

substance: titanium oxide (TiO₂)

property: crystal structure, lattice parameters and related parameters of brookite

crystal structure: orthorhombic, space group $D_{2h}^{15} - Pbca$, $Z = 2$ [79M1]. The bridging oxygens again have shorter O – O bonds (Fig. 1). Antiferroelectric displacements of the Ti⁴⁺ ions parallel to the *b*-axis (opposite to the arrows in the figure) produce three shorter Ti – Ti bonds. At RT, the Ti – Ti distances in zig-zag chains parallel to the *c*-axis (3.062(2) Å) are greater than the Ti – Ti distance (2.951(2) Å) across the third shared edge [79M2] of shared octahedral-site edges but the octahedral volume also decreases (Fig. 2).

lattice parameters

<i>a</i>	9.174(2) Å	<i>T</i> = 25 °C	79M1
<i>b</i>	5.449(2) Å		
<i>c</i>	5.138(2) Å		
<i>a</i>	9.175(4) Å	<i>T</i> = 280 °C	
<i>b</i>	5.459(4) Å		
<i>c</i>	5.149(2) Å		
<i>a</i>	9.191(4) Å	<i>T</i> = 425 °C	
<i>b</i>	5.463 (4) Å		
<i>c</i>	5.157(4) Å		
<i>a</i>	9.211(4) Å	<i>T</i> = 625 °C	
<i>b</i>	5.472(4) Å		
<i>c</i>	5.171(4) Å		

density

<i>d</i> _{calc}	4.133 g cm ⁻³	<i>T</i> = 250 °C	79M1
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interatomic distances and angles

(distances in Å, angles in °) (from [79M1]); * angles opposite shared edges, ** shared edges

	<i>T</i> = 25°C	<i>T</i> = 280°C	<i>T</i> = 425°C	<i>T</i> = 625°C
<i>d</i> (Ti–O _{Ia})	1.990(3)	1.989(3)	1.985(3)	1.991(5)
<i>d</i> (Ti–O _{Ib})	1.863(3)	1.870(4)	1.877(4)	1.881(5)
<i>d</i> (Ti–O _{Ic})	1.999(3)	2.000(3)	2.003(3)	2.005(5)
<i>d</i> (Ti–O _{IIa})	2.052(3)	2.043(3)	2.045(3)	2.050(5)
<i>d</i> (Ti–O _{IIb})	1.930(3)	1.938(3)	1.944(4)	1.945(5)
<i>d</i> (Ti–O _{IIc})	1.923(3)	1.928(3)	1.930(3)	1.937(4)
<i>d</i> (Ti–O) _{av}	1.960	1.961	1.964	1.968
<i>d</i> (O _{Ia} –O _{IIa})	2.734(4)	2.733(5)	2.736(5)	2.752(7)
<i>d</i> (O _{IIa} –O _{Ic})**	2.534(5)	2.533(5)	2.536(5)	2.548(7)
<i>d</i> (O _{Ic} –O _{IIb})	2.869(5)	2.874(5)	2.876(5)	2.872(7)
<i>d</i> (O _{IIb} –O _{Ib})	2.799(5)	2.800(5)	2.809(5)	2.806(7)
<i>d</i> (O _{Ib} –O _{IIc})	2.993(4)	3.000(5)	3.003(5)	3.016(7)
<i>d</i> (O _{IIc} –O _{IIb})	2.746(4)	2.751(2)	2.753(2)	2.756(2)
<i>d</i> (O _{Ib} –O _{IIc})	2.860(3)	2.870 (3)	2.873(3)	2.879(4)
<i>d</i> (O _{IIc} –O _{IIa})	2.982(3)	2.984(3)	2.989(4)	2.996(5)
<i>d</i> (O _{Ia} –O _{Ic})	2.794(2)	2.801(3)	2.805(3)	2.814(4)
<i>d</i> (O _{Ic} –O _{Ib})**	2.495(6)	2.496(6)	2.505(6)	2.509(8)
<i>d</i> (O _{Ib} –O _{Ia})	2.814(2)	2.820(2)	2.821(2)	2.827(3)
<i>d</i> (O _{Ia} –O _{IIc})**	2.534(5)	2.533(5)	2.536(5)	2.548(7)
<i>d</i> (O–O) _{av}	2.763	2.566	2.770	2.777
<i>d</i> (Ti–Ti)	2.951(2)	2.960(2)	2.965(2)	2.976(3)
<i>d</i> (Ti–Ti)	3.062(2)	3.060(2)	3.060(2)	3.063(2)

angles:

