

## Structural investigation of (130) twins and rutile precipitates in chrysoberyl crystals from Rio das Pratinhas in Bahia (Brazil)

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(Supplementary information)

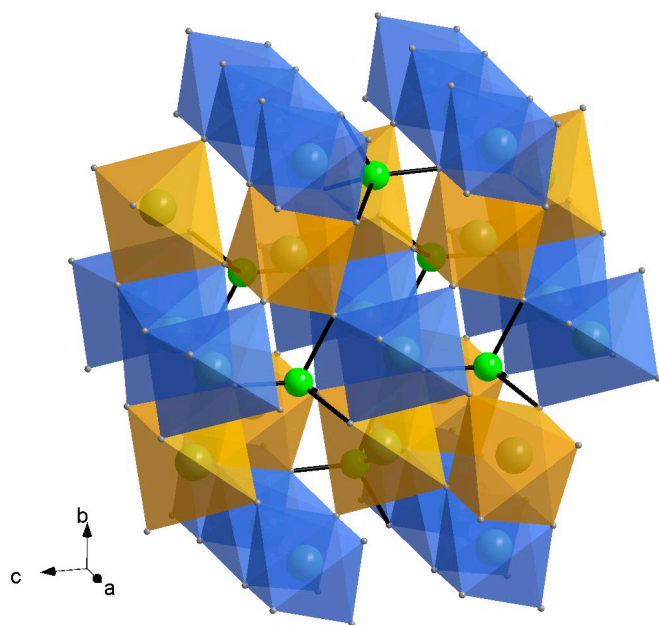
### Crystal structure of chrysoberyl from Rio das Pratinhas

For the purpose of atomic-scale determination of the twin boundary structure and structural characterization of rutile precipitates the structure of chrysoberyl was refined in the Pmnb(62) space group, as explained in the Crystallography section of the article, using previously reported crystallographic data (Hazen 1987). In the orthorhombic space group No.62 there are six possible subgroups: (i) Pbnm, (ii) Pcmn, (iii) Pmcn, (iv) Pmnb, (v) Pnam, and (vi) Pnma. Out of these, only (i) and (vi) were used to describe the chrysoberyl structure (see Table I).

**Table I:** Crystallographic data for chrysoberyl crystallizing in the olivine-type structure (s.g. No. 62) with space subgroup symbols, unit cell parameters, and reference.

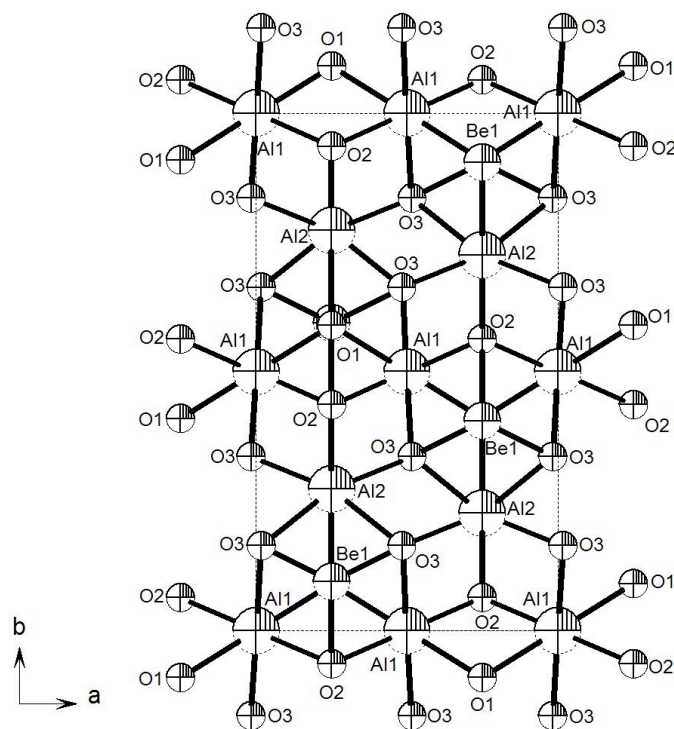
s.g.	a [Å]	b [Å]	c [Å]	Reference
Pbnm	4.42	9.39	5.47	Bragg & Brown (1926)
Pnma	9.404	5.476	4.427	Farrell <i>et al.</i> (1963)
Pbnm	4.428(1)	9.415(3)	5.481(2)	Hazen (1987)
Pbnm	4.424(1)	9.396(1)	5.471(2)	Hazen & Finger (1987)
Pnma	9.4082(2)	5.4790(2)	4.4288(1)	Weber <i>et al.</i> (2007)
Pnma	9.4203(9)	5.4871(5)	4.4331(4)	Lottermoser <i>et al.</i> (2011)

