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Structural control of polyhedral compression in synthetic braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{O}_8\text{SiO}_4$

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Abstract The compression of synthetic braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{O}_8\text{SiO}_4$, was studied by high-pressure single-crystal X-ray diffraction carried out in a diamond-anvil cell. The equation of state at room temperature (third-order Birch-Murnaghan equation of state: $V_0=1661.15(8) \text{ \AA}^3$, $K_{0.298}=180.7\pm 0.9 \text{ GPa}$, $K'=6.5\pm 0.3$) was determined from unit-cell volume data to 9.18 GPa. Crystal structures were determined at 6 different pressures to 7.69 GPa. Compression of the structure (space group $I4_1/acd$) was found to be slightly anisotropic ($a_0=9.4262(4) \text{ \AA}$, $K_a=499\pm 4 \text{ GPa}$, $K_a'=19.7\pm 0.9$; $c_0=18.6964(6) \text{ \AA}$, $K_c=657\pm 6 \text{ GPa}$, $K_c'=15.7\pm 1.4$) which can be attributed to the fact that the Mn^{3+} -O bonds, which are the most compressible bonds, are aligned closer to the (001) plane than to the c axis. The large bulk modulus is the result of the structural topology in which 2/3 and 1/2 of the edges of the Mn^{2+}O_8 and Mn^{3+}O_6 polyhedra share edges with other polyhedra. The Mn^{2+}O_8 polyhedra were found to compress isotropically, whereas anisotropic compressional behaviour was observed for all three Mn^{3+}O_6 octahedra. Although the polyhedral geometry of all three crystallographically independent Mn^{3+} sites shows the same type of uniaxially elongated distortion, the compression of the individual octahedral configurations was found to be strongly dependent upon both the geometry of the polyhedron itself and the types of, and the connectivity to, the neighbouring polyhedra. The differences in the configuration of the different oxygen atoms, and therefore the structural topology, is one of the major factors determining the type and degree of the pressure-induced distortion, while the Jahn-Teller effect plays a subordinate role.

Introduction

The dominant mechanism of compression in complex structures is usually one of polyhedral rotation and accompanying changes in interpolyhedral bond angles, with compression of the polyhedra usually playing only a secondary role. However, the bonding geometry is a major influence in determining the pressure-induced changes of the material's physical properties. Hazen and Finger (1978) suggested that bond-length distortion generally decreases with pressure as the anions tend to approximate close packing with pressure, and the tendency to achieve a more regular packing is even valid for open framework structures (e.g. Sowa 1988). Later Hazen and Finger (1982) revised their statement about the polyhedral distortion as they found examples (showing particular patterns of polyhedral connectivity) that revealed opposite trends of polyhedral bond-length distortion with pressure (Hazen and Finger 1982, and references therein). A considerable diversity in compressional behaviour can be expected for polyhedral coordinations which are distorted due to the Jahn-Teller (JT) effect (Jahn and Teller 1937) which is associated with the degeneracy of electronic ground states of d^9 and *high-spin* d^4 transition metal cations in holosymmetric (mostly octahedral) ligand fields. The influence of pressure on the type and degree of the JT distortion has not previously been investigated systematically.

We chose synthetic braunite, $\text{Mn}^{2+}\text{Mn}^{3+}_6\text{O}_8\text{SiO}_4$, in order to study the pressure dependence of the polyhedral geometries of the JT distorted Mn^{3+}O_6 octahedra because: (1) three crystallographically independent Mn^{3+} sites allow the influence of the topology on the polyhedral compression to be studied; (2) the common edge sharing by polyhedra should mean that intra-polyhedral changes dominate the compression mechanisms; (3) natural occurrences in high-grade metamorphic mineral associations (see Dasgupta and Manickavasagam 1981; Dasgupta et al. 1990) and experimental studies of the phase relations in the system Mn-Si-O (Abs-Wurmbach 1980; Abs-Wurmbach et al. 1983) indicate the stability of braunite over a wide range of P , T , and f_{O_2} .

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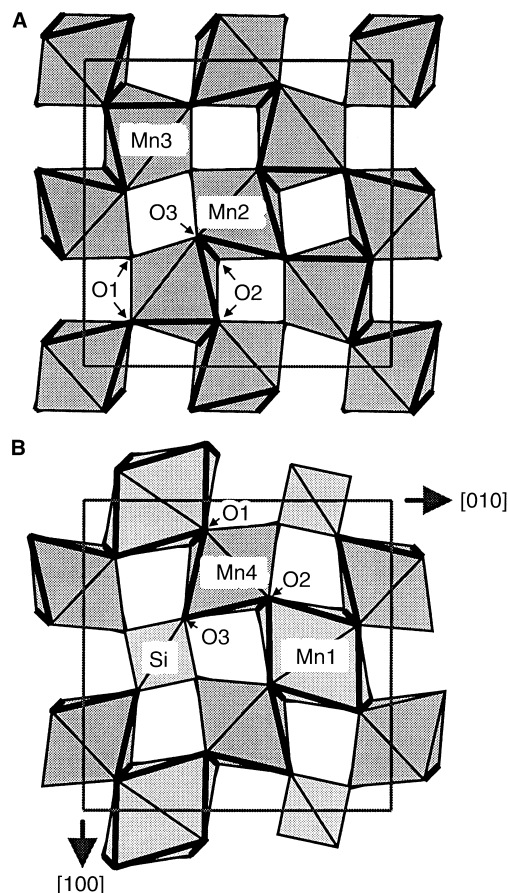


Fig. 1 A and B type layers of the braunite structure in a view down the *c* axis. Site notation follows the structure description by Moore and Araki (1976). Polyhedral edges which have edges shared with other polyhedra are drawn as **bold** lines. Graphic displayed with ATOMS (Dowty 1995)

The braunite structure type (space group $I4_1/acd$, $Z=8$) has a simple $(AB)_{4n}$ stacking sequence of two layer types (A, B; Fig. 1) along the 4_1 screw axis (De Villiers 1975; Moore and Araki 1976; Palvadeau et al. 1991). The type A layer consists only of distorted $Mn(2)^{3+}O_6$ and $Mn(3)^{3+}O_6$ octahedra, whereas the type B layer is built from $Mn(1)^{2+}O_8$, SiO_4 , and $Mn(4)^{3+}O_6$ polyhedra (site notation according to Moore and Araki 1976). All three

