Refinement of the crystal structure of calcium chondrodite $Ca_5[SiO_4]_2(OH)_2 = Ca(OH)_2 \cdot 2Ca_2SiO_4$

T. P. Kuznetsova, N. N. Nevskii, V. V. Ilyukhin, and N. V. Belov

Institute of Crystallography, Academy of Sciences of the USSR

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TABLE I. Coordinates of Basis Atoms, and Anisotropic Thermal Parameters of Ca Chondrodite*

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{13}
Ca_1	0	0	0	152(6)	112(4)	358(17)	11(6)	−56(11)	−143(16)
Ca_2	1875(1)	3301(1)	4(1)	152(7)	87(4)	550(37)	92(5)	53(18)	−53(16)
Ca_3	4185(1)	1195(1)	−100(1)	151(10)	122(5)	544(25)	104(5)	3(15)	123(18)
Si	2006(1)	1452(1)	4259(1)	107(7)	90(5)	212(22)	74(6)	16(10)	8(13)
O_1	2065(1)	156(2)	2946(4)	246(17)	116(11)	576(67)	146(23)	−15(46)	−29(53)
O_2	442(2)	1699(2)	2961(4)	166(18)	147(11)	704(69)	163(24)	77(46)	0(54)
O_3	3534(2)	2524(2)	2984(4)	148(18)	114(11)	779(70)	32(24)	32(46)	76(55)
O_4	1996(2)	1464(2)	7450(4)	238(18)	158(11)	452(67)	107(24)	68(44)	24(57)
O_5(OH)	4006(3)	4422(2)	7448(6)	367(41)	382(26)	3294(130)	1255(57)	1629(101)	4122(125)

*The coordinates of the basis atoms are augmented by a factor of 10^4, the thermal parameters by a factor of 10^5.

TABLE II. Interatomic Distances in Ca Chondrodite Polyhedra (Å)

Si–O_1	1.642	Ca_2–O_1	2.323	Ca_3–O_1	2.443
O_2	1.646	O_2	2.404	O_3	2.379
O_3	1.653	O_2*	2.312	O_3*	2.315
O_4	1.620	O_3	2.470	O_4	2.416
		O_4	2.501	O_5	2.343
O_1–O_2	2.612	O_5	2.325	O_5*	2.343
O_3	2.614				
O_4	2.744	O_1–O_2	3.791	O_1–O_3	2.614
		O_2*	3.292	O_4	3.176
O_2–O_3	2.620	O_3	3.675	O_5	3.522
O_4	2.724	O_5	3.176	O_5*	3.394
O_3–O_4	2.729	O_2–O_2*	3.367	O_3–O_3*	3.657
		O_3	2.620	O_4	3.194
Ca_1–O_1	2.335(×2)	O_4	3.171	O_5*	3.595
O_2	2.391(×2)				
O_4	2.404(×2)	O_2*–O_4	3.478	O_3*–O_4	3.796
		O_5	3.775	O_5	3.506
O_1–O_2	2.612(×2)			O_5*	3.075
O_2*	3.939(×2)	O_3–O_4	3.194		
O_4	3.176(×2)	O_5	3.496	O_4–O_5	3.364
O_4*	3.518(×2)				
		O_4–O_5	3.296	O_5–O_5*	3.141
O_3–O_4	3.171(×2)				
O_4*	3.596(×2)				

The results of a direct structural investigation of calcium chondrodite from x-ray data obtained by the photographic method were given in Ref. 1. To refine the crystal structure we used a single-crystal specimen of the products of hydrothermal reactions[2] (sphere with radius r = 0.017 cm). The experimental x-ray data amounted to 1646 independent reflections $I_{hkl} \geq 3\sigma(I)$, recorded on an Enraf-Nonius automatic diffractometer in Mo Kα radiation; $\sin\theta/\lambda \leq 0.75$ Å^{-1}, $\mu r = 0.6$. The parameters of the refined monoclinic cell were as follows: $a = 8.9207(35)$; $b = 11.4481(15)$; $c = 5.0759(8)$ Å; $\gamma = 108.32(3)°$; $V = 492$ Å^3; Fedorov group $C_{2h}^5 = P2_1/b$; $Z = 2$.

