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Structural Studies of the Natural Antimonian Pyrochlores

I. Mixed Valency, Cation Site Splitting, and Symmetry Reduction in Lewisite[1]

Roland C. Rouse,* Pete J. Dunn,† Donald R. Peacor,* and Liping Wang*

**Department of Geological Sciences, University of Michigan, Ann Arbor, Michigan 48109; and †Department of Mineral Sciences, Smithsonian Institution, Washington, D.C. 20560*

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A type sample of the natural pyrochlore-group mineral lewisite, $(Ca,Mn^{2+},Na)_{1.12}Sb^{3+}_{0.65}(Sb^{5+},Ti^{4+},Fe^{3+},Al)_2O_6(OH)_{0.91}$, is cubic, $F\bar{4}3m$ (pseudo-$Fd\bar{3}m$), with $a = 10.277(1)$ Å and $Z = 8$. The structure has been solved and refined in $Fd\bar{3}m$ ($R = 0.017$), $F\bar{4}3m$ ($R = 0.014$), and $F23$ ($R = 0.014$) using 218 (or 326) X-ray reflections $[I_{obs} > 2\sigma(I)]$ from a four-circle diffractometer and compositional constraints from electron microprobe and infrared spectroscopic analyses. Antimony is present in two valence states ($Sb^{5+} : Sb^{3+} = 60 : 40$), with Sb^{5+} ordered in the pyrochlore *B* site (16*c* in $Fd\bar{3}m$). To accommodate the different coordination requirements of Sb^{3+} (a lone-pair ion) and Ca^{2+}, the pyrochlore *A* site is split into 8-coordinated Ca^{2+} on *A*(16*d*) and Sb^{3+} on an asymmetrically 5-coordinated site, *A′*(96*g*), the *A*–*A′* separation being ca. 0.5 Å. The deviation from $Fd\bar{3}m$ symmetry is small, as shown by the fact that only two of the symmetry-forbidden reflections (200 and 420) have statistically significant intensities. The finding of $F\bar{4}3m$ symmetry in lewisite supports the choice of this space group for certain anomalous synthetic pyrochlores that have been characterized by powder diffraction methods. A previous study that purports to discredit lewisite as a two-phase mixture is shown to be in error. © 1998 Academic Press

INTRODUCTION

The literature on the synthetic cubic pyrochlores is replete with examples of compounds showing some anomalous crystal-chemical feature that sets such compounds apart from other members of the pyrochlore group. These anomalies are of three major types: (a) a reduction in space group symmetry below that of the conventional space group $Fd\bar{3}m$, as indicated by the presence of a few, low-intensity X-ray or neutron reflections that violate the *d*-glide extinction rules of $Fd\bar{3}m$ (1–8) or by physical tests that demonstrate the absence of a center of symmetry (9, 10); (b) positional disorder of the *A*-site cation, involving a displacement of that ion or ions, wholly or in part, from the conventional 16*d* position [or 16*c*, for the B_o or A_o settings of the structure, respectively (11)] onto 32*e* or 96*g* (9, 12–17); and (c) the presence of a post-transition series metal (Sn, Sb, Pb, or Bi) in two valence states, with a segregation of the two onto the *A* and *B* cation sites (9, 12, 14, 15, 18–26). In the following report we describe an example in which all three of these features occur simultaneously in a naturally occurring compound, the antimonian pyrochlore-group mineral lewisite.

Lewisite, which has been conventionally (and incorrectly) formulated as $(Ca,Fe^{2+},Na)_2(Sb^{5+},Ti^{4+})_2O_7$ (27), was originally described in 1895 by Hussak and Prior (28) from a cinnabar mine at Tripuhy (modern spelling "Tripuí"), near Ouro Preto, in the State of Minas Gerais, Brazil. The mineral occurs as orange to yellow-brown, euhedral crystals about 1 mm in size and of octahedral habit in an alluvial deposit, where it is associated with cinnabar, xenotime-(Y), monazite-(Ce), kyanite, rutile, hematite, magnetite, pyrite, and several minor species (28, 29).

From its chemical composition and crystal morphology, Hussak and Prior concluded that lewisite was "connected with the pyrochlore group of minerals," an assignment that was subsequently confirmed by the X-ray diffraction study of Machatschki and Zedlitz (30), who found a cubic unit cell with $a = 10.290 \pm 0.008$ Å (converted from *kX* units) using an NaCl standard. From the then-available data, Machatschki (31) proposed a conventional pyrochlore-type formula, $(Ca,Fe,Na,Mn)_2(Sb,Ti)_2(O,OH)_7$. Palache *et al.* (32) erroneously relegated lewisite to the status of a titanian variety of roméite, ideally $Ca_2Sb_2(O,OH,F)_7$. Most recently, a restudy of lewisite by Brugger *et al.* (29) yielded the approximate formula $(Ca,Mn,Na)_{2-m}(Sb,Ti,Al,Fe^{3+},Nb,As^{5+})_2O_6$, where $m \approx 1$ and the *Y*(8*b*) site is vacant. A study with the polarizing microscope led Brugger *et al.* to conclude that lewisite is a two-phase mixture and therefore not a valid mineral species. Our results on lewisite are at variance with this interpretation, but a discussion of the matter is deferred until a later section of this report.