$Mn^{3+}O_6$ octahedra (Fig. 2) are uniaxially elongated as expected from the JT theorem for *high-spin* d^4 transition metal cations and have site symmetries $\bar{1}$, $\bar{2}$, and $\bar{2}$, respectively. These sites can partially be substituted by Al^{3+} , Fe^{3+} , and $\frac{1}{2}Cu^{2+} + \frac{1}{2}Ti^{4+}$ (Seifert and Dasgupta 1982; Abs-Wurmbach 1987; Abs-Wurmbach and Amthauer 1988; Mouron et al. 1989). The eight-fold coordination (point symmetry 222) is also uniaxially elongated parallel to [110] along one of the two-fold axes and, therefore, can host not only Ca^{2+} and Mg^{2+} cations (Baudracco-Gritti et al. 1982; Baudracco-Gritti 1985; Cotkin 1989) but also JT cations like Cu^{2+} (Reinecke et al. 1991). A remarkable feature of the topology of the braunite structure is its high degree of polyhedral connectivity: 2/3 and 1/2 of all MnO_8 and MnO_6 polyhedral edges, respectively, are shared with other polyhedra. The braunite structure was also subject to low-temperature investigations (Ohmann et al. 1997) as antiferromagnetic ordering was found to occur below 93 K (Abs-Wurmbach et al. 1981) which corresponds to a λ transition reported from calorimetric measurements (Robie et al. 1995).

Experimental techniques

The single crystal used for the high-pressure X-ray diffraction study was synthesized from $MnCl_2$ (>96%, Merck), MnO_2 (99.99%, Aldrich), and SiO_2 (99.9%, 325 mesh, Alfa) by a chemical transport reaction with chlorine as described by Palvadeau et al. (1991) and Gueho et al. (1993). A pressed pellet of a homogeneous mixture of 1 $MnCl_2$ +5 MnO_2 +1 SiO_2 was heated in an evacuated quartz-glass tube to 880°C for 24 h and then continuously cooled down to 760°C over a further 24 h period. Euhedral crystals up to 300 μm in size were formed both on the pellet's surface and on the tube wall in contact with the pellet. Electron microprobe analysis (Cameca SX-50: 15 kV, 15 nA, 1 μm beam diameter, 20 s counting time, standard=synthetic rhodonite) yielded a composition $Mn^{2+}_{0.99(1)}Mn^{3+}_{5.98(1)}Si_{1.02(2)}O_{12}$ (averages and standard deviations of 11 analyses) which corresponds to the stoichiometric formula of the braunite end-member within the braunite-bixbyite ($=Mn_2O_3$) series of polysomatic intergrowth (De Villiers 1975, 1980; De Villiers and Buseck 1989). Selected area electron diffraction (SAED) and high-resolution transmission electron microscopy (HRTEM) images obtained with a Philips 200 kV field emission gun microscope revealed that the crystals have a perfectly ordered braunite structure which appears to be free of growth defects, dislocations, and mixed-layer polysomatism described by De Villiers and Buseck (1989).

Fig. 2 Polyhedral geometries of the three Mn^{3+} sites in braunite. The vertical axis corresponds to the direction along which the octahedra are uniaxially distorted according to the JT effect. Thick Mn-O bonds represent bonds of the square base, thin Mn-O bonds those to the apices of the resulting tetragonal-bipyramidal polyhedra. Dashed lines correspond to O...O distances which are shared edges with other $Mn^{3+}O_6$ octahedra, dotted lines are shared edges with the $Mn^{2+}O_8$ polyhedra

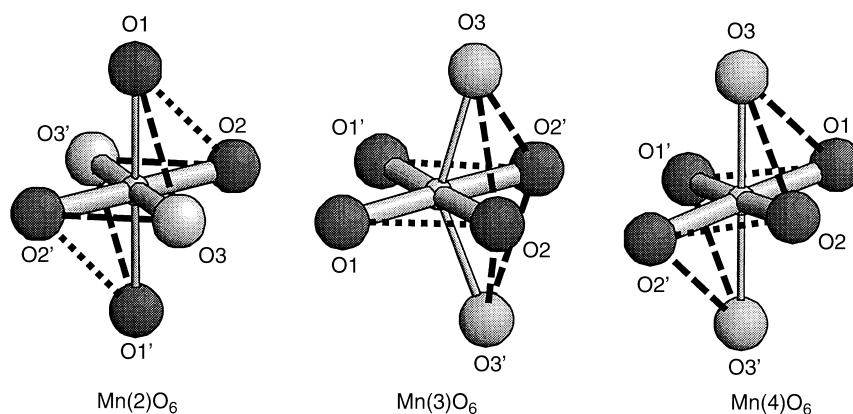


Table 1 Variation of the unit-cell parameters of synthetic braunite with pressure. Pressures were determined by using a CaF_2 (F) or SiO_2 (Q) internal diffraction standard by applying the equation of

states of Angel (1993) and Angel et al. (1997). Asterisks (*) mark pressures at which X-ray intensity data sets were measured for crystal structure determinations.

P (GPa)	Pressure standard			Braunite			
	Type	V ($\text{\AA}^3$)	n_{refl}	a ($\text{\AA}$)	c ($\text{\AA}$)	V ($\text{\AA}^3$)	n_{refl}
0.0001 ^{a*}	F	163.018 (18)	22	9.4264 (4)	18.6962 (6)	1661.29 (16)	57
0.0001 ^{b*}	F	163.022 (17)	8	9.4266 (5)	18.6952 (7)	1661.26 (18)	30
0.242 (13)	F	162.539 (18)	9	9.4212 (7)	18.6879 (9)	1658.72 (26)	28
0.721 (11)	F	161.609 (13)	9	9.4120 (7)	18.6760 (9)	1654.41 (25)	28
1.379 (12)*	F	160.385 (15)	9	9.4007 (6)	18.6574 (7)	1648.80 (20)	29
1.709 (13)	F	159.791 (14)	9	9.3945 (7)	18.6497 (9)	1645.98 (24)	26
2.323 (12)	F	158.723 (12)	9	9.3840 (5)	18.6309 (7)	1640.62 (18)	30
2.659 (12)*	F	158.156 (12)	9	9.3786 (5)	18.6234 (7)	1638.09 (18)	30
3.033 (14)	F	157.541 (15)	9	9.3725 (5)	18.6129 (6)	1635.03 (17)	29
3.566 (14)	F	156.688 (13)	9	9.3638 (6)	18.5979 (8)	1630.69 (22)	29
4.058 (14)	F	155.926 (13)	9	9.3555 (6)	18.5853 (7)	1626.68 (20)	28
4.512 (14)*	F	155.243 (13)	9	9.3480 (7)	18.5739 (9)	1623.08 (26)	27
4.849 (17)	F	154.747 (18)	9	9.3429 (7)	18.5649 (9)	1620.54 (23)	27
5.280 (17)	F	154.127 (18)	8	9.3356 (6)	18.5534 (8)	1616.99 (22)	27
5.630 (17)*	F	153.635 (17)	8	9.3309 (5)	18.5455 (7)	1614.69 (18)	28
6.054 (18)	F	153.053 (18)	9	9.3240 (6)	18.5355 (7)	1611.42 (19)	27
6.340 (17)	F	152.666 (16)	8	9.3192 (6)	18.5295 (8)	1609.24 (21)	27
6.737 (13)	Q	99.699 (13)	11	9.3138 (6)	18.5188 (7)	1606.47 (19)	24
7.189 (15)	Q	99.100 (15)	11	9.3074 (6)	18.5083 (8)	1603.33 (21)	25
7.689 (17)*	Q	98.462 (17)	11	9.2998 (7)	18.4957 (9)	1599.63 (23)	24
8.501 (15)	Q	97.476 (15)	11	9.2888 (6)	18.4768 (8)	1594.21 (21)	24
9.175 (18)	Q	96.700 (17)	11	9.2796 (8)	18.4609 (10)	1589.69 (29)	24

