SDPDRR-3

Sample 2 - $La_{18}W_{10}O_{57}$

Crystal Structure Determination

In a previous study [1] (from single crystal data though the structure determination was not completed because it was not possible to obtain good crystals), the commonest six-layered polytype was said to belong to the space group $P6_3/mmc$ (no piezoeffect detected) with cell parameters a = 9.04(1) Å and c = 32.60 – 33.65 Å depending on the composition of the crystal. This cell is confirmed here by a satisfying whole powder pattern fit (WPPF) by using the Le Bail method [2] through the Fullprof software [3]. The extracted intensities from the synchrotron powder pattern were then used for attempting the structure solution by direct space methods as embedded in the ESPOIR software [4], searching for the heavy W and La independent atoms by a Monte Carlo process. Nothing better than Rp > 35% could be obtained during various tests in the $P6_3/mmc$ or $P6_3mc$ space groups. Direct or Patterson methods failed as well to provide a satisfying starting model. Then the search for a solution was made in the c/6 subcell, in spite of the fact that very intense reflections had to be excluded (scaling the most intense 206 at I = 100, the 207 is at I = 13, the 217 is at I = 14), trying various space groups without extinction, a promising model leading to Rp = 22% on 220 remaining peaks was finally obtained from the ESPOIR software in the P-62m space group, corresponding to a La/W = 2 ratio (La_2WO_6 formula). No extension of that model in the large cell could be obtained in the $P6_3/mmc$ or $P6_3mc$ space groups. Then the other space groups compatible with the hh2-hl, l=2n reflection condition were examined (P-62c, P-31c, P31c). The small initial model could be extended in the large cell by using the acentric space groups, for instance with 4 La and 5 W independent atom sites in the general or special positions of P-62c. Using that estimation of the number of independent sites, ESPOIR provided new starting coordinates for the La and W atoms in the large cell, decreasing Rp to a satisfying 23%. Introducing these atomic coordinates into a Rietveld [5] refinement led then to R_B = 19.7 and R_F = 11.1 % when the thermal parameters were refined (most having negative values because of the absence of absorption correction at this stage). From a Fourier difference map, an additional W atom site was detected as well as all the oxygen atoms in ten independent sites. Further refinements suggested that this new W site had to be half occupied, leading to the $La_{18}W_{10}O_{57}$ formula with Z = 2. A part of the W atoms were found in octahedral coordination but the majority of them are in a unusual trigonal prismatic coordination. We then tried to confirm that by a new search for the oxygen atom position from the neutron data by using the ESPOIR software, fixing the La and W atoms to the positions obtained from the synchrotron data refinements. The same model was built up by ESPOIR from the neutron data. This unusual trigonal prismatic coordination was previously observed for the WO_6 group in the X-ray studies of $Pr_3WO_6Cl_3$ [6] and $La_3WO_6Cl_3$ [7], the latter structure being then confirmed from neutron powder diffraction data [8]. Indeed, the cell parameters of these halotungstates are similar to the c/6 subcell with a = 9.4048 and c = 5.4253 (S.G. $P6_3/m$), to be compared to a = 9.0443, c/6 = 5.4471 for the title compound. A

comparison of the La and W atom coordinates in both compounds is provided in Table 1. The W atom in $La_3WO_6Cl_3$ is at z = ¼ and ¾ whereas the corresponding W2 in the subcell of the title compound is exclusively at z =1/2 and there is an additional W1 at 0,0,0. This explains why early attempts to solve the $La_{18}W_{10}O_{57}$ structure by building a model from the $La_3WO_6Cl_3$ structure failed.