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EXPERIMENTAL

The lewisite crystals used in this study are part of a sample of the type (i.e., original) material obtained from its codescriber, Dr. E. Hussak, by Col. Washington Roebling. The Roebling Collection is now a part of the U.S. National Collection, which is housed in the Museum of Natural History, Smithsonian Institution. The USNM specimen number is R5741.

Electron Microprobe Analysis

Lewisite was chemically analyzed using an ARL-SEMQ electron microprobe operated at 15 kV and 0.025 μA sample current. The standards used were synthetic Sb_2O_3 (for Sb), manganite (for Mn), hornblende (for Fe, Ca, Na, Ti, and Al), and fluorapatite (for F). The data were corrected with a modified version of the program Magic-4. The resulting analysis, assuming all Fe as Fe^{2+} and all Sb as Sb^{5+}, was CaO 14.4, Na_2O 0.1, FeO 3.4, MnO 1.2, TiO_2 15.0, Al_2O_3 0.7, Sb_2O_5 65.8, F 0.0, sum 100.6 wt%. Subsequently, crystal-structure analysis showed the Fe to be Fe^{3+} and the Sb to be 39.7% Sb^{3+} and 60.3% Sb^{5+}, necessitating a recalculation of the analysis to CaO 14.4, Na_2O 0.1, Fe_2O_3 3.8, MnO 1.2, TiO_2 15.0, Al_2O_3 0.7, Sb_2O_3 23.5, Sb_2O_5 39.7, F 0.0, sum 98.4 wt%. The structure analysis further indicated 7.28 (OH) per unit cell, which corresponds to 2.0% H_2O and leads to a corrected sum of 100.4%. Previous chemical analyses of lewisite (28, 29) showed no H_2O (which was not experimentally determined) and apparently satisfactory analytical sums ranging from 100.38 to 100.72%. These latter results are artifacts produced by the erroneous assumption that all of the Sb is pentavalent, leading, in turn, to the mistaken belief that lewisite is an anhydrous phase (27–29).

From the recalculated microprobe analysis, the unit cell volume (Table 1) found in the X-ray diffraction study, and the density (Table 1) measured by Hussak and Prior (28), the unit cell contents of lewisite were calculated to be $Ca_{8.31}Na_{0.10}Fe_{1.53}Mn_{0.55}Ti_{6.07}Al_{0.44}Sb_{13.16}$, excluding O and H. These values for Ca, Mn, and Na were subsequently used in the structure refinement as compositional constraints on the atomic occupancy of the *A* site, and the values for Ti, Fe, and Al were used in like manner for the occupancy of *B*. The valence states of Mn, Fe, and Ti were assumed to be +2, +3, and +4, respectively, based on crystal-chemical considerations, the presence of numerous hematite (Fe_2O_3) and rutile (TiO_2) inclusions in lewisite crystals (28,29), and the association of lewisite with derbylite [$Fe_4^{3+}Ti_3^{4+}Sb^{3+}O_{13}(OH)$] at the type locality (33).

TABLE 1
Crystal-Chemical Data

Color	Orange-brown and translucent
Crystal habit	Euhedral octahedral
Optics	Isotropic
Formula	$[(Ca_{1.04}Mn_{0.07}^{2+}Na_{0.01})(Sb_{0.65}^{3+})]_{\sum 1.77}$ $(Sb_{0.99}^{5+}Ti_{0.76}^{4+}Fe_{0.19}^{3+}Al_{0.06})_{\sum 2}O_6(OH)_{0.91}$
Formula weight	405.81 with $Z = 8$
Space group	$F\bar{4}3m$ (pseudo-$Fd\bar{3}m$)
Unit cell	$a = 10.277(1)$ Å, $V = 1085.4(2)$ Å^3
$\|F\|_{000}$	1480.3
Density (g/cm^3)	4.950 (obs) and 4.966 (calc)

X-Ray Diffraction

Prior to measurement of intensity data, a film study of lewisite was performed using the precession and cone-axis methods and a crystal large enough to ensure overexposed diffraction patterns. The results were consistent with the classic pyrochlore space group, $Fd\bar{3}m$. A very small, optically isotropic fragment broken from an orange-brown octahedral crystal was then mounted on an Enraf-Nonius CAD4 diffractometer, and the intensities of 1241 reflections in one octant of reciprocal space to 90° 2θ were measured assuming only extinctions due to the lattice centering. The intensities were corrected for the Lorentz–polarization and absorption effects, the latter by the ψ-scan method (34) using 10 reflections. Symmetry-equivalent data were then averaged (merging $R = 0.034$), leaving a final data set of 273 reflections, of which 218 were considered "observed" at the $I(\text{obs}) > 2\sigma(I)$ threshold. The unit cell parameter $a = 10.277(1)$ Å was refined by leastsquares from the optimized setting angles of 25 reflections between 20° and 67° 2θ. An independent determination of *a* from a least-squares refinement of 24 reflections obtained with a 114.6-mm Gandolfi camera, a powdered sample, and Si as an internal standard yielded 10.2843(8) Å. The crystal structure was then solved and refined using the Enraf-Nonius crystallographic software package MolEN. Revised crystal-chemical data for lewisite are summarized in Table 1. Additional details of the data measurement and structure refinement procedures are given in Table 2.