^a Crystal mounted on fibre in air

^b Crystal mounted in DAC without pressure medium

Table 2 Details on data reduction and results of the structure refinements. Transmission (t) includes both crystal absorption and absorption by DAC components

P (GPa)	0.0001 ^a	0.0001 ^b	1.38 (2)	2.66 (2)	4.51 (2)	5.63 (2)	7.69 (2)
Total $ F $	2272	1421	1121	1189	1230	1379	1373
Averaged $ F $	580	428	420	346	365	344	332
$ F _{\text{obs}} (F > 4 \sigma)$	446	220	226	207	204	180	201
μ ($\text{MoK}\alpha$) (cm^{-1})	101.18	101.18	101.97	102.64	103.58	104.12	105.08
t_{min} (%)	41.8	17.9	16.1	18.1	17.9	17.7	17.0
t_{max} (%)	67.1	24.1	24.0	24.0	23.9	23.8	23.4
$R_{\text{int}} (F > 4 \sigma)$	0.0197	0.0247	0.0282	0.0289	0.0297	0.0320	0.0281
$ F _{\text{obs}}/n_{\text{var}}^c$	8.9	6.2	6.4	5.9	5.8	5.1	5.7
R	0.024	0.028	0.033	0.036	0.041	0.035	0.034
wR^d	0.025	0.027	0.033	0.030	0.036	0.034	0.037
Gof ^e	1.10	1.11	1.25	1.29	1.39	1.24	1.45
g ($\times 10^5$)	0.51 (7)	2.6 (2)	1.9 (2)	2.4 (2)	2.6 (3)	3.5 (3)	3.8 (4)

^a Crystal mounted on a glass fibre in air

^b Crystal mounted in the DAC without any pressure transmitting medium

^c $n_{\text{var}}=50$ (β_{ij} s for all atoms, + extinction coefficient g) for crystal on fibre

$n_{\text{var}}=35$ (β_{ij} s for cations, B_{iso} for oxygen atoms, + g) for crystal in DAC

^d $w = \sigma_F^2 + p F^2$, $p=0.005$

^e Gof goodness of fit

A (110) crystal plate ($95 \times 110 \times 35 \mu\text{m}^3$), oriented by X-ray film methods, was loaded in a diamond-anvil cell (Allan et al. 1996) together with a ruby chip for approximate pressure determination and either a fluorite or quartz crystal to act as internal diffraction standard. The crystals were secured in place on the $600 \mu\text{m}$ culet face of one diamond anvil by a thin film of petroleum jelly. For the experiments in the 0.0001 to 6.34 GPa pressure range, an inconel 750X gasket (which was pre-intended from $250 \mu\text{m}$ to $95 \mu\text{m}$ thickness) with a $220 \mu\text{m}$ hole was used. For pressures greater than 6.4 GPa a tungsten gasket (pre-intended to $100 \mu\text{m}$) with a $200 \mu\text{m}$ hole was used. A 4:1 methanol-ethanol mixture was used as pressure transmit-

ting medium for all experiments. Up to 9.2 GPa the peak profiles of both the braunite and quartz/fluorite crystals showed no broadening which would be indicative of non-hydrostatic stresses. The pressure range of this study was restricted to 9.2 GPa because the sample crystal was bridged between the two diamond anvils at ~ 9.5 GPa.

Unit-cell parameters of braunite and of the respective pressure calibrant crystals were determined using a customized HUBER four circle diffractometer operated with unmonochromatized Mo X-ray radiation. Details of the diffractometer and the centering procedure are given in Angel et al. (1997). To prevent crystal-offset errors and diffractometer aberrations affecting the results, the technique of

Table 3 Refined positional and displacement parameters for braunite. Estimated standard deviations are given in parenthesis, anisotropic displacement parameters are given in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$; $B_{eq} = 4/3 (\beta_{11}a^2 + \beta_{22}a^2 + \beta_{33}c^2)$. Refinement of the crystal in air marked with an asterisk (*)