Tests in order to see if reducing the symmetry would allow the half occupied W site to become fully ordered were made in P31c and in various subgroups of P-62c and P31c (Ama2, Cc) with no convincing result : the number of atomic coordinates to be refined becomes prohibitive. From the low-resolution powder pattern, it was hardly possible to refine all thermal parameters independently. The details of the Rietveld refinements, the atomic coordinates and the interatomic distances and angles are gathered respectively in Tables 2, 3 and 4. The W4 atom which has half of the times W6 as a neighbour is the only tungsten atom presenting a high thermal parameter (from the synchrotron data refinement). It is clear that according to the presence of W6 or not, then the W4 position will be modified along z. Accordingly, the very short W4-W6 interactomic distance (2.42 Å) should be considered cautiously. These two WO_6 octahedra sharing a face are also a very unusual feature of the title compound. See the Rietveld plots below, and the drawings of the projections along [001] and [110] of the crystal structures of $La_{18}W_{10}O_{57}$ and $La_3WO_6Cl_3$.

The neutron data fit is under the expected quality with Rp = 12.9 %. This is due to inhomogeneities in the sample which could not be prepared in large quantity without some composition variation. In spite of this problem, the atomic coordinates from the synchrotron and neutron fits compare well. Anyway, the current description of that structure, having resisted up to now to characterization attempts, is the best we can do with these data and samples.

References

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Table 1
Initial model for $La_{18}W_{10}O_{57}$ in the c/6 subcell in the P-62m space Group, compared to the W and La positions in the $La_3WO_6Cl_3$ structure described in the $P6_3/m$ space group.

Atom	Wyckoff Position	x	y	z
c/6 subcell of $La_{18}W_{10}O_{57}$				
W1	1a	0	0	0
W2	2d	1/3	2/3	1/2
La1	3f	0.429	0	0
La2	3g	0.743	0	1/2
$La_3WO_6Cl_3$				
W	2c	1/3	2/3	1/4
La	6h	0.0906	0.6865	3/4

Table 2
Rietveld refinements with the Fullprof program

			Synchrotron	Neutron
Wavelength (Å)			0.60044	1.5944
Absorption correction			muR-eff = 4.95	none
Space group			P-62c (No 190)	
Cell parameters	a(Å)		9.04428(4)	9.0518(2)
	c(Å)		32.6829(1)	32.708(1)
Volume			2315.26(2)	2320.9(1)
No of fitted parameters			89	70
No of background parameters			25	14
No of reflections			1086	943
Zeropoint (°)			0.0012(2)	0.168(3)
Eta (Pseudo-Voigt)			0.574(12)	0.53(2)
Halfwidth parameters		U	0.00241(6)	0.102(6)
		V	0	-.26(1)
		W	0.000150(1)	0.299(8)
Average FWHM			0.0193	0.441
Asymmetry parameters			0.035(3)	0.089(9)
			0.0080(3)	0.026(4)
X parameters			0.0011(6)	0
Reliability factors for points with Bragg contribution				
N-P+C			13417	2749
R-factors (not corrected for background)				
	Rp		7.03	5.91
	Rwp		9.44	7.71
	Rexp		9.52	1.41
	Chi2		0.983	29.8
Conventional Rietveld R-factors				
	Rp		17.9	12.9
	Rwp		17.6	15.1
	Rexp		17.8	2.76
	Chi2		0.983	29.8
Bragg R-factors				
	RB		5.91	6.45
	RF		4.93	3.87

Table 3.
Atomic coordinates in the P-62c space group from X-ray synchrotron and neutron data.