Infrared Spectroscopy

Four octahedral crystals were doubly polished simultaneously to obtain parallel surfaces, and their thicknesses were measured with a digital micrometer. The inclusion-free region of one such crystal having a thickness of 136 μm was used for near-infrared measurements using a Nicolet 60-SX Fourier transform infrared spectrometer equipped with an InSb detector. An aperture of 50 μm was used to delimit the beam. In the typical spectrum shown in Fig. 1, there is one large peak at $\sim 3590\ \text{cm}^{-1}$ and a small shoulder at $\sim 3560\ \text{cm}^{-1}$. Both peaks are in the O–H stretching region

TABLE 2
Experimental Details

Crystal size	$0.14 \times 0.16 \times 0.19$ mm
Data measurement	
Radiation	Monochromatized Mo$K\alpha$ at 50 kV and 30 mA
Temperature	24°C
Index limits	$0 \leq h, k, l \leq 20$
Maximum 2θ	90.00°
Scan type	$\omega/2\theta$
Scan rates	Between 0.4 and 5.5/min in ω
Scan widths	$0.73 + 0.35 \tan\theta$
Intensity monitoring	3 reflections every 3 h
Orientation monitoring	3 reflections every 400 reflections
Data Corrections	Lorentz–polarization and absorption ($\mu_1 = 109$ cm^{-1}) effects
Structure Refinement	
Type	Full matrix least squares
Function minimized	$\sum w(\lvert F\rvert_{obs} - \lvert F\rvert_{cal})^2$
Reflection weights	$4F^2_{obs}/\sigma^2(F^2_{obs})$
Anomalous dispersion	For all atoms
Extinction parameter (g)	$2.38(7) \times 10^{-6}$ [a], $2.13(5) \times 10^{-6}$ [b,c]
Observations	218[a,b] or 326[c] reflections with $I > 2\sigma(I)$
Variables	20,[a] 28,[b] 33[c]
R (observed data)	0.017,[a] 0.014,[b] 0.014[c]
wR (observed data)	0.026,[a] 0.019,[b] 0.020[c]
R (all data)	0.022,[a] 0.026,[b] 0.029[c]
Esd obs of unit weight	1.066,[a] 0.821,[b] 0.799[c]
Largest shift/error	0.00,[a] 0.01,[b] 0.02[c]
Largest $\Delta\rho(x, y, z)$	$+0.64$ and -1.2 e/Å^3 [a] $+0.83$ and -0.61 e/Å^3 [b] $+0.70$ and -0.27 e/Å^3 [c]
Diffractometer	Enraf-Nonius CAD4
Crystallographic software	MolEN system

[a] For the refinement in $Fd\bar{3}m$.
[b] For the refinement in $F\bar{4}3m$.
[c] For the refinement in $F23$.

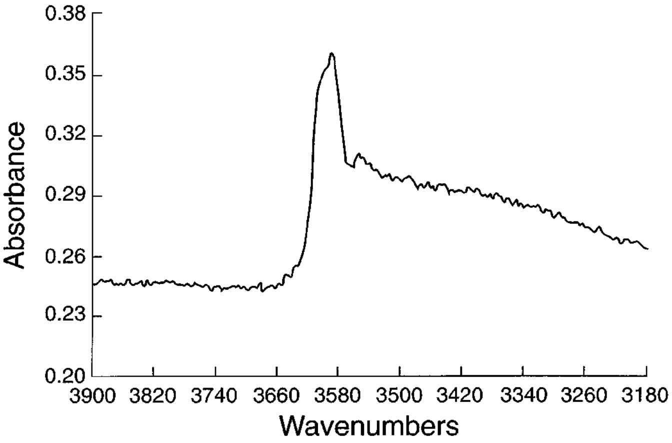

FIG. 1. Infrared spectrum from a single crystal of lewisite demonstrating the presence of structural (OH) groups.

and are assigned to structural OH groups. The periodic oscillations are interference fringes.

RESULTS

Symmetry-Forbidden Reflections

Three types of "symmetry-forbidden" reflections have been reported for the cubic pyrochlores: (a) violations of the lattice-centering extinction rule of $Fd\bar{3}m$ (e.g., (3, 4)); (b) violations of the d-glide extinction rules of $Fd\bar{3}m$ (1–8); and (c) violations of the special extinction rules (11) that apply to the classic cubic pyrochlore structure by virtue of the fact that all of its atoms occupy special positions in $Fd\bar{3}m$ (e.g., (2, 3, 17)). In lewisite, reflections of the third type are rather weak, but numerous, a consequence of the presence of a heavy atom on a nonconventional site. Reflections of the second type are few in number and of very low intensity. Of the 23 unique (after averaging symmetry equivalents) reflections inconsistent with d-glide symmetry, only six (200, 600, 14,0,0, 420, 820, 14,4,0) have $F > 1.00\sigma(F)$, and of these only 200 and 420 have $F > 2.00\sigma(F)$ and are therefore considered statistically significant. This fact is ascribed both to the small deviation of the structure from centrosymmetry and to the small size of the crystal fragment used for intensity measurement. In addition to 200 and 420, the forbidden reflections 600, 820, 640, and 860 have also been observed from certain synthetic pyrochlores (1–8).