Chrysoberyl crystallizes in the olivine-type structure where Mg and Si atoms are replaced by Al and Be cations, respectively (Bragg and Brown 1926) in hexagonal close-packed (*hcp*) O-sublattice. In this sublattice aluminium atoms occupy two different octahedral sites Al(1) and Al(2), whereas Be atoms reside in tetrahedral interstices interconnecting the Al-octahedra (Figure S1). Al(1) occupies special positions on the inversion centers and the two-fold screw axes ( $\bar{1}$ ), whereas Al(2) lie on the mirror planes (*m*). Less pronounced deviations in the interatomic Al(1)-O distances, 1.876(2)-1.930(3) Å, compared to the Al(2)-O distances, ranging from 1.868(5)-1.961(4) Å, indicate that Al(2)-centered octahedra possess a higher degree of geometric distortion than the Al(1)-octahedra. The Al(2)-sites are accommodating a small amount of Fe-atoms (Fe/Al atomic ratio of 0.01), which contributes to the more pronounced distortion. These two types of Al-octahedra are arranged in the following manner: (i) Al(1)O<sub>6</sub> form straight chains of edge-sharing octahedra running along the *a*-axis, whereas (ii) *cis* corner-shared Al(2)O<sub>6</sub> type of octahedra form zig-zag chains along the *c*-direction. The arrangement of Al-octahedra is illustrated in supplemental Figure S1. Bridging O atoms, which interconnect Al(2) atoms is of  $\mu^4$ -type coordinated also with one Al(1) and one Be(1) atom, respectively.

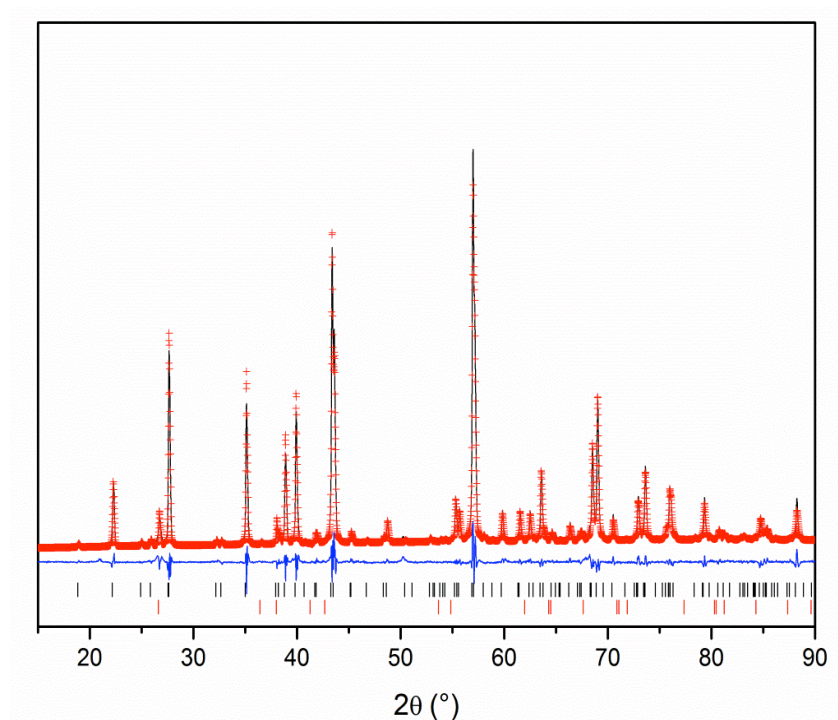


**Figure S1.** Arrangement of two types of Al-octahedra in the chrysoberyl structure (Pnmb) where first type (Wickoff position 4a) forms chains of edge-sharing Al(1)O<sub>6</sub> octahedra along the *a*-axis (blue) and the second type (Wickoff position 4c) forms zig-zag chains of edge sharing Al(2)O<sub>6</sub> octahedra with a larger geometric distortion lined along the *c*-axis (brown). Be-atoms (green) occupy tetrahedral sites (Wickoff position 4c) connecting the octahedra.

Beryllium atoms occupy distorted tetrahedral coordination geometry located on mirror planes with Be-O distances ranging between 1.500(9) and 1.704(9) Å forming O-Be-O angles between 96.18(9)° and 120.54(8)°. Such arrangement of Al- and Be-based polyhedra produces distortions of the *hcp* O-sublattice, as shown in an ORTEP-type schematic of the chrysoberyl structure, Figure S2.



**Figure S2.** ORTEP-type scheme of the chrysoberyl structure projected along the *c*-axis with atom numbering.



**Figure S3.** Final Rietveld plot of chrysoberyl sample with rutile inclusions from Rio das Pratinhas. Observed plot – black line; calculated plot – red crosses; difference plot – blue line; calculated reflection positions for chrysoberyl – black tick marks; calculated reflection positions for rutile – red tick marks.