Atom	Wyckoff position		x	y	z	B
La1	12i	X	0.6151(3)	0.0401(3)	0.58377(8)	1.40(4)
		N	0.6174(10)	0.0416(9)	0.5826(2)	0.88(6)
La2	12i	X	0.2776(2)	0.0367(2)	0.33203(7)	0.82(3)
		N	0.2747(9)	0.0308(8)	0.3305(3)	0.88(6)
La3	6h	X	0.3704(4)	0.4291(5)	1/4	1.07(5)
		N	0.3728(15)	0.4276(16)	1/4	0.88(6)
La4	6g	X	0.2567(4)	0	0	1.19(6)
		N	0.2570(14)	0	0	0.88(6)
W1	4e	X	0	0	0.58496(8)	0.91(4)
		N	0	0	0.5873(8)	0.76(12)
W2	4f	X	1/3	2/3	0.33313(7)	0.87(3)
		N	1/3	2/3	0.3335(9)	0.76(12)
W3	4f	X	1/3	2/3	0.00314(5)	0.82(4)
		N	1/3	2/3	0.0032(6)	0.76(12)
W4	4f	X	1/3	2/3	0.63634(8)	2.50(5)
		N	1/3	2/3	0.6384(6)	0.76(12)
W5	2b	X	0	0	1/4	0.73(6)
		N	0	0	1/4	0.76(12)
W6*	4f	X	1/3	2/3	0.7186(1)	0.92(7)
		N	1/3	2/3	0.7123(14)	0.76(12)
O1	12i	X	0.8309(33)	0.9826(33)	0.2130(7)	0.97(10)
		N	0.8334(17)	0.9872(15)	0.2137(3)	1.02(4)
O2	12i	X	0.9759(33)	0.8256(31)	0.6204(8)	0.97(10)
		N	0.9763(17)	0.8256(19)	0.6212(3)	1.02(4)
O3	12i	X	0.6869(38)	0.5043(32)	0.7069(6)	0.97(10)
		N	0.6975(16)	0.5126(16)	0.7047(3)	1.02(4)
O4	12i	X	0.5216(28)	0.7090(30)	0.0445(6)	0.97(10)
		N	0.5147(15)	0.7051(17)	0.0454(3)	1.02(4)
O5	12i	X	0.6834(32)	0.4980(27)	0.6314(6)	0.97(10)
		N	0.6751(13)	0.5010(13)	0.6298(3)	1.02(4)
O6	12i	X	0.1509(32)	0.1829(31)	0.5456(7)	0.97(10)
		N	0.1578(15)	0.1811(17)	0.5444(3)	1.02(4)
O7	12i	X	0.4758(29)	0.1799(29)	0.3932(6)	0.97(10)
		N	0.4718(15)	0.1848(14)	0.3908(3)	1.02(4)
O8	12i	X	0.1392(24)	0.6003(26)	0.9718(6)	0.97(10)
		N	0.1425(14)	0.5995(12)	0.9777(3)	1.02(4)
O9	12i	X	0.5176(23)	0.3720(26)	0.3246(6)	0.97(10)
		N	0.5137(13)	0.3672(13)	0.3241(3)	1.02(4)
O10	6h	X	0.4628(38)	0.1699(39)	1/4	0.97(10)
		N	0.4678(20)	0.1767(20)	1/4	1.02(4)

* half occupied site

Table 4
Selected interatomic distances (La-O < 3.2 A) and angles (from neutron data)

La1-O4	2.403(13)	La2-O3	2.386(18)	La3-O1 x2	2.498(14)	La4-O6 x2	2.367(13)
-O5	2.501(16)	-O1	2.479(18)	-O3 x2	2.51(2)	-O4 x2	2.426(16)
-O6	2.511(18)	-O5	2.485(17)	-O3 x2	2.583(15)	-O6 x2	2.660(13)
-O4	2.517(19)	-O7	2.555(13)	-O10	2.70(2)	-O8 x2	2.794(16)
-O8	2.521(11)	-O1	2.558(13)	-O10	2.80(3)		
-O2	2.523(19)	-O2	2.574(15)	-O9 x2	2.915(15)		
-O5	2.772(12)	-O2	2.63(2)				
-O7	2.788(12)	-O9	2.722(11)				
-O7	2.803(15)	-O9	2.873(14)				
		-O10	3.071(11)				

