JOURNAL OF SOLID STATE CHEMISTRY 39, 94–99 (1981)

# The 1-6 Weberite $Na_2Te_2O_7$ and Some Observations on Compounds with the Weberite Structure

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Received December 15, 1980; in final form March 5, 1981

The 1-6 weberite $Na_2Te_2O_7$ ($Imm2$, $a$ = 7.233 Å, $b$ = 10.104 Å, $c$ = 7.454 Å) has been prepared by high-pressure synthesis. It is shown that $\bar{a}$ (the mean unit-cell dimension per formula unit) of oxide weberites $A_2B_2O_7$ can be represented as a linear function of the effective ionic radii of $A$ and $B$. The problem of the true space-group symmetry of weberite is discussed.

The existence of the weberites $A_2^{2+}Sb_2^{5+}O_7$ ($A$ = Ca, Sr, Cd) is well documented (*1*). Experiments designed to obtain mixed weberites containing Te(VI), $NaASbTeO_7$ ($A$ = Ca, Sr, Cd), have recently been described by Burchard and Rüdorff (*2*). The X-ray powder diffraction patterns of the products formed by firing mixtures of $Na_2CO_3$, $ACO_3$, $Sb_2O_3$, and $TeO_2$ in a stream of oxygen at atmospheric pressure were of the weberite type, but the lines were not sufficiently sharp for determining the unit-cell dimensions. Efforts to obtain well-crystallized products failed; the weberite phases decomposed above 800°C. However, preparation of the $Na_{0.5}A_{1.5}(B_{0.5}Te_{1.5})O_7$ ($A^{2+}$ = Ca, Cd; $B^{3+}$ = Mn, Fe, Co) weberites was successful. The Fe products were pure phases, but the Co and Mn products contained some $A_3TeO_6$. These results suggested that it should be possible to obtain the pure 1-6 weberite $Na_2Te_2O_7$ if sufficiently oxidizing conditions could be maintained at a high enough temperature.

A stoichiometric mixture of $Na_2O_2$ and $TeO_2$ was heated with an excess of $NaClO_3$ in a sealed gold capsule for 20 min at ~800°C and 60 kbar in a belt-type apparatus. The charge was then quenched by cutting the furnace power but the pressure was maintained for another 10 min before being slowly reduced. In the diffractogram of the resulting slightly greenish powder only peaks of NaCl and those of a well-defined phase indexable on an orthorhombic body-centered unit cell were visible. A determination of the unit-cell dimensions from 27 single reflections ($10° < 2\theta < 70°$; Ge internal standard, $a$ = 5.6575 Å; $\lambda(CuK\bar{\alpha})$ = 1.54178 Å) resulted in $a$ = 7.233(5) Å, $b$ = 10.104(7) Å and $c$ =

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0022-4596/81/100094-06$02.00/0

7.454(5) Å. The quantity of the product was too small for an accurate chemical analysis and the powder was too fine to contain usable single crystals. However, the systematic absences ($h + k + l = 2n + 1$) are consistent with the space group of weberite, *Imm*2 (No. 44) (see below); the unit-cell dimensions closely resemble those reported in Ref. (*2*) for the two $Na_{0.5}A_{1.5}(Fe_{0.5}Te_{1.5})O_7$ phases, both of which had been analyzed chemically; and the observed intensities agree satisfactorily with the intensities calculated for $Na_2Te_2O_7$ on the assumption that this compound is isostructural with the weberite $Ca_2Sb_2O_7$ (*3*) and has the same positional parameters (Table I). From this (and taking account of the conditions under which the product formed) we conclude that the product was in fact the expected weberite $Na_2Te_2O_7$.

The weberite structure requires the Te atoms (in equipoints 4(*c*) and 4(*d*) of *Imm*2) to be six-coordinated. $Na_2Te_2O_7$ thus furnishes yet another example of the preference which Te(VI) in oxides has for octahedral coordination: $TeO_3$ (*4*), $Te_2O_5$ (*5*), $Li_2TeO_4$ (*6*), and $Na_3TeO_4$ (*7, 8*) all contain $TeO_6$ octahedra. Although six-coordination would also be satisfied if $Na_2Te_2O_7$ were a 1-6 pyrochlore, the criterion in Ref. (*1*) shows why of the two alternatives the weberite is the preferred structure.