The possibility that the symmetry-forbidden reflections in lewisite are spurious observations produced by the Renninger effect (double diffraction) was considered and rejected for two reasons: (1) The same set of reflections also appears, with statistically significant intensities ($>2\sigma$, with many $>4\sigma$), in four-circle diffractometer data we have obtained from roméite crystals from localities in Italy, Brazil, and Sweden. These violations of d-glide symmetry are far too numerous and persistent to be Renninger reflections. (2) The reflections in question are, as noted above, the same ones observed from certain synthetic pyrochlores using various powder diffraction methods (conventional X-ray, neutron, and synchrotron), which are not subject to the Renninger effect.

Structure Refinement in $Fd\bar{3}m$

From the unit cell contents calculated from the chemical analysis, the site contents were initially assumed to be $A(16d) = (\text{Ca}_{8.31}\text{Sb}_{5.20}\text{Mn}_{0.55}\text{Na}_{0.10})_{\sum 14.16}$, $B(16c) = (\text{Sb}_{7.96}\text{Ti}_{6.07}\text{Fe}_{1.53}\text{Al}_{0.44})_{\sum 16}$, $X(48f) = 48$ O, and $Y(8b) = 8$ O. Refinement of this model with isotropic displacement factors and neutral atom scattering factors yielded a residual of 0.13 and a conspicuously high value of 3.4 Å^2 for B_{iso} of the A site. The site multiplicities of the dominant cations, Ca(A) and Sb(B) (i.e., Ca in the A site and Sb in the B site), were refined as variables, with the multiplicities of all other cations being fixed at the values from the chemical analysis.

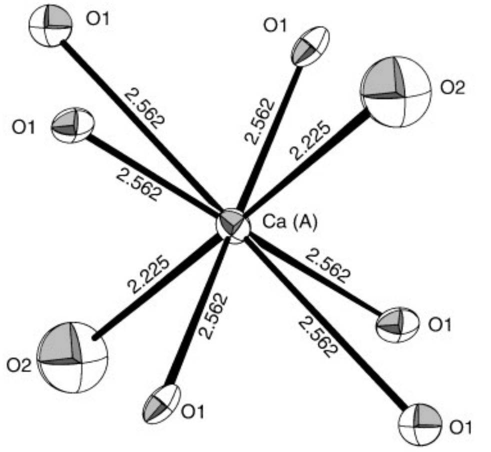

FIG. 2. Coordination of the Ca(*A*) site in lewisite in the $Fd\bar{3}m$ model.

Conversion to anisotropic displacement factors reduced the residual to 0.065, but a difference Fourier synthesis revealed a set of symmetrically equivalent peaks at (0.49, 0.49, 0.56) clustered around the conventional *A* site (1/2, 1/2, 1/2) and separated from it by 0.46 Å. This indicated a splitting of the pyrochlore large-cation site into two, i.e., Ca on the conventional *A* site (16*d*) and Sb as Sb^{3+} on an alternative site, *A*′(96*g*). Such partitioning is reasonable given the very different coordination requirements of Ca^{2+} and Sb^{3+} (a lone-pair ion) and the fact that *A*′ has a highly asymmetrical, "one-sided" coordination (Figs. 2 and 3) well-suited to a lone-pair ion. The Sb in the symmetrically coordinated (octahedral) *B* site is then Sb^{5+}.

With Ca and Sb^{3+} now properly assigned to *A* and *A*′, respectively, and refining the multiplicity factors of Sb(*A*′), Sb(*B*), and O2(*Y*), the residual decreased from 0.065 to 0.036. A comparison of observed and calculated structure factors indicated that an extinction correction was needed, and this reduced the residual to its final value of 0.017. At this point, a final difference Fourier revealed a very small peak of height 0.6 e/Å^3 on 32*e* (0.40, 0.40, 0.40) 0.48 Å from O2(*Y*) on 8*b* (3/8, 3/8, 3/8). This feature may represent a small amount of positional disorder of the *Y*-site anion, or it may be nothing more than a fortuitously situated "noise peak" in the difference Fourier. Attempts to refine the peak as a partially occupied "O(*Y*′)" site and as the H atom of a hydroxyl group, which is known to be present from the IR study, were not successful.

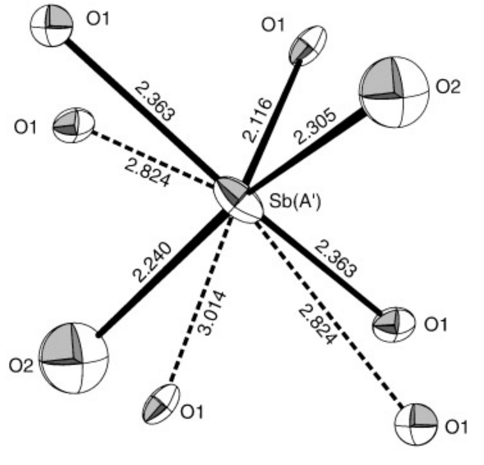

FIG. 3. Coordination of the Sb(*A*′) site in lewisite in the $Fd\bar{3}m$ model.