<i>P</i> (GPa)		0.0001*	0.0001	1.38 (2)	2.66 (2)	4.51 (2)	5.63 (2)	7.69 (2)
Mn1	$\beta_{11}=\beta_{22}$	0.00316 (6)	0.00354 (14)	0.00370 (15)	0.00352 (19)	0.00366 (22)	0.00322 (27)	0.00354 (20)
	β_{33}	0.00074 (2)	0.00069 (5)	0.00079 (5)	0.00077 (6)	0.00083 (7)	0.00094 (7)	0.00072 (6)
	β_{12}	-0.00115 (5)	-0.00145 (22)	-0.00098 (22)	-0.00101 (23)	-0.00032 (38)	-0.00051 (46)	-0.00073 (29)
	B_{eq}	1.09	1.16	1.24	1.18	1.24	1.20	1.14
Mn2	β_{11}	0.00213 (6)	0.00219 (19)	0.00263 (21)	0.00241 (27)	0.00272 (32)	0.00218 (33)	0.00214 (27)
	β_{22}	0.00220 (6)	0.00253 (18)	0.00234 (21)	0.00255 (26)	0.00221 (32)	0.00248 (32)	0.00298 (25)
	β_{33}	0.00059 (2)	0.00060 (4)	0.00062 (4)	0.00069 (5)	0.00061 (6)	0.00073 (7)	0.00056 (6)
	β_{12}	-0.00030 (3)	-0.00024 (14)	-0.00038 (14)	-0.00043 (15)	-0.00083 (23)	-0.00065 (30)	-0.00043 (19)
	β_{13}	-0.00011 (2)	-0.00006 (7)	-0.00007 (8)	0.00009 (9)	0.00012 (12)	-0.00013 (16)	-0.00004 (20)
	β_{23}	0.00005 (2)	0.00005 (6)	-0.00002 (10)	0.00004 (8)	0.00001 (11)	0.00006 (10)	0.00010 (9)
	B_{eq}	0.79	0.84	0.87	0.90	0.86	0.88	0.85
Mn3	<i>y</i>	0.21663 (7)	0.21626 (16)	0.21611 (17)	0.21589 (21)	0.21626 (21)	0.21645 (25)	0.21651 (21)
	β_{11}	0.00211 (6)	0.00229 (21)	0.00214 (24)	0.00237 (28)	0.00132 (31)	0.00220 (39)	0.00226 (31)
	β_{22}	0.00206 (7)	0.00252 (23)	0.00244 (25)	0.00228 (29)	0.00241 (35)	0.00179 (43)	0.00230 (34)
	β_{33}	0.00063 (2)	0.00057 (4)	0.00057 (4)	0.00071 (4)	0.00072 (5)	0.00068 (6)	0.00063 (5)
	β_{13}	0.00008 (2)	0.00015 (6)	0.00001 (6)	0.00012 (7)	0.00000 (9)	0.00028 (10)	0.00025 (8)
	B_{eq}	0.79	0.83	0.81	0.87	0.77	0.77	0.81
	B_{eq}/B_{iso}	0.79	0.83	0.81	0.87	0.77	0.77	0.81
Mn4	<i>x</i>	0.23282 (5)	0.23261 (11)	0.23242 (12)	0.23263 (15)	0.23269 (17)	0.23277 (22)	0.23225 (17)
	$\beta_{11}=\beta_{22}$	0.00207 (4)	0.00227 (10)	0.00234 (12)	0.00226 (14)	0.00275 (16)	0.00249 (21)	0.00278 (15)
	β_{33}	0.00059 (2)	0.00056 (4)	0.00056 (4)	0.00066 (4)	0.00061 (5)	0.00071 (5)	0.00055 (5)
	β_{12}	-0.00011 (4)	-0.00027 (11)	-0.00015 (12)	-0.00016 (13)	0.00008 (18)	-0.00003 (22)	0.00008 (17)
	$\beta_{13}=\beta_{23}$	0.00003 (2)	0.00004 (5)	0.00005 (6)	0.00016 (7)	0.00026 (10)	0.00004 (11)	0.00007 (7)
	B_{eq}	0.77	0.80	0.81	0.84	0.92	0.90	0.89
	B_{eq}/B_{iso}	0.77	0.80	0.81	0.84	0.92	0.90	0.89
Si	$\beta_{11}=\beta_{22}$	0.00170 (8)	0.00212 (22)	0.00225 (24)	0.00251 (33)	0.00313 (38)	0.00240 (45)	0.00232 (30)
	β_{33}	0.00063 (3)	0.00070 (8)	0.00062 (8)	0.00077 (10)	0.00072 (12)	0.00083 (12)	0.00052 (10)
	B_{eq}	0.70	0.83	0.82	0.94	1.06	0.94	0.77
	B_{eq}/B_{iso}	0.70	0.83	0.82	0.94	1.06	0.94	0.77
O1	<i>x</i>	0.15074 (17)	0.14972 (38)	0.14963 (47)	0.14971 (53)	0.14947 (55)	0.15033 (66)	0.14978 (56)
	<i>y</i>	0.85526 (16)	0.85504 (41)	0.85538 (47)	0.85484 (48)	0.85480 (57)	0.85425 (72)	0.85459 (57)
	<i>z</i>	0.94565 (8)	0.94605 (17)	0.94580 (21)	0.94579 (21)	0.94564 (26)	0.94610 (30)	0.94608 (28)
	β_{11}	0.00264 (15)						
	β_{22}	0.00249 (15)						
	β_{33}	0.00081 (4)						
	β_{12}	-0.00018 (12)						
	β_{13}	-0.00005 (7)						
	β_{23}	0.00020 (6)						
	B_{eq}/B_{iso}	0.99	1.08 (7)	1.06 (8)	0.92 (9)	0.76 (10)	0.95 (12)	0.91 (10)
	B_{eq}/B_{iso}	0.99	1.08 (7)	1.06 (8)	0.92 (9)	0.76 (10)	0.95 (12)	0.91 (10)
O2	<i>x</i>	0.14441 (16)	0.14524 (38)	0.14506 (42)	0.14422 (47)	0.14438 (59)	0.14437 (67)	0.14455 (53)
	<i>y</i>	0.07326 (16)	0.07341 (38)	0.07319 (51)	0.07201 (51)	0.07212 (63)	0.07238 (73)	0.07296 (58)
	<i>z</i>	0.05673 (7)	0.05680 (16)	0.05720 (19)	0.05673 (20)	0.05728 (28)	0.05742 (28)	0.05744 (26)
	β_{11}	0.00261 (16)						
	β_{22}	0.00283 (16)						
	β_{33}	0.00070 (4)						
	β_{12}	-0.00021 (12)						
	β_{13}	-0.00012 (7)						
	β_{23}	0.00005 (7)						
	B_{eq}/B_{iso}	0.97	1.02 (7)	0.96 (8)	1.04 (9)	1.16 (11)	0.93 (13)	0.98 (9)
	B_{eq}/B_{iso}	0.97	1.02 (7)	0.96 (8)	1.04 (9)	1.16 (11)	0.93 (13)	0.98 (9)
O3	<i>x</i>	0.07780 (18)	0.07798 (45)	0.07862 (47)	0.07885 (53)	0.07936 (64)	0.08029 (80)	0.08100 (61)
	<i>y</i>	0.13403 (16)	0.13404 (43)	0.13392 (50)	0.13328 (57)	0.13283 (57)	0.13196 (73)	0.13172 (62)
	<i>z</i>	0.92521 (8)	0.92544 (17)	0.92569 (21)	0.92554 (21)	0.92549 (28)	0.92564 (29)	0.92504 (28)
	β_{11}	0.00244 (17)						
	β_{22}	0.00320 (16)						
	β_{33}	0.00077 (4)						
	β_{12}	0.00027 (13)						
	β_{13}	-0.00003 (7)						
	β_{23}	0.00018 (7)						
	B_{eq}/B_{iso}	1.03	1.00 (7)	0.94 (8)	1.10 (9)	0.93 (10)	0.98 (11)	1.21 (10)
	B_{eq}/B_{iso}	1.03	1.00 (7)	0.94 (8)	1.10 (9)	0.93 (10)	0.98 (11)	1.21 (10)
Note	Mn1 at 8 <i>b</i> :	0, 1/4, 1/8	(point symmetry: 2.22)	$\beta_{11}=\beta_{22}$; $\beta_{13}=\beta_{23}=0$				
	Mn2 at 16 <i>c</i> :	0, 0, 0	(point symmetry: 1)					
	Mn3 at 16 <i>e</i> :	1/4, <i>y</i> , 0	(point symmetry: .2.)	$\beta_{12}=\beta_{23}=0$				
	Mn4 at 16 <i>f</i> :	<i>x</i> , <i>x</i> +1/4, 1/8	(point symmetry: .2)	$\beta_{11}=\beta_{22}$; $\beta_{13}=-\beta_{23}$				
	Si at 8 <i>a</i> :	0, 1/4, 3/8	(point symmetry: 4)	$\beta_{11}=\beta_{22}$; $\beta_{12}=\beta_{13}=\beta_{23}=0$				
	O1, O2, O3 at 32 <i>g</i> :	<i>x</i> , <i>y</i> , <i>z</i>	(point symmetry: 1)					