The mean linear unit-cell dimension per formula unit, $\bar{a} = (V/Z)^{1/3}$, of the weberites

TABLE I

X-RAY POWDER PATTERN OF $Na_2Te_2O_7$

| *hkl* | $d_{obs}$ | $d_{calc}$ | $I_{obs}$[a] | $I_c$ |
|---|---|---|---|---|
| 011 | 6.02 | 6.00 | 85 | 77 |
| 110 | — | 5.881 | — | 0 |
| 101 | 5.197 | 5.196 | 60 | 61 |
| 020 | — | 5.052 | — | ~0 |
| 002 | — | 3.727 | — | <1 |
| 121 | 3.622 | 3.622 | 59 | 49 |
| 200 | | 3.618 | | ~0 |
| 211 | 3.099 | 3.096 | 36 | 38 |
| 031 | 3.069 | 3.069 | 28 | 21 |
| 022 | 2.998 | 2.998 | 100 | 100 |
| 220 | 2.941 | 2.941 | 64 | 95 |
| 202 | 2.596 | 2.596 | 43 | 39 |
| 040 | 2.524 | 2.527 | 17 | 18 |
| 103 | 2.352 | 2.350 | 9 | 7 |
| 141 | 2.272 | 2.271 | 5 | 5 |
| 123 | 2.133 | 2.131 | 5 | 6 |
| 042 | 2.090 | 2.091 | 12 | ~0 |
| 321 | | 2.089 | | 10 |
| 033[b] | 2.001 | 1.999 | (13) | 9 |
| 312 | 1.985 | 1.985 | 1 | 1 |
| 051 | 1.950 | 1.951 | 1 | 4 |
| 004 | 1.864 | 1.863 | 9 | 15 |
| 242 | 1.810 | 1.810 | 45 | 66 |
| 400 | | 1.809 | | 17 |
| 233 | 1.750 | 1.750 | 8 | 6 |
| 024 | | 1.748 | | ~0 |
| 411 | 1.731[c] | 1.731 | | 5 |
| 303 | | 1.730 | | 1 |
| 143 | 1.720[c] | 1.720 | | 6 |
| 251 | 1.716[c] | 1.717 | | 3 |
| 420 | —[d] | 1.703 | | ~0 |
| 341 | 1.699 | 1.698 | 3 | 7 |
| 161 | 1.602 | 1.602 | 2 | 4 |
| 224 | 1.574 | 1.574 | 26 | 33 |
| 431 | 1.558 | 1.558 | 4 | 6 |
| 350 | 1.549 | 1.549 | 16 | 0 |
| 422 | | 1.549 | | 27 |
| 062 | 1.535 | 1.535 | 15 | 15 |
| 260 | 1.527 | 1.527 | 7 | 10 |
| 044 | 1.500 | 1.500 | 11 | 10 |
| 440 | 1.470 | 1.470 | 9 | 10 |
| 105 | 1.460 | 1.460 | 1 | 2 |
| 253 | 1.438 | 1.438 | 6 | 4 |
| 343 | 1.428 | 1.428 | 4 | 5 |
| 125 | 1.403 | 1.403 | 4 | 5 |
| 215 | 1.366 | 1.366 | 7 | 5 |

[a] $I_{obs} = 100I(hkl)/I(022)$, from estimated peak heights.

[b] Coincided with Ge(111) and NaCl(220).

[c] Overlap with neighboring peak(s).

[d] Coincided with Ge(311).