The final values of the multiplicity factors of Sb(*A*′), Sb(*B*), and O2(*Y*), which were all included as variables in the refinement, are (expressed as atoms/cell with esd's) 5.22(2) Sb, 7.93(1) Sb, and 7.28(9) O, respectively. Separate attempts were made to refine the multiplicities of Ca(*A*) and O1(*X*) simultaneously with those of the foregoing three sites, but these attempts failed, owing, in the case of Ca(*A*), to a high correlation between *A* and *A*′. An independent refinement of the multiplicity of Ca(*A*) holding that of Sb(*A*′) constant yielded 8.41(5) Ca atoms. A refinement of the multiplicity of O1(*X*) holding those of all other sites constant yielded 48.0(2) O atoms. Agreement between the numbers of Ca, Sb, and O1(*X*) atoms from the refinement and those derived from the chemical analysis and the requirement for B_2X_6 pyrochlore framework stoichiometry is excellent; e.g., the Sb totals from the refinement and the chemical analysis are 13.15 and 13.16 atoms, respectively.

The result of the foregoing analysis is the optimal chemical formula for lewisite of $[(Ca_{8.31}Mn^{2+}_{0.55}Na_{0.10})(Sb^{3+}_{5.22})]_{\sum 14.18}(Sb^{5+}_{7.93}Ti^{4+}_{6.07}Fe^{3+}_{1.53}Al_{0.44})_{\sum 15.97}O_{48}(OH)_{7.28}$, which is (probably fortuitously) charge balanced at $\sum v_c = +103$ and $\sum v_a = -103$ vu. Refined atomic parameters are listed in Table 3, structure factors are available as supplementary material, and selected interatomic distances are listed in Table 4.

Structure Refinement in $F\bar{4}3m$

Having obtained a satisfactory refinement of the lewisite structure in its pseudo-space group, $Fd\bar{3}m$, additional refinements were carried out in the relevant subgroups $F\bar{4}3m$ and $F23$, which are the only ones that retain cubic symmetry but lack the *d*-glide planes inconsistent with the observed forbidden reflections. These possibilities were recognized in 1978 by Sleight *et al.* (10), who noted that among certain AM_2X_6 defect pyrochlores "The acentric cubic phases must have point groups of $\bar{4}3m$ or 23 since these are the only two cubic point groups which allow a second harmonic signal." In 1984, Beyerlein *et al.* (4) successfully solved the structure of $Pb_2Ru_2O_{6.5}$ in $F\bar{4}3m$ using neutron powder diffraction data, and all subsequent refinements of noncentrosymmetric cubic pyrochlore structures (5–8) have been carried out in this space group using a structure setting derived from the A_o setting in $Fd\bar{3}m$. This precedent has also been followed in the present case, the starting atomic parameter set in $F\bar{4}3m$

TABLE 3
Atomic Coordinates and Displacement Factors (Å^2) in Lewisite[a]

Site		x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}	B_{eq}
$Fd\bar{3}m$ Refinement											
A	16d	1/2	1/2	1/2	0.0105(2)	U_{11}	U_{11}	− 0.0012(1)	U_{12}	U_{12}	0.830(4)
A'	96g	0.4835(2)	x	0.5386(2)	0.0206(3)	U_{11}	0.0084(5)	− 0.0117(4)	0.0004(3)	U_{13}	1.31(1)
B	16c	0	0	0	0.00405(4)	U_{11}	U_{11}	− 0.00049(3)	U_{12}	U_{12}	0.3195(9)
O1	48f	0.3242(1)	1/8	1/8	0.0148(5)	0.0124(2)	U_{22}	0	0	0.0074(4)	1.04(1)
O2	8b	3/8	3/8	3/8	0.0418(15)	U_{11}	U_{11}	0	0	0	3.30(4)
$F\bar{4}3m$ Refinement											
A	16e	0.8720(1)	x	x	0.0078(2)	U_{11}	U_{11}	− 0.0007(1)	U_{12}	U_{12}	0.612(3)
A'	48h	0.8918(1)	x	0.8415(1)	0.0378(2)	U_{11}	0.0120(4)	− 0.0342(3)	0.0031(2)	U_{13}	2.30(1)
B	16e	0.37522(3)	x	x	0.00424(3)	U_{11}	U_{11}	− 0.00056(2)	U_{12}	U_{12}	0.3346(7)
O1a	24f	0.3046(2)	0	0	0.0152(9)	0.0219(5)	U_{22}	0	0	− 0.0154(7)	1.55(2)
O1b	24g	0.4512(2)	1/4	1/4	0.0086(6)	0.0044(3)	U_{22}	0	0	− 0.0030(4)	0.46(2)
O2a	4d	3/4	3/4	3/4	0.0422(39)	U_{11}	U_{11}	0	0	0	3.33(9)
O2b	4a	0	0	0	0.0391(20)	U_{11}	U_{11}	0	0	0	3.04(4)
$F23$ Refinement											
A	16e	0.8723(1)	x	x	0.0081(1)	U_{11}	U_{11}	− 0.0006(1)	U_{12}	U_{12}	0.640(3)
A'	48h	0.8913(2)	0.8920(2)	0.8414(1)	0.0387(4)	0.0375(4)	0.0120(3)	− 0.0345(2)	0.0021(3)	0.0040(3)	2.32(1)
B	16e	0.37519(3)	x	x	0.00423(2)	U_{11}	U_{11}	− 0.00054(2)	U_{12}	U_{12}	0.3337(5)
O1a	24f	0.3040(2)	0	0	0.0152(7)	0.0243(7)	0.0192(6)	0	0	− 0.0156(6)	1.55(3)
O1b	24g	0.4509(2)	1/4	1/4	0.0092(5)	0.0029(4)	0.0059(4)	0	0	− 0.0029(4)	0.48(2)
O2a	4d	3/4	3/4	3/4	0.0416(30)	U_{11}	U_{11}	0	0	0	3.29(7)
O2b	4a	0	0	0	0.0391(15)	U_{11}	U_{11}	0	0	0	3.08(3)