Trigonal prisms

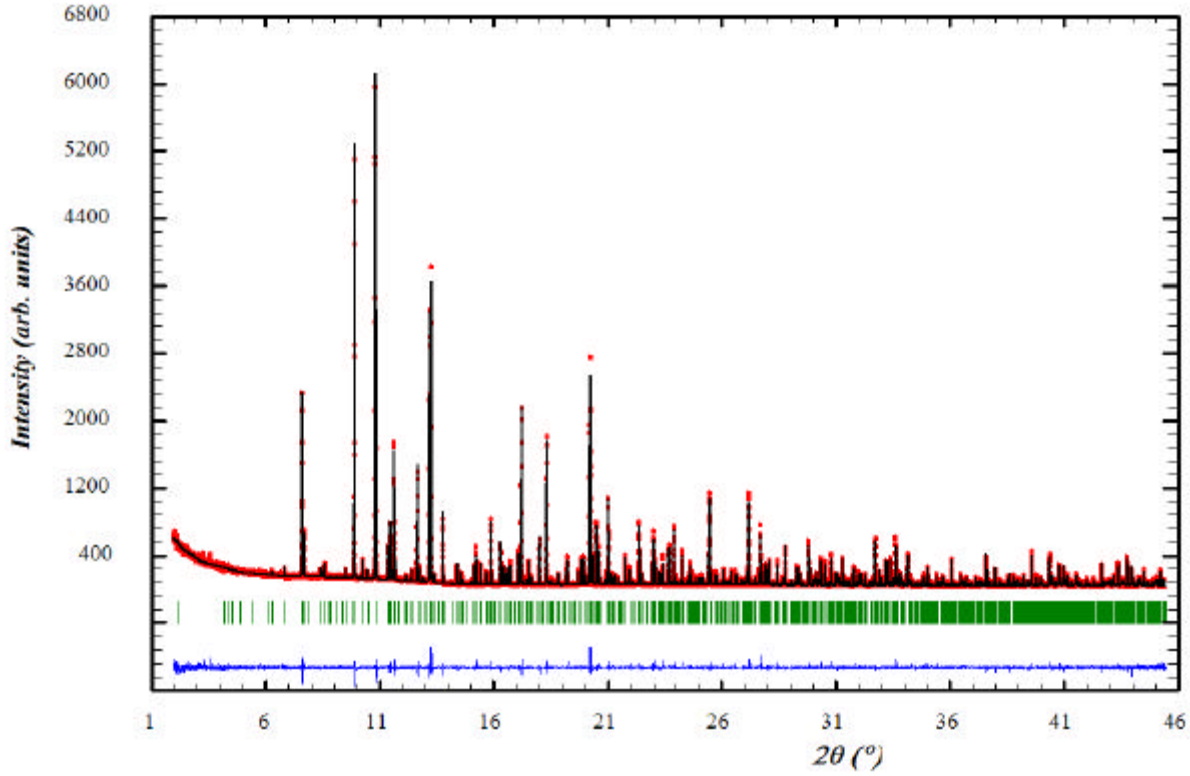
W1-O2 x3	1.85(2)	O2-W1-O2	87.8(13)	O2-W1-O6	144.5(14)	O2-W1-O6	124.5(15)
W1-O6 x3	2.09(2)	O6-W1-O1	79.7(10)	O2-W1-O6	80.1(11)		
W2-O5 x3	1.91(1)	O3-W2-O3	83.5(11)	O3-W2-O5	139.4(12)	O3-W2-O5	129.7(14)
W2-O3 x3	1.95(2)	O5-W2-O5	84.6(11)	O3-W2-O5	79.0(11)		
W5-O1 x6	1.877(10)	O1-W5-O1	84.2(12)	O1-W5-O1	78.5(8)	O1-W5-O1	134.4(11)

Octahedra

W3-O8 x3	1.732(13)	O4-W3-O4	79.1(12)	O4-W3-O8	85.6(10)	O4-W3-O8	95.3(11)
W3-O4 x3	2.037(17)	O8-W3-O8	98.7(13)	O4-W3-O8	164.5(13)		
W4-O7 x3	1.860(14)	O7-W4-O7	96.0(11)	O7-W4-O9	86.9(9)	O7-W4-O9	90.8(10)
W4-O9 x3	1.985(15)	O9-W4-O9	85.8(11)	O7-W4-O9	172.2(10)		
W6-O9 x3	1.96(3)	O9-W6-O9	86.9(15)	O9-W6-O10	91.7(13)	O9-W6-O10	93.7(13)
W6-O10 x3	2.05(3)	O10-W6-O10	87.7(16)	O9-W6-O10	178.4(18)		