The final Rietveld plot of chrysoberyl sample (supplemental Figure S3) corresponds to satisfactory model indicators and figures of merit. Al(2) sites were identified to accommodate a small fraction of Fe-atoms. After refining the chrysoberyl structure, rutile precipitates, based on HRTEM information were also included in final refinement (see Table II). Refined atomic positions, bond lengths and principal angles are given in Tables III to V.

**Table II.** Crystal data and structure refinement details for chrysoberyl sample with rutile inclusions including 54 structural parameters, GoF = 2.34, Rwp = 0.078, Rp = 0.058 and RBragg = 0.0252.

	chrysoberyl	rutile
formula	(Al <sub>1.99</sub> Fe <sub>0.01</sub> )BeO <sub>4</sub>	TiO <sub>2</sub>
temperature	RT	RT
wavelength [Å]	1.5406	1.5406
symmetry	orthorhombic	tetragonal
space group	Pmnb (No. 62)	P4 <sub>2</sub> /mnm (No. 136)
a [Å]	5.4825(1)	4.7331(4)
b [Å]	9.4163(2)	4.7331(4)
c [Å]	4.4308(1)	2.880(2)
V [Å <sup>3</sup> ]	228.74(1)	64.52(2)
Z, calc. density [g/cm <sup>3</sup> ]	4, 3.695	2, 4.102
2θ range [°]	15 to 90.0	15 to 90.0
number of reflections	100	21
phase composition [%]	98.0(9)	2.0(9)

**Table III.** Wickoff positions, Fractional coordinates, and isotropic displacement parameters for different atom types determined for chrysoberyl from Rio das Pratinhas. Special positions were not refined.

Atom	Wickoff	x	y	z	occ.	Beq [ $\text{\AA}^2$ ]
Al(1)	4a	0	0	0	1	1.43(5)
Al(2)	4c	0.25	0.2735(2)	0.9960(7)	0.99	1.21(5)
Fe(2)	4c	0.25	0.2735(2)	0.9960(7)	0.01	1.21(5)
Be(1)	4c	0.25	0.0950(8)	0.446(2)	1	2.3(2)
O(1)	4c	0.25	0.0906(4)	0.7844(7)	1	1.1(1)
O(2)	4c	0.25	0.4360(5)	0.2377(6)	1	0.8(1)
O(3)	8d	0.0168(6)	0.1640(3)	0.2604(5)	1	0.7(1)

Symmetry codes: (i)  $x, y, z$ ; (ii)  $-x+1/2, y+1/2, -z+1/2$ ; (iii)  $x+1/2, -y, -z$ ; (iv)  $-x, -y+1/2, z+1/2$ ; (v)  $-x, -y, -z$ ; (vi)  $x+1/2, -y+1/2, z+1/2$ ; (vii)  $-x+1/2, y, z$ ; (viii)  $x, y+1/2, -z+1/2$ .

**Table IV.** Interatomic distances for chrysoberyl [ $\text{\AA}$ ].

Al1 <sup>i</sup> —O1 <sup>i</sup>	1.876 (2)
Al1 <sup>ii</sup> —O2 <sup>ii</sup>	1.895 (2)
Al1—O3	1.930 (3)
Al2—O1	1.961 (4)
Al2—O2	1.868 (5)
Al2 <sup>ii</sup> —O3 <sup>ii</sup>	1.891 (4)
Be1—O1	1.500 (9)
Be1 <sup>iii</sup> —O2 <sup>iii</sup>	1.704 (9)
Be1—O3	1.653 (6)

Symmetry codes: (i)  $x+1/2, -y, -z$ ; (ii)  $-x, -y+1/2, z+1/2$ ; (iii)  $-x+1/2, y+1/2, -z+1/2$ ; (iv)  $-x, -y, -z$ ; (v)  $-x+1/2, y, z$ .

**Table V.** Selected principal angles [ $^\circ$ ].

O1—Al1 <sup>iii</sup> —O2 <sup>iii</sup>	85.90 (1)
O1—Al1—O3	95.41 (8)
O2 <sup>iii</sup> —Al1 <sup>iii</sup> —O3 <sup>iv</sup>	98.44 (8)
O1—Al2—O2	173.6 (2)
O1 <sup>ii</sup> —Al2 <sup>ii</sup> —O3	90.54 (8)
O2—Al2—O3 <sup>ii</sup>	93.53 (8)
O1—Be1—O2 <sup>iii</sup>	116.9 (5)
O1—Be1—O3 <sup>v</sup>	120.54 (8)
O2 <sup>v</sup> —Be1 <sup>v</sup> —O3 <sup>iii</sup>	96.18 (9)

Symmetry codes: (i)  $x+1/2, -y, -z$ ; (ii)  $-x, -y+1/2, z+1/2$ ; (iii)  $-x+1/2, y+1/2, -z+1/2$ ; (iv)  $-x, -y, -z$ ; (v)  $-x+1/2, y, z$ .