(O _{Ia} –Ti–O _{IIa})	85.14(13)	85.36(14)	85.50(14)	85.87(19)
(O _{IIa} –Ti–O _{Ic})*	77.43(12)	77.57(13)	77.58(13)	77.88(18)

(O _{Ic} -Ti-O _{Ib})	93.76(13)	93.71(14)	93.52(14)	93.27(20)
(O _{Iib} -Ti-O _{Ib})	95.07(13)	94.60(15)	94.61(15)	94.30(21)
(O _{Ib} -Ti-O _{Iic})	104.49(13)	104.33(14)	104.14(14)	104.33(20)
(O _{Iic} -Ti-O _{Iia})*	80.70(12)	80.56(13)	80.72(14)	80.87(19)
(O _{Iia} -Ti-O _{Iib})	87.13(8)	87.37(9)	87.26(9)	87.19(12)
(O _{Iib} -Ti-O _{Iic})	95.85(7)	95.85(8)	95.72(9)	95.71(12)
(O _{Iic} -Ti-O _{Iia})	97.20(13)	97.38(14)	97.50(14)	97.38(20)
(O _{Ia} -Ti-O _{Ic})	88.94(12)	89.21(14)	89.39(15)	89.54(20)
(O _{Ic} -Ti-O _{Ib})*	80.41(13)	80.29(13)	80.38(13)	80.08(18)
(O _{Ib} -Ti-O _{Ia})	93.78(5)	93.78(7)	93.82(7)	93.77(8)
(Ti-O _{Ib} -Ti)	99.59(13)	99.71(13)	99.62(13)	99.92(18)
(Ti-O _{Ic} -Ti)	100.26(16)	100.21(16)	100.20(17)	100.08(23)
(Ti-O _{Ia} -Ti)	159.20(16)	159.07(17)	159.17(17)	158.97(23)
(Ti-O _{Iia} -Ti)	123.92(15)	124.16(15)	124.11(15)	124.10(21)
(Ti-O _{Iib} -Ti)	134.80(16)	134.50(16)	134.67(17)	134.83(23)
(Ti-O _{Iic} -Ti)	100.72(14)	100.76(15)	100.63(16)	100.35(22)

References:

- 79M1 Meagher, E. P., Lager, G. A.: Can. Mineral. 17 (1979) 77.
- 79M2 Mitsuhashi, T., Kleppa, O. J.: J. Am. Ceram. Soc. 62 (1979) 356.

Fig. 1.

TiO₂, brookite. Crystal structure. Shared edges are labelled Sh [79M1].

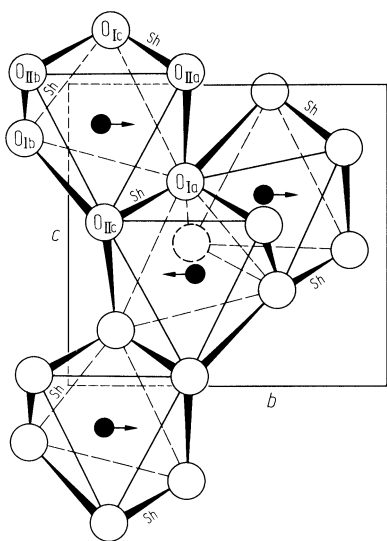


Fig. 2.

TiO₂. Octahedral volumes in the three polymorphs vs. temperature [79M1].