diffracted-beam centering (King and Finger 1979) was employed to obtain correct setting angles. The lattice parameters constrained to the respective symmetries were obtained by a vector-least-squares fit (Ralph and Finger 1982) to the corrected reflection positions. The unit-cell parameters of braunite were determined from the corrected positions of 24 to 30 accessible reflections within the 11.6–26.7° range in 2θ (at 0.0001 GPa). Equation-of-state parameters were determined by a least-squares fit of a third-order Birch-Murnaghan equation of state (Birch 1947) to the P - V data set (Table 1) with pressures determined from the fluorite (Angel 1993) and quartz unit-cell volumes (Angel et al. 1997).

X-ray intensity data sets were collected at 6 pressures to a maximum of 7.69 GPa in addition to two data collections at ambient pressure (10^{-4} GPa), one in the DAC without any pressure medium and one with the crystal mounted on a glass fibre in air. All intensity data collections were carried out on an Enraf Nonius CAD4 four-circle diffractometer using graphite-monochromatized $\text{MoK}\alpha$ radiation from an X-ray tube operated at 50 kV and 50 mA. The intensity measurements were carried out with ω -scans (scan range: $0.66^\circ + 0.35^\circ \tan \theta$, $+0.16^\circ$ background on each side; scan time: 12 to 600 s) at the position of least attenuation of the pressure cell, according to the fixed- ϕ technique (Finger and King 1978). All symmetry-allowed accessible reflections within the $\pm h$, $+k$, $\pm l$ hemisphere were collected for $2\theta \leq 60^\circ$. Integrated X-ray intensities were obtained from the scan data using a modified Lehmann-Larsen algorithm (Grant and Gabe 1978). Intensities were corrected for Lorentz and polarization effects, crystal absorption and, in the case of the HP experiments, for absorption effects of the diamond and beryllium components of the pressure cell by a modified version of the program ABSORB (Burnham 1966). Averaged structure factors were obtained by averaging symmetry equivalent reflections in Laue group $4/mmm$ following the averaging criteria recommended by Blessing (1987). The structure refinements were carried out with RFINE90, a development version of RFINE4 (Finger and Prince 1975). The atomic coordinates given by Moore and Araki (1976) were used as a starting model. The coefficients for scattering factors of neutral atoms and the coefficients for dispersion corrections were taken from the International Tables for Crystallography (Maslen et al. 1992; Creagh and McAuley 1992). The final refinements were carried out with anisotropic displacement parameters for the cations and isotropic B 's for the oxygen atoms. Refinement of the anisotropic displacement parameters for the oxygen atoms was only carried out with the data collected for the crystal in air. All refinements included a correction for secondary isotropic extinction (Lorentzian type I distribution, Becker and Coppens 1974). Details of the data reduction and refinements are given in Table 2, the resulting structural parameters are listed in Table 3, bond distances and angles are summarized in Table 4.¹

Results and discussion

Equation of state at 298 K and axial compressibilities

For a third-order Birch-Murnaghan equation of state we obtain $V_0 = 1661.15(8) \text{ \AA}^3$, $K_{T,0} = 180.7(9) \text{ GPa}$, and $K' = 6.51(25)$ from the P - V data (Table 1) at $T = 298(1) \text{ K}$. The χ_w^2 of 0.29 from the 3 parameters fitted to the 20 data points indicates that the esds of the unit-cell volumes of braunite and the pressure calibrants derived from the least-squares fit might be overestimated. The equation of state parameters of braunite are similar to those reported for structures of similar connectivity and polyhedral types, such as the high-pressure polymorph of Mn_3O_4 ($K_0 = 166 \pm 3 \text{ GPa}$ assuming $K' = 4$; Paris et al. 1992) or sil-

icate garnets (139 to 212 GPa: Hazen and Finger 1978; Leger et al. 1990; Zhang et al. 1996).

The variation of the braunite unit-cell parameters with pressure can be described by the second-order polynomial equations:

$$a = 9.42595(21) \text{ \AA} - 0.01856(11) \text{ \AA GPa}^{-1} \cdot P + 2.86(14) \cdot 10^{-4} \text{ \AA GPa}^{-2} \cdot P^2$$

$$c = 18.69557(37) \text{ \AA} - 0.02824(21) \text{ \AA GPa}^{-1} \cdot P + 2.95(24) \cdot 10^{-4} \text{ \AA GPa}^{-2} \cdot P^2$$

The pressure dependencies of the a and c axes are significantly non-linear as indicated by the terms in P^2 being more than 10 times their esds. On the other hand, a fit of the P - a and P - c data sets to a third-order polynomial yielded third-order terms of the same order of their uncertainties. The pressure variation of the unit-cell parameters can also be expressed by a formulation (equivalent to the Murnaghan equation of state)

$$-1/x \, dx/dP = 1/(K_{x,0} + K'_x \cdot P)$$

where x corresponds to the lattice parameter a or c . The linear moduli K_x , their derivatives K'_x , and the values for a_0 and c_0 obtained for fits to this formulation are: $a_0 = 9.4262(4) \text{ \AA}$, $K_a = 498.8(3.5) \text{ GPa}$, $K'_a = 19.7(9)$; $c_0 = 18.6964(6) \text{ \AA}$, $K_c = 656.9(5.7) \text{ GPa}$, $K'_c = 15.7(1.4)$. The χ_w^2 values obtained for these fits are 0.58 and 0.85, respectively. Axial compression is therefore significantly anisotropic with a higher compressibility along the a axis as indicated by the $K_a:K_c$ ratio being close to 3:4.