[a] Anisotropic displacement factors are of the form $\exp[-2\pi^2\{h^2a^2U_{11} + k^2b^2U_{22} + l^2c^2U_{33} + 2hkabU_{12} + 2hlacU_{13} + 2klbcU_{23}\}]$.The B_{eq} are the equivalent isotropic displacement factors. The coordinate transformations for $Fd\bar{3}m$ (B_o, $\bar{3}m$ origin) to $F\bar{4}3m$ (O_o, $F\bar{4}3m$ origin) are $(x, y, z) = (x + 0.375, y + 0.375, z + 0.375)$ or $(\bar{x} + 0.375, \bar{y} + 0.375, \bar{z} + 0.375)$, with further transformations to symmetry-equivalent positions in the case of 24f and 24g of $F\bar{4}3m$.

being derived from the $Fd\bar{3}m$ (B_o) refinement of lewisite by the appropriate coordinate transformations.

In the $Fd\bar{3}m \rightarrow F\bar{4}3m$ transformation, three of the five atomic sites in lewisite split into pairs, i.e., $A'(96g) \rightarrow A'(a)(48h) + A'(b)(48h)$, $O1(48f) \rightarrow O1a(24f) + O1b(24g)$, and $O2(8b) \rightarrow O2a(4d) + O2b(4a)$. Of these, only the two A' sites presented a problem in the refinement, that being whether the ca. 5 Sb^{3+}/cell are (a) entirely ordered in A'(a) at (0.86, 0.86, 0.91), (b) entirely ordered in A'(b) at (0.89, 0.89, 0.84), or (c) disordered over both positions. Attempts to refine the disordered model produced residuals as low as 0.013 with anisotropic displacement factors, but one or both A' sites and the O1a site tended to become non-positive definite. An attempt to refine the site multiplicity factors of A'(a) and A'(b) simultaneously produced a negative value for A'(a) followed by a catastrophic failure of least squares. Likewise, refinement of the model with all Sb^{3+} in A'(a) caused the latter site, and often O1a as well, to become non-positive definite. The only consistently well-behaved refinement occurred when all Sb^{3+} was ordered in A'(b), convergence being reached at a residual of 0.014. The A'(b) model was therefore accepted as the correct choice and is the one reported in Table 3. The cation assignments to the solid solution sites A and B are the same as in the $Fd\bar{3}m$ refinement.

The multiplicity factors of Sb(A'), Sb(B), O2a, and O2b were treated as variables in all three of the models just described, their final values for the A'(b) model being 5.57(2) Sb(A'), 8.52(1) Sb(B), 2.42(7) O2a, and 4.20(6) O2b atoms/cell. Note that the Y-site anion vacancies are evidently ordered in O2a, both O2 sites being fourfold equipoints. The agreement between the Sb totals from the $F\bar{4}3m$ structure refinement and the chemical analysis, 14.09 and 13.16 Sb/cell, respectively, is not as good as it is for $Fd\bar{3}m$, and the total (O2a + O2b) = 6.62 O/cell is slightly less than the 7.28 O/cell indicated by the $Fd\bar{3}m$ refinement. Consequently, the sums of the formal ionic charges are now +107 and −103 vu. Refined atomic parameters are listed in Table 3, structure factors are available as supplementary material, and selected interatomic distances are listed in Table 4.

Structure Refinement in F23

Michel *et al.* (1) proposed that the hydrated pyrochlore $NaNbWO_6 \cdot H_2O$ has $F23$ symmetry, as evidenced by the presence of the same forbidden reflections described above