In the refinement of the structure we used the coordinates of the basis atoms, given in Ref. 1, as the initial ones. Refinement by the one third of least-squares in the anisotropic approximation[3] leads to $R_{hkl} = 0.04$.

TABLE III. Valence Angles in the Structure of Ca Chondrodite

O_1–Si–O_2	105°12′	O_2–Ca_2–O_4	80°31′
O_1–Si–O_3	105°00′	O_2*–Ca_2–O_4	92°26′
O_1–Si–O_4	114°34′	O_2*–Ca_2–O_5	108°59′
O_2–Si–O_3	105°10′	O_3–Ca_2–O_4	79°57′
O_2–Si–O_4	113°01′	O_3–Ca_2–O_5	93°34′
O_3–Si–O_4	113°00′	O_4–Ca_2–O_5	86°03′
O_1–Ca_1–O_2	67°06′	O_1–Ca_3–O_3	65°38′
O_1–Ca_1–O_2*	112°54′	O_1–Ca_3–O_4	81°38′
O_1–Ca_1–O_4	84°09′	O_1–Ca_3–O_5	94°45′
O_1–Ca_1–O_4*	95°51′	O_1–Ca_3–O_5*	90°18′
O_2–Ca_1–O_4	82°48′	O_3–Ca_3–O_5*	102°21′
O_2–Ca_1–O_4*	97°12′	O_3–Ca_3–O_4	83°33′
O_1–Ca_2–O_2	106°38′	O_3–Ca_3–O_5*	99°09′
O_1–Ca_2–O_2*	90°31′	O_3*–Ca_3–O_4	106°43′
O_1–Ca_2–O_3	100°06′	O_3*–Ca_3–O_5	97°38′
O_1–Ca_2–O_5	86°11′	O_3*–Ca_3–O_5*	82°37′
O_2–Ca_2–O_2*	91°05′	O_4–Ca_3–O_5	89°57′
O_2–Ca_2–O_3	65°01′	O_5–Ca_3–O_5*	84°09′

Table I lists the final coordinates of the basis atoms and the anisotropic thermal parameters; the interatomic

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distances and valence angles are given in Tables II and III, respectively.

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Crystal structure of $Cs_2Hf(MoO_4)_3$

R. F. Klevtsova, A. A. Antonova, and L. A. Glinskaya

Institute of Inorganic Chemistry, Siberian Branch, Academy of Sciences of the USSR

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Single crystals of the double molybdate $Cs_2Hf(MoO_4)_3$ have been synthesized by the solution in a melt method. They are colorless transparent plates.[1]

The experimental data for the structural investigation were obtained from a selected specimen measuring 0.1 × 0.2 × 0.3 mm on a Syntex $P2_1$ automatic diffractometer. The intensities of 2206 independent nonzero reflections with $\sin\theta/\lambda \leq 0.71$ Å^{-1} were recorded by the $\theta:2\theta$ method at a variable scanning rate in Mo Kα radiation. In the subsequent calculations we used an array of 1882 F_{hkl} with $I > 3\sigma(I)$.

All the structural calculations were performed by the programs in Refs. 2 and 3, and the intensities were converted to $|F_{hkl}|$ without allowing for absorption (owing to the absence of the corresponding programs for specimens of arbitrary shape) on the XTL Syntex specialized calculation system.

The monoclinic unit-cell dimensions refined on the automatic diffractometer were as follows: a = 19.341(6); b = 6.950(2); c = 10.782(2) Å; β = 105.4°. With a volume V = 1396.8 Å^3 and four $Cs_2Hf(MoO_4)_3$ formula units in the unit cell, the density d_x = 4.41 g/cm^3 (the pycnometric density is 4.40 g/cm^3).