Structural compression

Our structure refinement of the room-pressure structure is in agreement with, and even improves the precision of the previously reported structural data of natural (De Villiers 1975; Moore and Araki 1976) and synthetic (Palvadeau et al. 1991) braunite. The high-pressure study to the maximum pressure of 9.2 GPa reveals only continuous changes of both the unit-cell and the atomic arrangement and no pressure-induced phase transition is evident. As expected from both the topological connectivity of polyhedra and the fact that the braunite structure can be derived from the fluorite structure (Moore and Araki 1976), the pressure-induced changes of inter- and intra-polyhedral bond angles (Table 5) are insignificantly small.¹ The largest changes affect the O3 inter-polyhedral bond angles, as the SiO_4 tetrahedron is the only polyhedron exclusively interconnected via corners, and the Si-O3-Mn2 [$131.2(3) \rightarrow 129.5(4)^\circ$] and the Mn3-O3-Mn4 [$90.6(2) \rightarrow 91.9(3)^\circ$] bond angles have significant changes with pressure (Table 5).¹ By contrast, all types of interatomic distances (M-O bond distances: Table 4; M...M inter-cation distances, O...O contacts: Table 6)¹ reveal significant changes with pressure. The linear compressibility coefficients for the cation-cation distances, $\beta_{\text{M} \cdots \text{M}}$, were found

¹ Can be obtained from the authors on request

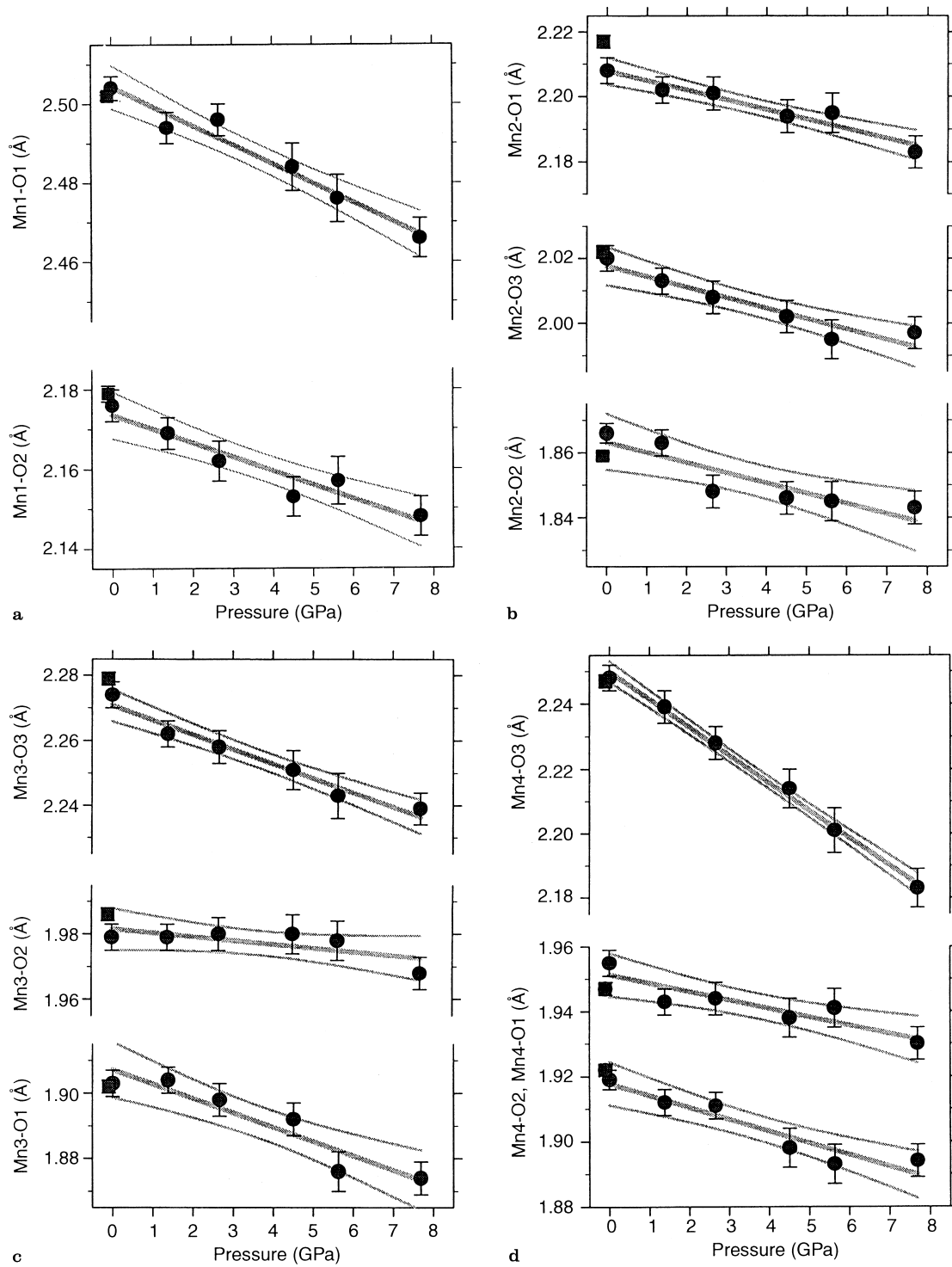


Fig. 3a–d Variation of the Mn²⁺-O and Mn³⁺-O bond distances with pressure for: **a** the Mn(1)²⁺; **b** the Mn(2)³⁺; **c** the Mn(3)³⁺; **d** the Mn(4)³⁺ sites. **Bold lines** represent the fits of a linear function to the data points applying $1/\sigma^2$ weights (σ =uncertainty in the bond distance X–O); **fine lines** represent the 95% confidence limits of the fit. Errors in pressure are smaller than the symbol size (see Table 1). **Circles** represent data points from the measurements of the crystal in the DAC, **squares** of the crystal in air

to lie between $1.45(10)$ and $1.86(11) \times 10^{-3} \text{ GPa}^{-1}$. The corresponding linear compression moduli (690 ± 45 and $540 \pm 35 \text{ GPa}$) show the expected good correspondence with the axial moduli K_a and K_c because most of the fractional coordinates of the cations are, because of their site symmetries, constrained to be invariant parameters (Table 2).

Significant changes with pressure can be observed for the Mn²⁺-O and Mn³⁺-O bond distances (Fig. 3) whereas the Si–O distance appears to be invariant as pressure in-

creases. The $\text{Mn}^{2+}\text{-O}$ bonds (Fig. 3a) show shortening by 1.4% over the pressure range 0.0001 to 7.7 GPa. The mean linear Mn-O compressibility coefficients of 1.7 ± 0.2 and $1.9 \pm 0.2 \times 10^{-3} \text{ GPa}^{-1}$ are the same within their uncertainty and indicate isotropic compression of the Mn^{2+}O_8 polyhedron. However, $\text{Mn}^{3+}\text{-O}$ bond distances (Fig. 3b–d) show a large variational range of the linear bond compressibilities which vary from 0.6 ± 0.3 to $3.8 \pm 0.2 \times 10^{-3} \text{ GPa}^{-1}$. The fact that the most compressible $\text{Mn}^{3+}\text{-O}$ bonds are aligned closer to the (001) plane than to the c axis explains the compressional anisotropy of the unit-cell parameters.