$A_2Sb_2O_7$ ($A$ = Ca, Sr, Cd) (*1*), $CaPbSb_2O_7$ (*2*), $NaLnSb_2O_7$ (*2*, *9*), and $KLnTa_2O_7$ (*10*) may be represented as $\bar{a} = 2.360 + 0.879r^{\mathrm{viii}}(A) + 3.111r^{\mathrm{vi}}(B)$, where $r^{\mathrm{viii}}(A)$ and $r^{\mathrm{vi}}(B)$ are Shannon's (*11*) effective ionic radii (or the average values, for mixed phases) except for $r^{\mathrm{viii}}(Cd^{2+})$ and $r^{\mathrm{vi}}(Sb^{5+})$, which are taken as 1.063 and 0.59 Å, respectively (*1*). The $\bar{a}$ values calculated from this empirical relation (Fig. 1) correlate very well with the observed values: $r^2 = 0.999$, $\sigma = 0.005$ Å. The point for $Na_2Te_2O_7$ falls within $\sim 1\sigma$ of the regression line; the $\bar{a}_{\mathrm{calc}}$ values for $Na_{0.5}Ca_{1.5}Fe_{0.5}Te_{1.5}O_7$ and $Na_{0.5}Cd_{1.5}Fe_{0.5}Te_{1.5}O_7$ are about 0.025 Å, $\sim 5\sigma$ higher than the respective $\bar{a}_{\mathrm{obs}}$. By contrast, this correlation fails to accommodate the orthorhombic phases $Ln_3BO_7$ ($B$ = Sb, Nb, Ta), where dimensional similarity to the weberites might be conducive to formulating them as mixed weberites $Ln_2(LnB)O_7$: the $\bar{a}_{\mathrm{calc}}$ values obtained on this formulation are much too large to fall on the regression line of Fig. 1.[1]

The $\bar{a} - r(A),r(B)$ correlation occasions a number of remarks. In Ref. (*1*) the $r^{\mathrm{vi}}(Bi^{5+})$ in the weberite $Sr_2Bi_2O_7$ was estimated, from comparisons with $Na_3BiO_4$ and the corresponding Sb(V) compounds, to be 0.64 Å. When this value is used in the regression equation the $\bar{a}_{\mathrm{calc}}$ is only 0.02 Å larger than the $\bar{a}_{\mathrm{obs}}$. This agreement reinforces the validity of the correlation for oxide weberites; conversely, it confirms that $Sr_2Bi_2O_7$ is a weberite. The regression equation permits the $r^{\mathrm{vi}}(Bi^{5+})$ estimate to be improved from 0.64 to 0.635 Å. This effective radius is significantly smaller than the estimate obtained by Shannon (*11*) from $Ba_2LaBiO_6$, 0.76 Å.

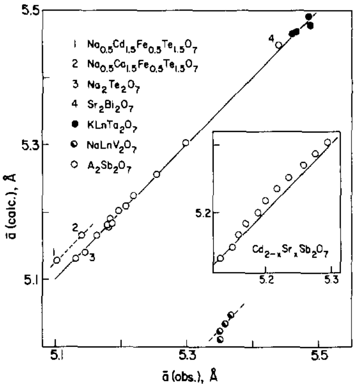

FIG. 1. Regression of $\bar{a}_{calc}$ on $\bar{a}_{obs}$ for the weberites $A_2B_2O_7$ ($B$ = $Sb^{5+}$, $Ta^{5+}$, $Te^{6+}$) (see text). The $\bar{a}_{\mathrm{calc}}$ values for $NaLnV_2O_7$ are based on Shannon's $r^{\mathrm{vi}}$ ($V^{5+}$) = 0.54 Å. Inset: Effect of ordering in $Cd_{2-x}Sr_xSb_2O_7$ on $\bar{a}$ (data from Ref. (*15*)).

Secondly, the unit-cell dimensions reported by Gade and Chincholkar (*10*) for $NaLnV_2O_7$ ($Ln$ = Nd, Sm, Gd, Dy) cannot be reconciled with Shannon's $r^{\mathrm{vi}}(V^{5+})$ = 0.54 Å. Values between 0.64 and 0.65 Å, i.e., comparable to $r^{\mathrm{vi}}$ of $Nb^{5+}$ and $Ta^{5+}$, would be required to satisfy the regression equation. While it is recognized that V–O distances in $V^{5+}O_6$ may vary considerably depending on the distortion of the octahedron, a variation amounting to 0.1 Å is certainly unexpected, as is the result that $b$ (the largest dimension of the unit cell) in the $NaLnV_2O_7$ series is the same, for a given $Ln$, as that in the $KLnTa_2O_7$ series.

