	−8	0	24
4*c*	(2)		(2)	(1)	(1)	(1)		(1)		(1)
Mg(1)	0	0	$\frac{1}{2}$	5	4	8	−1	0	1	6
4*b*				(1)	(1)	(1)	(1)	(1)	(1)	(1)
In(1)	2619	$\frac{1}{4}$	7495	11	9	12	0	0	0	10
4*c*	(1)		(1)	(1)	(1)	(1)		(1)		(1)
F(1)	3574	$\frac{1}{4}$	5082	24	21	13	0	2	0	19
4*c*	(3)		(3)	(1)	(1)	(1)		(1)		(1)
F(2)	1625	$\frac{1}{4}$	9834	21	28	12	0	3	0	20
4*c*	(3)		(3)	(1)	(1)	(1)		(1)		(1)
F(3)	4706	$\frac{1}{4}$	0569	36	9	36	0	15	0	27
4*c*	(3)		(5)	(2)	(1)	(2)		(1)		(1)
F(4)	3738	0241	8029	21	20	23	−3	−8	7	21
8*d*	(2)	(3)	(3)	(1)	(1)	(1)	(1)	(1)	(1)	(1)
F(5)	3648	9501	1750	21	15	31	3	13	−4	22
8*d*	(2)	(2)	(3)	(1)	(1)	(1)	(1)	(1)	(1)	(1)

Crystallography" (17). First a statistical test for centrosymmetry (Howells, Phillips, and Rogers test (18)) was performed on the structure factor's intensities of the X-ray data collection: it showed unambiguously the centrosymmetry of the crystal structure. Therefore, the structure was solved in the space group *Pnma* (No. 62). All the refinement calculations were performed with the SHELX-97 programs (19). Sodium, magnesium, and indium atoms were first located using the direct method analysis (TREF instruction), and

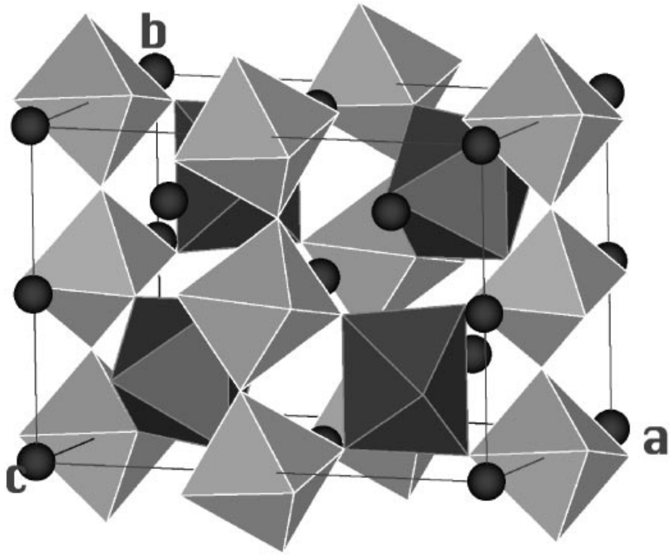

FIG. 1. The unit cell of Na_2MgInF_7 (magnesium octahedra are light gray and indium octahedra dark gray; sodium atoms are represented as black circles).

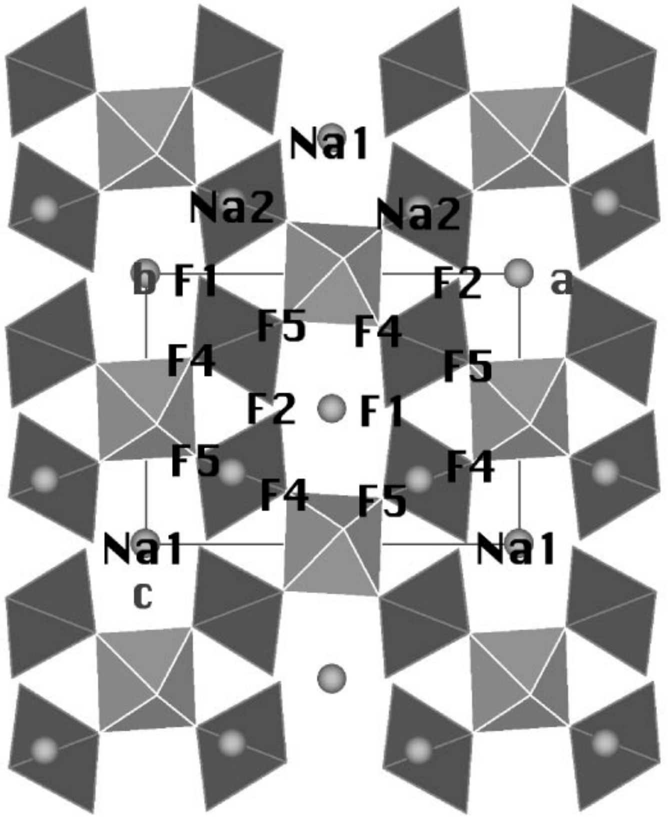

FIG. 2. (010) Projection of the structure of Na_2MgInF_7 (magnesium octahedra are light gray and indium octahedra dark gray; sodium atoms are represented as circles).