Mn^{2+}O_8 and Mn^{3+}O_6 polyhedral bulk moduli

No experimentally determined data have previously been reported in the literature for the compression of either of these polyhedral types because they are relatively rare. Eight-coordinated Mn^{2+} is known in only a few oxygen-based compounds including $\text{Mn}_3\text{Y}_2(\text{ZrO}_4)_3$ garnets (Lind and Geller 1969; Novak and Gibbs 1971; Fujino et al. 1986), the high-pressure polymorph of Mn_3O_4 (Ross et al. 1990), and $\text{Mn}(\text{Mn,Cu})\text{Te}_2\text{O}_5$ (Miletich 1993). Paris et al. (1992) modelled the pressure dependence of the structure of the marokite-type Mn_3O_4 (Ross et al. 1990) and we derived a value of 174 GPa for the polyhedral modulus from their calculated MnO_8 polyhedral volumes. This compares to our measured K_p of 200 ± 17 GPa for the MnO_8 polyhedron in braunite (Fig. 4). Paris et al. (1992) also calculated volumes for the Mn^{3+}O_6 polyhedra in both the high- P and low- P polymorphs of Mn_3O_4 from which polyhedral bulk moduli of 188 and 230 GPa can be obtained, similar to the range of 146 ± 8 to 210 ± 25 GPa (mean value: 180 ± 33 GPa) that we have found for the three Mn^{3+}O_6 polyhedra in braunite (Fig. 4). All of these values fall between the 143 ± 7 GPa value for six-coordinated Mn^{2+} in rock-salt MnO (Clendenen and Drickamer 1966) and that of 280 ± 10 GPa for the Mn^{4+}O_6 octahedron in rutile-type MnO_2 (Bassett and Takahashi 1974).

Mn^{3+}O_6 polyhedral distortion and anisotropic compression

Although the coordination polyhedra of all three crystallographically independent Mn^{3+} sites show the same type of uniaxial elongation (as expected for the *high-spin* $3d^4$ electronic configuration due to the JT effect) at room pressure, the detailed geometry of the three polyhedra are different, and these differences have a significant effect on their behaviour under compression (Figs. 3–5). There are three geometrical factors that distinguish the polyhedra (Fig. 2) and we will discuss the influences of each of them on the polyhedral compression in turn.

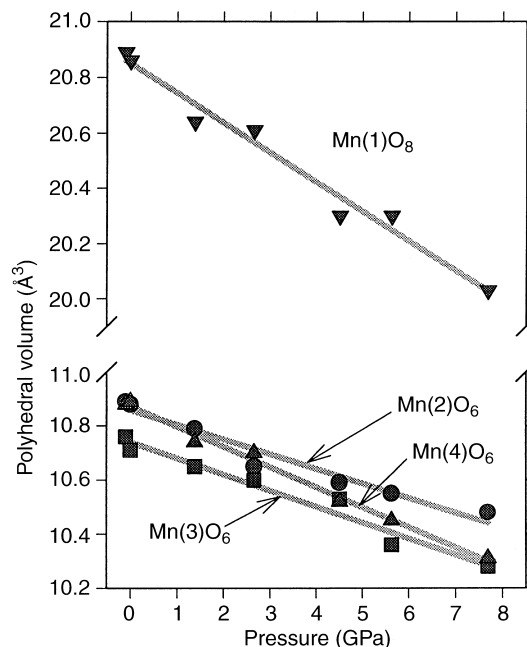


Fig. 4 Variation of the polyhedral volumes with pressure. Lines represent linear fits with unit weights

Different oxygen-configuration types

Each of the three Mn^{3+}O_6 octahedra in braunite are coordinated by two of the three symmetrically distinct oxygen atoms. These oxygens can be divided into two types by their own coordination environment. The O1 and O2 atoms are coordinated by 3 Mn^{3+} + 1 Mn^{2+} whereas the O3 atom is coordinated by 3 Mn^{3+} + 1 Si^{4+} . Because the bond valence for a $^{4}\text{Si-O}$ bond is greater than that for a $^{8}\text{Mn}^{2+}\text{-O}$ bond, the Mn-O3 bonds are generally longer than the Mn-O1 and Mn-O2 bonds to prevent oversaturation of the O3 oxygens. These bonding requirements contribute to the axial elongation of the $\text{Mn}(3)\text{O}_6$ and $\text{Mn}(4)\text{O}_6$ octahedra in which the O3 atoms form the apices (Fig. 2). In the $\text{Mn}(2)\text{O}_6$ octahedron the O3 oxygens lie within the equatorial plane, and the bond-length distortion arising from valence requirements of the O3 itself is reflected by the strong differences in bond length within the equatorial plane.

In the $\text{Mn}(3)\text{O}_6$ and $\text{Mn}(4)\text{O}_6$ octahedra the Mn-O3 bonds are the most compressible bonds, and in the $\text{Mn}(2)\text{O}_6$ octahedra they are as compressible (within the experimental uncertainties) as the Mn-O1 bonds, in spite of the fact that in the $\text{Mn}(2)\text{O}_6$ octahedron the Mn-O3 bond is not the longest bond. This differential compression of the Mn-O3 bonds therefore contributes to a decrease in the distortion of the $\text{Mn}(3)\text{O}_6$ and $\text{Mn}(4)\text{O}_6$ octahedra with increasing pressure. A similar, but smaller, regularization occurs within the equatorial plane of $\text{Mn}(2)\text{O}_6$. However, in this case, the fact that the longest Mn-O1 bond has the smallest bond compressibility is responsible for the increasing overall polyhedral bond-length distortion of the $\text{Mn}(2)\text{O}_6$ polyhedron with pressure (Fig. 5a).