W-W short distances

W6-W4	2.42(5)	W6-W6	2.46(6)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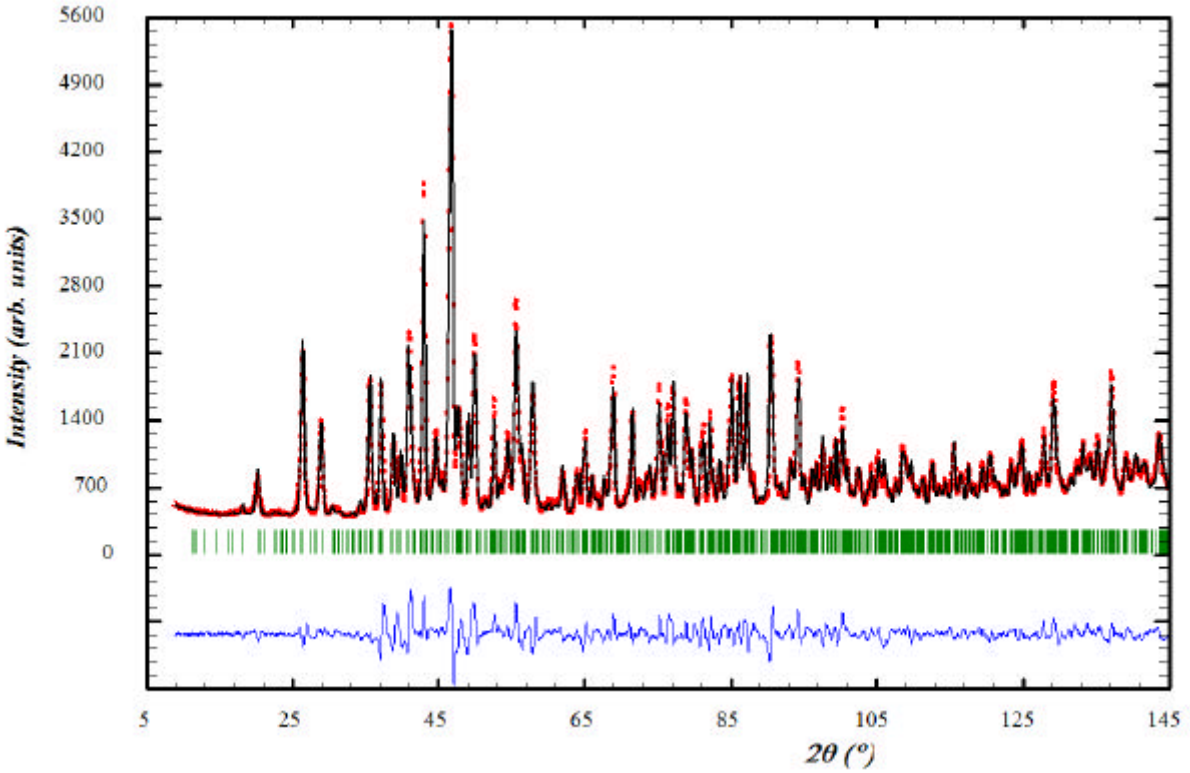
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