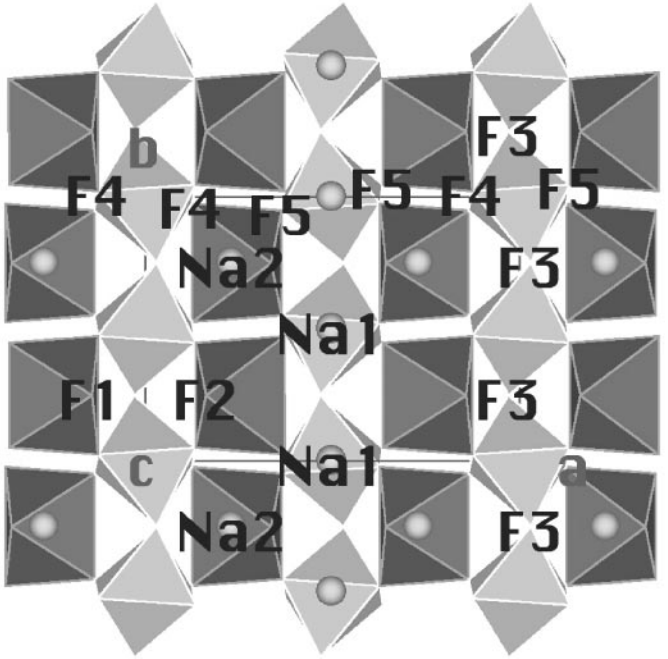

FIG. 3. (001) Projection of the structure of Na_2MgInF_7 (magnesium octahedra are light gray and indium octahedra dark gray; sodium atoms are represented as circles).

TABLE 4
Interatomic Distances (Å) and Bond Angles (°) in the $[MgF_6]$ Octahedron

Mg(1)	F(3)	F(3)	F(5)	F(5)	F(4)	F(4)
F(3)	**1.911(1)**	3.821	2.860	2.620	2.730	2.795
F(3)	180.0	**1.911(1)**	2.620	2.860	2.795	2.730
F(5)	95.0	85.0	**1.968(2)**	3.935	2.739	2.864
F(5)	85.0	95.0	180.0	**1.968(2)**	2.864	2.739
F(4)	88.7	91.3	87.5	92.5	**1.995(2)**	3.991
F(4)	91.3	88.7	92.5	87.5	180.0	**1.995(2)**

Note. Mean ⟨Mg–F⟩ = 1.958 Å.

then the positions of the five independent fluorine atoms were found by successive difference Fourier syntheses. The refinement of all anisotropic thermal parameters for all atoms leads to $R_1(F_o) = 0.034$ and $wR_2(F_o^2) = 0.096$ for 1183 unique reflections with $F_o > 4\sigma(F_o)$ and 62 refined parameters. The atomic coordinates and the anisotropic displacement parameters are listed in Table 3. In opposition to the crystal structure determination of Na_2NiFeF_7 (7), all atoms, including fluorine, have here suitable anisotropic displacement parameters. The simulated powder pattern of Na_2MgInF_7, using the atomic coordinates of the crystal structure determination (program Fullprof (20)), is similar to the observed one (Table 1). One can also observe that the strong and medium lines are all indexed with a body-centered condition: (*hkl*): $h + k + l = 2n$. The nine lines indexed with a body-centered absence condition are weak; therefore, these lines could have been ignored in the indexation of weberite-type compounds by previous authors.

A list of structure factors may be obtained from the authors on request.

DESCRIPTION OF THE STRUCTURE AND DISCUSSION

The three-dimensional network of Na_2MgInF_7 (Fig. 1) is built up from tilted chains of trans corner-sharing $[MgF_6]$ octahedra running along the *b* axis of the cell. These chains are linked with each other roughly in the [101] and $[10\bar{1}]$ directions through corners of $[InF_6]$ octahedra, as shown on the (010) projection of the structure (Fig. 2). Each $[InF_6]$ octahedron connects two chains of $[MgF_6]$ octahedra via four of its corners (Fig. 3). The magnesium and indium fluorine octahedra are fairly regular, with mean Mg–F and In–F distances (1.958 and 2.062 Å) shorter than the sum of the ionic radii calculated with Shannon's table (2.03 and 2.11 Å) (21). Bond lengths and angles observed in the $[MgF_6]$ and $[InF_6]$ octahedra are gathered in Tables 4 and 5. The sodium atoms, inserted between the chains, ensure the electroneutrality and the cohesion of the structure. They exhibit 8 and 7 coordination (Table 6). The sodium polyhedra can be described as a distorted cube for $[Na(1)F_8]$ (Fig. 4) and as a pentagonal bipyramid for $[Na(2)F_7]$ (Fig. 5). It is useful to observe that the shortest Na–F bond is now 2.211 Å, instead of 2.160 Å in Na_2NiFeF_7 (7), but remains very short.