Thirdly, $b$ in both the $NaLnV_2O_7$ and $KLnTa_2O_7$ series is reported (*10*) to *decrease* with increasing $r^{\mathrm{viii}}(Ln^{3+})$ (Fig. 2). This is contrary to what is observed in the $NaLnSb_2O_7$ weberites (*2*, *9*). A decrease in $b$ with the increasing mean size of $A^{2+}$ is documented for the mixed weberites $Cd_{2-x}Sr_xSb_2O_7$ (*15*) (cf. inset of Fig. 1). It has been explained as follows. The weberite structure contains two types of $A$ sites. For $0 \leq x \leq 1$, Cd is progressively replaced by Sr in sites of one type; an ordered arrangement is reached at $x = 1$, beyond which Sr begins to replace Cd in sites of the second type, and it is this last process which is associated with a slight

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[1] Although these phases are now known to have different symmetries (*Cmcm* and $C222_1$) and structural arrangements (*12*, *13*), they were in fact at one time thought to be weberites (*14*).

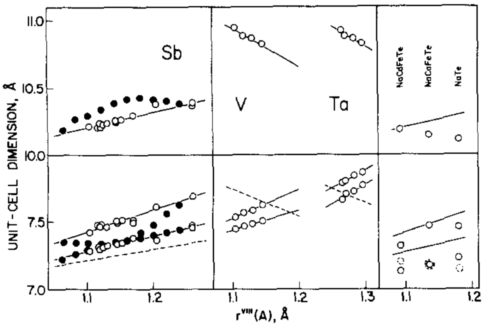

FIG. 2. Variation of the unit-cell dimensions of the weberites $A_2B_2O_7$ ($B$ = $Sb^{5+}$, $V^{5+}$, $Ta^{5+}$, $[Fe_{0.5}Te_{1.5}]^{5.25+}$, $Te^{6+}$) with $r^{viii}(A)$. The broken lines represent $b/2^{1/2}$; in the right-hand section the regression lines for $A_2Sb_2O_7$ are shown for comparison. Full circles, $Cd_{2-x}Sr_xSb_2O_7$ (*15*).

reduction of $b$. Although in $NaLnV_2O_7$ and $KLnTa_2O_7$ preferential occupancy of the two $A$ sites (whose degree depends on the size of the $Ln$) *might* in principle account for the decrease in $b$ with increasing $r^{viii}(Ln^{3+})$, the question remains why a similar decrease is not observed in the $NaLnSb_2O_7$ series, considering that the preparative conditions for the three classes of compounds were much the same; Desgardin *et al.* (*9*) regard the $NaLnSb_2O_7$ phases as disordered. Resolution of these discrepancies is desirable, since $NaLnV_2O_7$ and $KLnTa_2O_7$ appear to be the first reported instances of $A_2B_2O_7$ weberites in which $B$ is exclusively a transition element.

For the two $Na_{0.5}A_{1.5}Fe_{0.5}Te_{1.5}O_7$ ($A$ = Ca, Cd) phases of Ref. (*2*), $\bar{a}_{calc} > \bar{a}_{obs}$ (Fig. 1), which indicates that the mean ionic radius assumed for $\frac{1}{4}(Fe^{3+} + 3Te^{6+})$ is too large. Furthermore, while $\bar{a}_{obs}(Cd) < \bar{a}_{obs}(Ca)$, $b(Cd) > b(Ca)$ and $b(Ca)/2^{1/2} = a(Ca)$ (Fig. 2). If these effects are real, they may point to the existence of partial order (cf. Ref. (*15*) for a discussion of some of the points concerning order in the weberite structure).

A final remark concerns the true space group of weberite. The only systematic absences in Brosset's (*16*) Weissenberg photographs of the type compound, the mineral weberite ($Na_2MgAlF_7$), where $h + k + l = 2n + 1$, from which he deduced *Immm* (No. 71), *Imm*2 (No. 44), *I*222 (No. 23) and $I2_12_12_1$ (No. 24) as possible space groups.[2] He specifically mentioned the reflections 110 and 011 as observed. Byström (*3*) confirmed the systematic absences and chose, on the assumed similarity to the pyrochlore structure,[3] *Imm*2 as the applicable space group. This assumption turned out to be wrong, but Byström nevertheless succeeded in proposing a reasonable structure in *Imm*2. However, the values he gave for the positional parameters in both weberite and $Ca_2Sb_2O_7$ in fact are such that the structure would be more properly described in the centrosymmetric space group *Imma* $\supset$ *Imm*2; he noted that any deviation from a centrosymmetric arrangement would be slight, the presence of the very faint 390 reflection being his only evidence for the noncentrosymmetric group.