The systematic absences, revealed in the F_{hkl} array, satisfy two Fedorov groups: C_{2h}^6 = C2/c and C_s^4 = Cc. Taking account of the positive result from measurement of the piezoelectric effect, the final refinement of the structure and its description were performed in the acentric group Cc. Check refinement of the structure in the C2/c group led to R = 0.056, i.e., differing markedly from the acentric version (R = 0.049). However, a comparison of the atomic coordinates of the two aspects revealed that the Hf and Mo atoms practically comply with the centrosymmetric version, but the Cs and O atoms deviate significantly from it.

The structure of $Cs_2Hf(MoO_4)_3$ was solved by the heavy atom method. The coordinates of the cations (hafnium, cesium, and molybdenum) were determined from the three-dimensional Patterson function. The oxygen atoms were readily revealed from electron density difference and ordinary syntheses. Refinement of the structure by the

TABLE I. Coordinates of Basis Atoms, Standard Deviations, and Temperature Parameters in the $Cs_2Hf(MoO_4)_3$ Structure

Atom	x	y	z	B_{iso}	B_{11}	B_{22}	B_{33}	B_{12}	B_{23}	B_{31}
Hf	0	0.0007(3)	0	1.01	0.11	0.53	0.14	0	0	0.05
Mo(1)	−0.0019(2)	0.3865(2)	0.2505(4)	1.60	0.18	0.57	0.28	−0.07	−0.07	0.10
Mo(2)	−0.1321(1)	−0.0910(3)	0.1844(2)	2.45	0.17	1.31	0.44	−0.04	0	0.10
Mo(3)	0.1294(1)	−0.0922(2)	0.1390(2)	1.21	0.09	0.75	0.25	−0.04	−0.04	0.05
Cs(1)	0.3363(1)	0.0171(2)	0.4286(2)	2.66	0.19	1.59	0.62	0.09	−0.31	0.06
Cs(2)	0.1638(1)	0.5303(2)	0.0646(2)	2.48	0.18	1.54	0.46	0.11	−0.18	0.05
O(1)	−0.0726(8)	0.5383(20)	0.2317(13)	2.1	0.16	1.34	0.23	0.09	−0.14	0.04
O(2)	0.0751(12)	0.5203(31)	0.2820(20)	2.5	0.29	1.41	0.51	−0.09	0.08	0.15
O(3)	−0.0020(9)	0.2470(25)	0.1111(16)	2.1	0.21	1.18	0.42	0.03	−0.35	0.11
O(4)	0.0136(9)	0.2424(24)	0.3963(16)	2.5	0.19	1.27	0.59	0.15	0.41	0.14
O(5)	−0.0805(10)	−0.1405(26)	0.0625(16)	2.4	0.19	1.34	0.45	−0.02	0.08	0.11
O(6)	−0.1748(11)	0.1340(30)	0.1394(17)	2.2	0.15	1.42	1.03	0.05	0.29	0.11
O(7)	−0.2021(9)	−0.2452(22)	0.1589(15)	1.9	0.07	0.85	0.29	−0.03	0.14	−0.01
O(8)	−0.0785(8)	−0.1076(22)	0.3471(15)	2.1	0.18	1.75	0.34	−0.10	−0.29	0.01
O(9)	0.0840(11)	−0.1052(31)	0.1489(21)	2.4	0.15	1.64	0.47	0.04	0.31	0
O(10)	0.0764(9)	−0.1298(24)	0.4265(15)	1.9	0.16	0.92	0.44	0.03	−0.05	0.13
O(11)	0.2088(9)	−0.2408(25)	0.3572(16)	2.5	0.27	1.51	0.68	0.07	−0.05	0.11
O(12)	0.1569(11)	0.1325(29)	0.3383(19)	1.9	0.42	1.17	0.60	−0.01	−0.14	0.22

$T=[\exp-1/2(B_{11}h^2+B_{22}k^2+B_{33}l^2+2B_{12}hk+2B_{13}hl+2B_{23}kl)]$

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