TABLE 5
Interatomic Distances (Å) and Bond Angles (°) in the $[InF_6]$ Octahedron

In(1)	F(2)	F(5)	F(5)	F(4)	F(4)	F(1)
F(2)	**2.049(3)**	2.769	2.769	3.078	3.078	4.125
F(5)	84.9	**2.055(2)**	2.939	4.114	2.677	3.021
F(5)	84.9	91.3	**2.055(2)**	2.677	4.114	3.021
F(4)	96.8	171.9	81.0	**2.069(2)**	3.318	2.782
F(4)	96.8	81.0	171.9	106.7	**2.069(2)**	2.782
F(1)	178.3	93.9	93.9	84.3	84.3	**2.077(3)**

Note. Mean ⟨In–F⟩ = 2.062 Å.

TABLE 6
Interatomic Na–F Distances (Å) in the Sodium Coordination Polyhedra

Na(1) polyhedron	(CN = 8)	Na(2) polyhedron	(CN = 7)
F(1)	2.364(2)	F(2)	2.211(3)
F(1)	2.364(2)	F(1)	2.249(3)
F(2)	2.503(2)	F(5)	2.468(2)
F(2)	2.503(2)	F(5)	2.468(2)
F(4)	2.646(2)	F(3)	2.515(4)
F(4)	2.646(2)	F(4)	2.547(3)
F(5)	2.855(2)	F(4)	2.547(3)
F(5)	2.855(2)		

Note. Mean: ⟨Na(1)–F⟩ = 2.592 Å; ⟨Na–F⟩ = 2.49 Å [21]. Mean: ⟨Na(2)–F⟩ = 2.429 Å. ⟨Na–F⟩ = 2.43 Å [21].

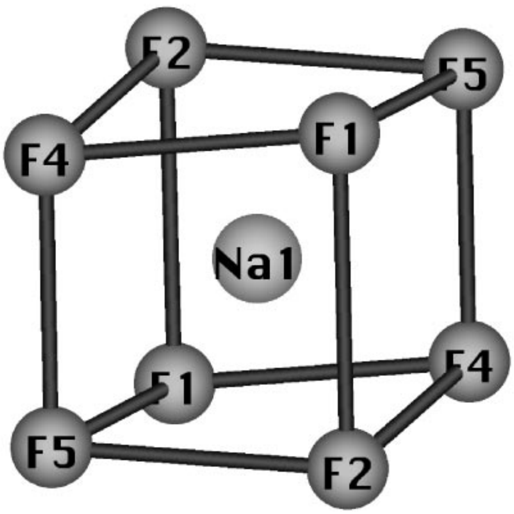

FIG. 4. The $[Na(1)F_8]$ distorted cube in Na_2MgInF_7.

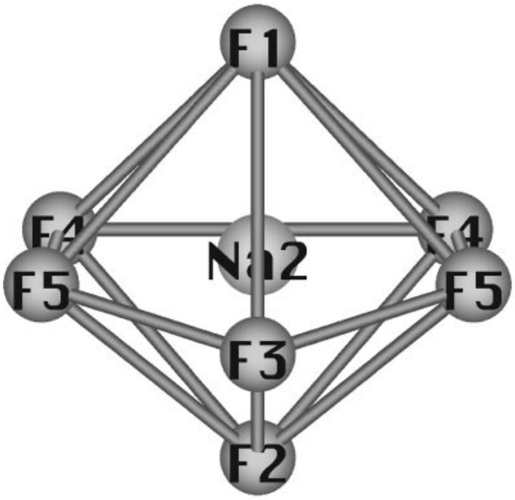

FIG. 5. The [Na(2)F_7] pentagonal bipyramid in Na_2MgInF_7.

The crystal structure of Na_2MgInF_7 (space group *Pnma*) and of its homologs, Na_2CuCrF_7, Na_2NiInF_7, and Na_2CuInF_7, can be considered as a new structure-variant for weberite, if it is admitted that a body-centered cell is well assumed for the hitherto resolved structures of Na_2MgAlF_7 (1, 2, 8) and Na_2NiFeF_7 (7, 9).

It is here useful to mention for comparison that the RE_3NbO_7 oxides ($RE = \mathrm{La}$, Nd, Sm) have the weberite structure (space group *Imm*2) for (22) and an orthorhombic cell (nonconventional space group *Pnam*) for (23). In addition, a series of niobium–samarium oxides Sm_2RENbO_7 was found to be orthorhombic, with weberite-type cell parameters, space group *Pnam* (24). Unfortunately, the X-ray powder patterns of all these compounds are not available (23,24).

Discussion is open to answer two queries: Is the crystal structure of orthorhombic weberite well body-centered? and Do different space groups exist for the orthorhombic weberite structure? A partial response was given by Frenzen *et al.* (12), who conclude that the indium weberites are different from the others, due to the large size of the trivalent cation. Copper weberites are isostructural, due to the Jahn–Teller effect (11,13).

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