Ferguson (*17*) failed to observe, for natural weberite from the same locality (Ivigtut), any systematic absences other than $h + k + l = 2n + 1$ and deduced *Imma* and *Ima*2 (No. 46) as possible space groups. No further structure work has been done on weberite and its analogs until the appearance of the two recent determinations, of Ivigtut weberite (*18*) and $Na_2NiFeF_7$ (*19*), the declared purpose of which was to resolve the space-group ambiguity. Curiously, their conclusions disagree. Giuseppetti and Tadini (*18*) concluded from the systematic absences $h + k + l = 2n + 1$ and a centrosymmetric $E$ statistic that the applicable space group was *Imma*. They determined the atomic positions from three-dimensional Patterson and Fourier maps without prior assumptions

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[2] The Miller indices have been converted to the standard settings throughout. They correspond to $b > c > a$.

[3] The pyrochlore structure is describable in *Imm*2, for $Fd3m \supset Imma \supset Imm2$.

and refined the (ordered) structure to $R = 0.036$. Haegele *et al.* (*19*) considered Byström's structure as basically correct and concerned themselves merely with the choice between *Imm*2 and Ferguson's *Imma* and *Ima*2. They settled the problem in favor of *Imm*2: a number of *hk*0 with *h*,*k* odd were observed which, in addition to the presence of odd *h*0*l* and 0*kl* reflections, ruled out all but four of the nine body-centered orthorhombic space groups and specifically *Imma* and *Ima*2. Starting from Byström's positional parameters for weberite they refined the (ordered) $Na_2NiFeF_7$ structure to $R = 0.029$. The refined positional parameters in the two determinations are very similar.[4] The *Imm*2 structure is obtainable from the *Imma* structure by displacing the cations slightly from the twofold axes and splitting up centrosymmetric pairs of F atoms into separate sets. This reduces the symmetries of the coordination polyhedra about the cations from $2/m$ to $m$, but the overall distortion of the *Imma* structure is slight.

Scrutiny of single reflections in the powder patterns of the oxide weberites narrows down the choice of space group to *Imma*, *Immm*, *Imm*2, *I*222, and $I2_12_12_1$. There is no mention in the literature of any attempt to arrive, without prior assumptions, at a reasonable structure of a weberite in *Immm*, $I222 \subset Immm$ or $I2_12_12_1 \subset Imma$. However, if Byström's structure is accepted as essentially correct, the choice is between *Imma* and *Imm*2 and hinges on the presence of *hk*0 reflections with *h* and *k* both odd. $Na_2NiFeF_7$, for which such reflections were observed, must then belong to *Imm*2. As for $Na_2MgAlF_7$, the scattering factors of Fe and Ni are about 2½ times larger than those of Mg and Al, but the difference in the contribution of these atoms in *Imm*2 to *F*(*hk*0) with *h*,*k* odd is not such as to make the intensities of these reflections in $Na_2MgAlF_7$ unobservable, unless the departure from centrosymmetry are much smaller in the MgAl than in the NiFe compound, i.e. unless the MgAl structure *has* effectively the *Imma* symmetry. This possibility cannot be excluded, in view of the difference in the effective radii of six-coordinated $Al^{3+}$ (0.535 Å) and $Fe^{3+}$HS (0.645 Å). Giuseppetti and Tadini do not cite observability of *hk*0 reflections with *h*,*k* odd among the criteria which led them to adopt the space group *Imma* as applicable.

It is hoped that the new redetermination of the structure of Ivigtut weberite which is now in progress (T. S. Cameron and O. Knop, to be published) will provide satisfactory answers to the above queries.

## Acknowledgment

Financial support received by one of us (O. K.) under the CNRS/NRCC agreement on cooperative research during his stay at the Laboratoire de Chimie du Solide du CNRS is gratefully acknowledged.

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[4] The atomic coordinates in *Imma* are converted to the corresponding coordinates in *Imm*2 by subtracting (0, ¼, ¼).

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