TABLE 4
Selected Interatomic Distances in Lewisite

$Fd\bar{3}m$		$F\bar{4}3m$		$F23$	
A–O2	2.225[a] × 2	*A*–O2a	2.172(3)	*A*–O2a	2.177(2)
–O1	2.562(1) × 6	–O2b	2.278(3)	–O2b	2.273(2)
Mean	2.478	–O1b	2.538(6) × 3	–O1b	2.542(5) × 3
		–Ola	2.599(7) × 3	–O1a	2.594(5) × 3
		Mean	2.483	Mean	2.482
A′–O1	2.116(3)	*A′*–Ola	2.174(7)	*A′*–Ola	2.171(5)
–O2	2.240(3)	–O2b	2.263(6)	–O2a	2.263(5)
–O2	2.305(4)	–O2a	2.266(5)	–O2b	2.266(5)
–O1	2.363(3) × 2	–O1b	2.369(6) × 2	–O1b	2.366(9)
Mean	2.277	Mean	2.288	–Olb	2.375(9)
–O1	2.824(4) × 2	–Ola	2.821(7) × 2	Mean	2.288
–O1	3.014(4)	–Olb	2.964(6)	–Ola	2.814(9)
				–Ola	2.822(9)
				–Olb	2.966(4)
B–O1	1.9701(8) × 6	*B*–O1a	1.953(3) × 3	*B*–O1a	1.956(2) × 3
		–O1b	1.980(3) × 3	–O1b	1.979(2) × 3
		Mean	1.966	Mean	1.968
A–*A*	3.633[a]	*A*–*A*	3.546(8)	*A*–*A*	3.554(6)
–*A′*	0.463(4)[b]	–*A′*	0.426(6)[b]	–*A′*	0.424(4)[b]
–*B*	3.633[a]	–*B*	3.634(4)	–*B*	3.634(3)
A′–*A′*	0.467(6)[b]	*A′*–*A′*	0.731(8)[b]	*A′*–*A′*	0.731(5)[b]
–*B*	3.241(4)[b]	–*B*	3.274(4)[b]	–*B*	3.272(6)[b]
B–*B*	3.633[a]	*B*–*B*	3.627(2)	*B*–*B*	3.628(1)
O1–O1	2.673(1)	O1a–O1a	2.840(12)	O1a–O1a	2.848(8)
–O2	3.092(2)	–O1b	2.677(1)	–O1b	2.676(1)
		–O2a	3.676(1)	–O2a	3.676(1)
		–O2b	3.130(9)	–O2b	3.124(6)
		O1b–O1b	2.925(9)	O1b–O1b	2.920(7)
		–O2a	3.070(7)	–O2a	3.074(5)
		–O2b	3.668(1)	–O2b	3.668(1)
O2–O2	4.450[a]	O2a–O2a	7.267[a]	O2a–O2a	7.267[a]
		–O2b	4.450[a]	–O2b	4.450[a]
		O2b–O2b	7.267[a]	O2b–O2b	7.267[a]

[a] Distances between atoms on symmetry-fixed equipoints.
[b] Shortest cation-cation distances involving Sb(*A′*).

in its X-ray powder pattern. It therefore seemed advisable to attempt a refinement of the lewisite structure in this space group. The atomic coordinate transformations and structure setting for the case $Fd\bar{3}m \rightarrow F23$ are the same as those for $F\bar{4}3m$, and indeed the only fundamental difference between the two noncentrosymmetric models is that the *A′*, O1a, and O1b sites in the $F23$ model acquire additional degrees of freedom relative to those in $F\bar{4}3m$ (Table 3). Reference to the refined atomic parameters in Table 3 shows no salient differences between the $F\bar{4}3m$ and $F23$ models, the maximum difference in their positional parameters being three esd's. The final values of the three residuals in Table 2 are negligibly different from those for the $F\bar{4}3m$ model. The same may also be said of the interatomic distances in Table 4. A list of structure factors is available as supplementary material.[2] The other enantiomer in $F23$ was also refined, but the resulting residuals were negligibly different from those listed for $F23$ in Table 2.

DISCUSSION

On the basis of the foregoing evidence, i.e., the optical isotropy of the crystal fragment studied, the anomalous reflections forbidden in $Fd\bar{3}m$, and the essential identity of the $F\bar{4}3m$ and $F23$ structure models, we conclude that $F\bar{4}3m$ is the "true" space group symmetry of lewisite insofar as this property can be determined by X-ray diffraction. This result, obtained from a high-resolution single-crystal data set, supports the choice of $F\bar{4}3m$ for those synthetic pyrochlores (4–8) that show the same anomalous reflections but for which only X-ray or neutron powder data are available. The qualification concerning the limitations of X-ray diffraction is included because the structure we have described for lewisite is necessarily an average structure, the two *A*-site cations Ca^{2+} and Sb^{3+} being in such close proximity to one another as to preclude their coexistence in any given unit cell. The possibilities for the real structure(s), which may or may not have $F\bar{4}3m$ symmetry, are similar to those outlined in general terms by Ercit *et al.* (17) for the natural inverse pyrochlore cesstibtantite, $(Na,Sb^{3+},Pb^{2+},Bi^{3+},Ca,Sn^{2+})(Ta,Nb)_2(O,OH,F)_6(Cs,K,OH,F)$. These are (a) *short-range ordering* of Ca^{2+} and Sb^{3+}, yielding coexisting regions of pure Ca and pure Sb^{3+} end-member phases on a submicron scale, i.e., a domain structure; and (b) *long-range ordering* involving Ca, Sb^{3+}, and *A*-site cation vacancies, producing a superstructure that is not observable in the X-ray diffraction data.

The $Fd\bar{3}m \rightarrow F\bar{4}3m$ symmetry reduction phenomenon is usually ascribed to ordering of *Y*-site anion vacancies coupled with a positional shift of the *A*-site cation by ~0.04 Å (relative to its position in the $Fd\bar{3}m$ structure) toward its associated anion vacancy (4–8). In these studies, all involving synthetic pyrochlores of the type $A_2B_2X_6Y_{0.5}$, the vacancies are confined to the 4*a* (0, 0, 0) position, the other half of the *Y*-site, 4*d* (3/4, 3/4, 3/4), being fully occupied. An exception is $Pb_2(TiSb)O_{6.5}$ (5), in which 4*a* is occupied and 4*d* is vacant. Lewisite is similar to the latter compound both in its vacancy ordering pattern and in its *B*-site contents, but the 4*d* (O2a) site is only partially vacant, its contents being 2.42(7) atoms or ~60% occupancy. Comparison of the *A*–O2 ($Fd\bar{3}m$) and *A*–O2a,O2b ($F\bar{4}3m$) distances in Table 4 shows that Ca(*A*) has moved 0.053 Å toward the O2a vacancy and away from the fully occupied O2b position by the same amount. With regard to the Sb(*A′*) site, the $F\bar{4}3m$ model equalizes the *A′*–O2a and *A′*–O2b distances [2.266(5) and 2.263(6) Å] relative to their counterparts in $Fd\bar{3}m$ [2.240(3) and 2.305(4) Å]. It should also be noted that in some $A_{2-x}B_2X_6Y_{7-y}$ pyrochlores (6, 7, 35–37) the Y-site vacancies are evidently disordered, as no forbidden reflections are observed and hence $Fd\bar{3}m$ symmetry is maintained.