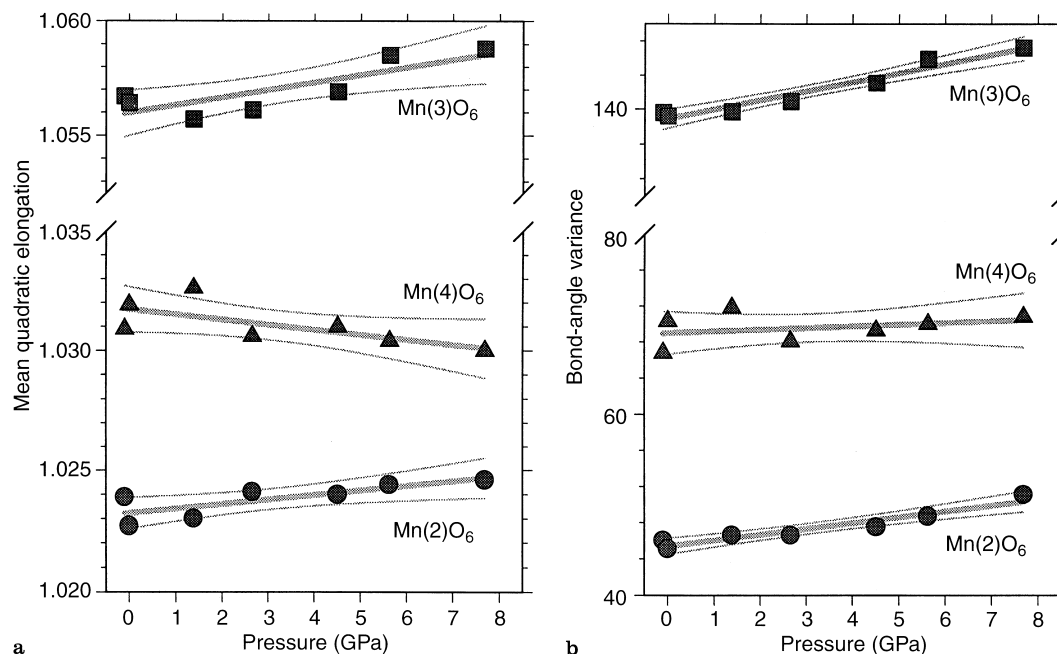


Fig. 5a, b Variation of the polyhedral distortion parameters (Robinson et al. 1971) with pressure: **a** mean quadratic elongation; **b** bond-angle variance. **Bold lines** represent linear fits with unit weights, **fine lines** are 95% confidence limits

Differences in the connectivity

There are two distinct arrangements by which the MnO₆ octahedra share edges with other polyhedra. The Mn(2)O₆ and Mn(4)O₆ octahedra have a *trans*-configuration of shared edges in which all of the edges shared with Mn³⁺O₆ octahedra occur in pairs opposite one another across the centre of the octahedron (Fig. 2). By contrast, the Mn(3)O₆ octahedron has a *cis*-configuration in which all such shared edges occur on one side of the octahedron. These differences between the connectivity of Mn(3) and Mn(4) sites appear to be responsible for their different compressional behaviour despite having the same arrangement of the two oxygen configurations.

Angular distortion

The asymmetric *cis*-configuration of the shared edges of the Mn(3)O₆ octahedron (Fig. 2) also seems to be responsible for its significant angular distortion with the axial angle O3-Mn3-O3 being reduced to 140.0° (at room pressure) compared to the symmetry-constrained 180° at Mn(2) and the 178.7° in Mn(4). The differences in the connectivity and the angular distortion are, of course, strongly correlated and both contribute to the observed differences between the lengths of the various O...O edges of the octahedra. The role of this factor in compression can be estimated by comparing the compressional behaviour of the Mn(3)O₆ and Mn(4)O₆ which have the same arrangement of O3 apical oxygens: both the polyhedral

bulk moduli (Fig. 4) and the mean quadratic elongation (Fig. 5a) show significant differences. In the Mn(3)O₆ octahedron, any decrease in the O3-Mn-O3 angle would lead to a rapid increase in the O3...O2 repulsion compared to those for the O3...O1 contacts. As a consequence, the Mn3-O1 and Mn3-O2 bonds within the equatorial plane display a very strong compressional anisotropy (Fig. 3c) which leads to an increase of the bond-length distortion within this plane. This increase in the equatorial plane distortion with increasing pressure dominates over the intrinsic tendency for the distortion to decrease as a result of the shortening of the apical Mn-O3 bonds. Consequently, the bond-length distortion of Mn(3) increases with pressure, in contrast to the decrease for the Mn(4) site even though both sites have the same arrangements of coordinating oxygens. In addition, the Mn(3)O₆ polyhedral bulk compression is smaller relative to that of the Mn(4)O₆ polyhedron (Fig. 4).

Concluding remarks

The braunite structure was found to be ideal for the study of continuous changes of the polyhedral geometry of uniaxially elongated Mn³⁺O₆ octahedra as it undergoes no phase transition in the pressure range 0.0001 to 9.2 GPa. The compression of the unit cell was found to be anisotropic as a result of the fact that the most compressible bonds, the Mn³⁺-O bonds, are aligned closer to the (001) plane than to the *c* axis. The large bulk modulus, $K=180.7\pm0.9$ GPa, can be related to the fact that structural connectivity is achieved to a high degree by edge-sharing as 2/3 and 1/2 of the polyhedral edges of the Mn²⁺O₈ and Mn³⁺O₆ polyhedra are shared edges with other polyhedra. The Mn²⁺O₈ polyhedron were found to compress isotropically with increasing pressure, whereas all Mn³⁺O₆ oc-

tahedra are characterized by a strong anisotropic compression. The SiO_4 tetrahedron reveals no significant compression.

In addition to the electronic distortion due to the JT effect, topologically induced distortion was found to contribute significantly to the compressional behaviour of the polyhedra. These topologically related distortions have to be differentiated into the distortion induced by the bonding of the polyhedral ligands to other types of cations and the distortion induced by the patterns of connectivity, in this case by *cis*- and *trans*-configuration of shared edges. This second type of topologically induced distortion was found to be related closely to the angular distortion of the polyhedra themselves. The distortion due to the bonding topology was found to decrease with pressure, whereas angular distortion related to asymmetric connectivity (*cis*-configured type) was found to be responsible for the increasing bond-length distortion.

The influence of pressure on the JT effect can therefore only be determined quantitatively for coordinations essentially free of any type of topologically induced distortion, which is not the case for the Mn(3) and Mn(4) sites in braunite. In contrast, the absence of topological constraints in the basal O2 and apical O1 atoms of the Mn(2)O_6 octahedron allow the changes in the electronic distortion with pressure to be studied directly. Because the O1 and O2 atoms have equivalent bonding to further cations ($3 \text{ Mn}^{3+} + 1 \text{ Mn}^{2+}$), the Mn(2)O_6 octahedron has no axial bond-angle distortion (point symmetry: $\bar{1}$), and the individual bond angles deviate by less than 10.5° from an ideal of 90° ; the small but significant differences in the Mn3-O1 and Mn3-O2 bond compression indicate that the electronically driven distortion increases slightly with pressure. The increase of the JT distortion with pressure is therefore opposite to, and competing with, the compressional changes induced by normal bond shortening with pressure.

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