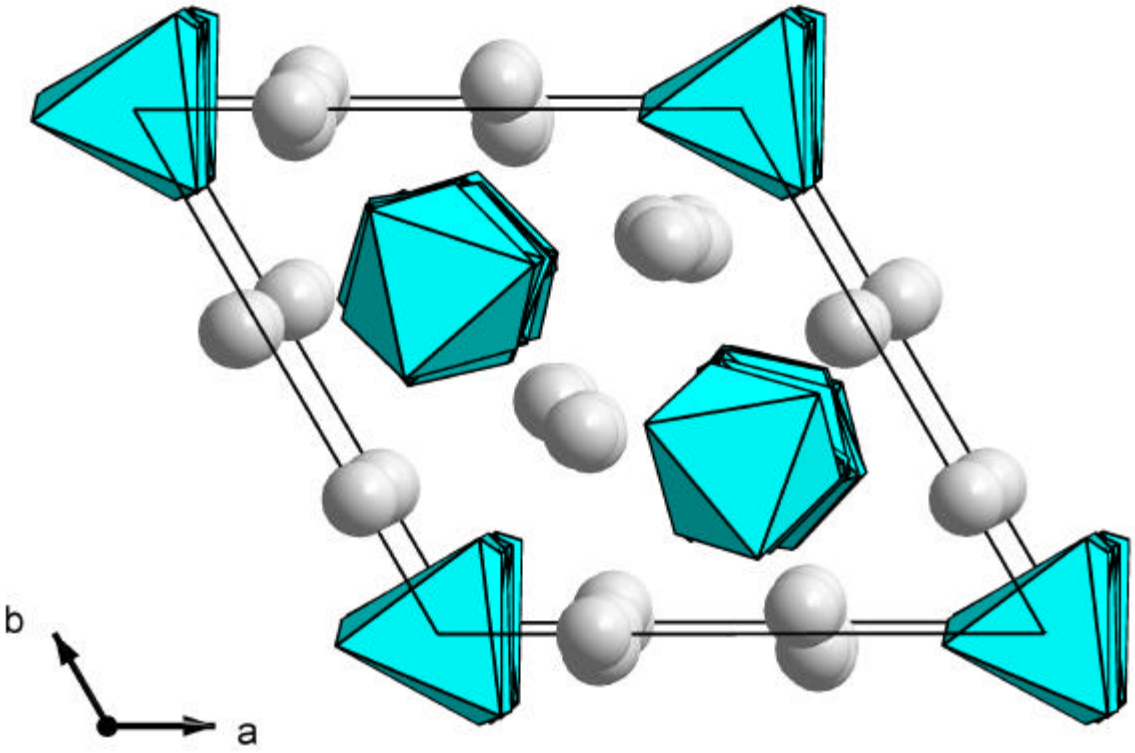
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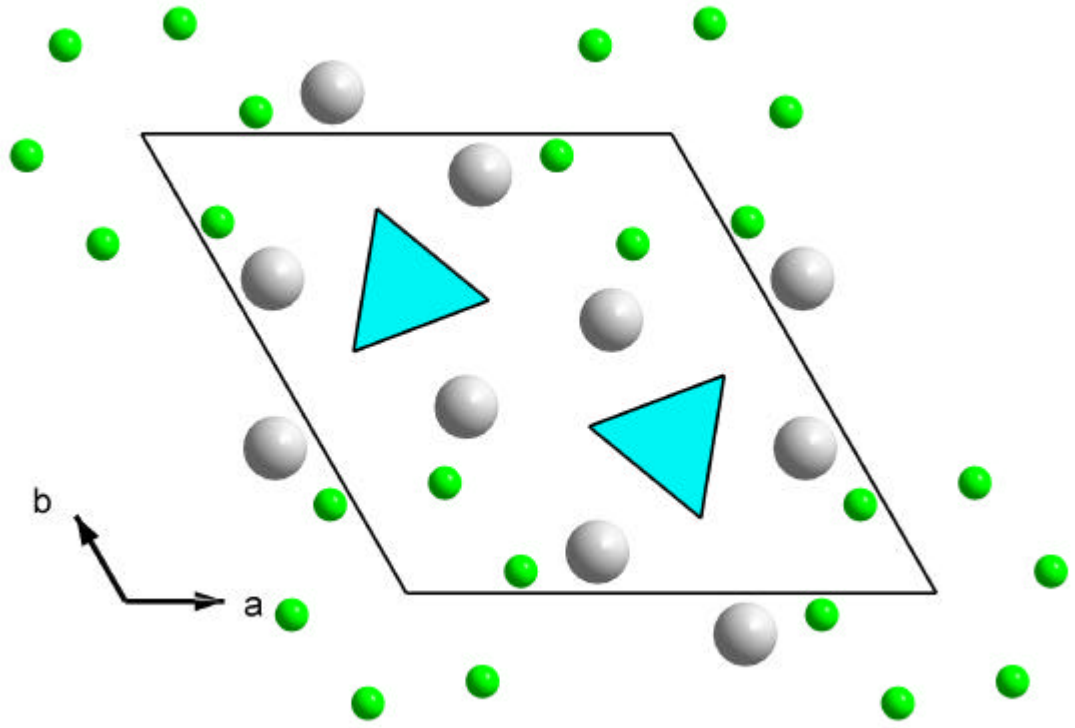
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