The splitting of the A site and the segregation of Sb^{3+} and Sb^{5+} onto separate positions in lewisite have some precedents among the natural and synthetic pyrochlores. Synthetic $K_{0.51}Sb^{3+}_{0.67}Sb^{5+}_2O_{6.26}$ (14) and $Tl_{0.51}Sb^{3+}_{0.71}Sb^{5+}_2O_{6.32}$ (15) both contain Sb^{3+} on $96g$ (0.49, 0.49, 0.54), which is identical to the A' site in lewisite, and Sb^{5+} on $16c$, the B site in $Fd\bar{3}m$. However, both compounds are inverse pyrochlores, with K^+ and Tl^+ located on $32e$ and $96g$ sites that are slightly displaced from the standard Y($8b$) position and with their $A(16d)$ sites entirely vacant. A third precedent is in the structure of cesstibtantite (17), which has a mixed normal and inverse character and a $96g$ (0.48, 0.48, 0.54) site that again serves as a collection point for lone-pair cations, in this case (Sb^{3+},Pb^{2+},Bi^{3+}, …).

From their observations with the polarizing light microscope, Brugger *et al.* (29) concluded that "Our data suggest that 'lewisite' is a mixture of roméite and a phase which is structurally related to pyrochlore and develops at the expense of roméite." Our results are inconsistent with this interpretation in three respects: (a) Their proposed chemical formula, $(Ca,Mn,Na)_{2-m}(Sb,Ti,Al,Fe^{3+},Nb,As^{5+})_2O_6$ with $m \approx 1$, while agreeing with our cation site assignments, is in error on two counts. First, it requires that lewisite be an anhydrous phase, with a Y site that is entirely vacant. As we have just shown, this formulation is clearly in error, being the result ultimately of an erroneous assumption about the valence state of Sb in lewisite. Secondly, $m \approx 1$ in their empirical formula leaves only 8 (Ca,Mn,Na) atoms on the A site. The crystal structure analysis proves that the X-ray scattering power of this site ($A + A'$) is far greater than this and is equivalent to 9.0 (Ca,Mn,Na) + 5.2 Sb. (b) The optical study of Brugger *et al.* indicates that lewisite crystals are optically anisotropic aggregates of very small grains, possibly representing a mixture of hexagonal and cubic phases. However, Hussak and Prior (28) reported lewisite to be optically isotropic, with no mention of any microscopic grain structure or any other optical anomalies. Optical examination of our crystals shows them to be homogeneous, except for the presence of numerous minute inclusions of other minerals. (c) The lewisite crystals used in our study are part of the type (original) material studied by Hussak and Prior (28), whereas those studied by Brugger *et al.* are not; at least no such claim for their specimens' provenance is made in their paper. Since the results of a study of type material are considered definitive relative to those on nontype material when the validity of a mineral species is in question, this challenge to the validity of lewisite cannot be sustained. That is, whereas we accept the validity of Brugger *et al.*'s optical characterization *of their crystals*, those results cannot be used to discredit lewisite as a unique chemical compound.

Lastly, one might ask what significance the lewisite structure has within the larger framework of pyrochlore-group crystal chemistry. Does it, in fact, contribute anything new to the already voluminous body of knowledge on that subject? Our response is that the lewisite structure illustrates one possible solution to the following problem: How can a compound for which the pyrochlore structure is the stable form accommodate two (or more) different cations that are too large for the B site, but whose bond-valence and coordination geometry requirements are so different as to prohibit their co-occupancy of the A site, i.e., no simple solid solution on A is possible. The most obvious solution to the problem is to segregate the incompatible components by formation of more than one pyrochlore-type phase. A second solution is to segregate them within the same phase, i.e., by formation of an inverse pyrochlore structure, in which very large monovalent cations, e.g., the larger alkali metal ions, occupy the Y-anion site, leaving somewhat smaller or higher valence cations to occupy A. A third possibility is to split the A site into two (or more) sites, each having a different coordination geometry that is appropriate to one of the incompatible ionic types. This third solution should be especially applicable to cases in which one of the large cations involved has a stereochemically active lone pair, the A' site of lewisite being well-suited to accommodate such ions. It is this third solution that is realized in the structure of lewisite and defines the crystal-chemical significance of that compound. The relative stabilities of the foregoing alternatives can be assessed quantitatively from a consideration of the Madelung energies of pyrochlore compounds (38), but this aspect is beyond the scope of the present work.

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