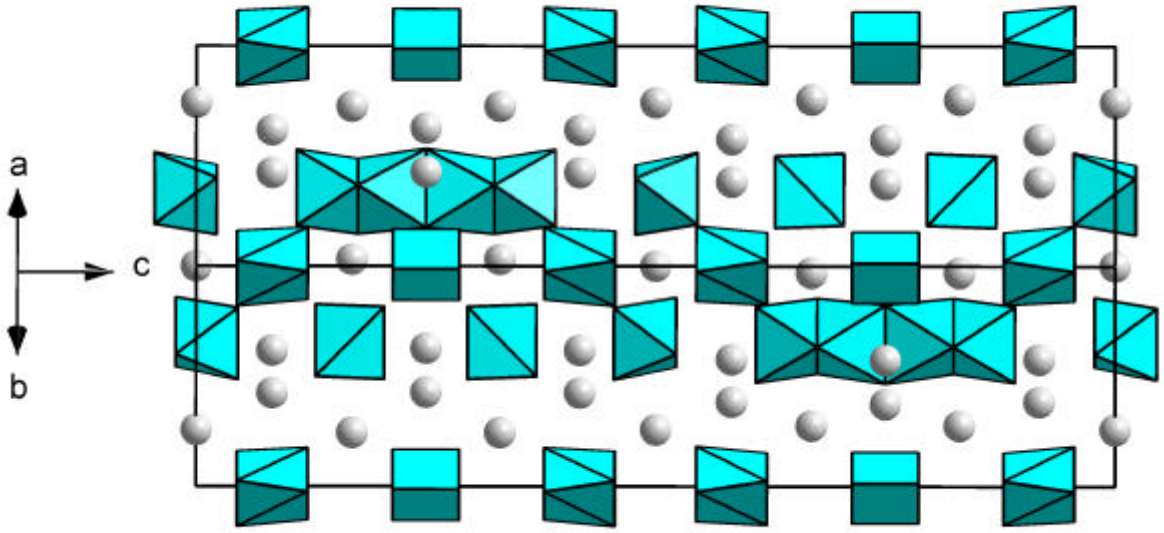
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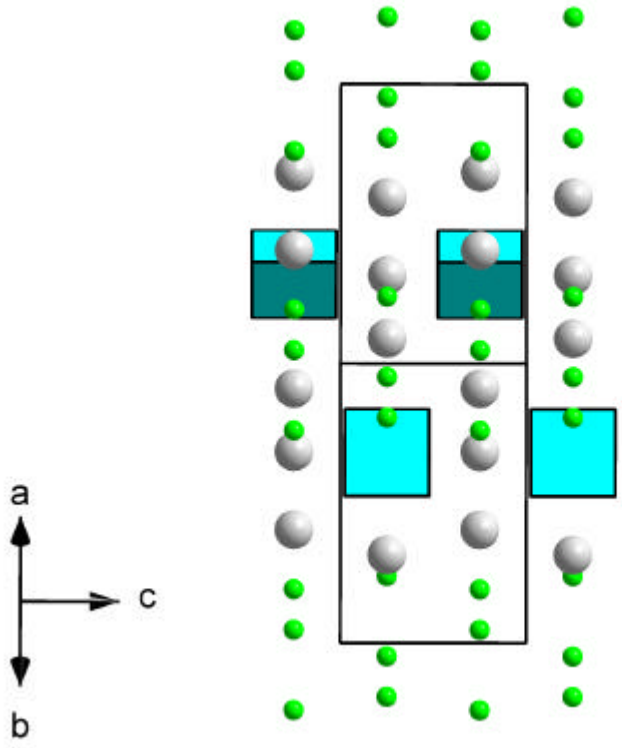
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