

Compression of the perovskite-related mineral bernalite $\text{Fe}(\text{OH})_3$ to 9 GPa and a reappraisal of its structure

M. D. WELCH^{1,*}, W. A. CRICHTON² AND N. L. ROSS³

¹ Department of Mineralogy, The Natural History Museum, Cromwell Road, London SW7 5BD, UK

² European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, 38043 Grenoble, France

³ Department of Geological Sciences, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, USA

ABSTRACT

The octahedral-framework mineral bernalite, $\text{Fe}(\text{OH})_3$, provides a rare opportunity to examine directly the effects of a vacant *A* site upon the physical properties of perovskite-like structures. Here, we report the effect upon compressibility. Bernalite has been reported previously as having space group *Immm* (Birch *et al.*, 1993), but numerous reflections violating *I*-centering were observed in the present study. A case is presented for bernalite having orthorhombic space group *Pmnm*. Lattice parameters were refined using the Le Bail method for a metrically tetragonal cell and their variation with pressure at room temperature was determined from 17 measurements at pressures from 10^{-4} to 9.3 GPa using synchrotron X-ray powder diffraction. No discontinuities in the compression curves of lattice parameters were observed. Fitting to a second-order Birch-Murnaghan equation-of-state ($K_{T0}' = 4$) gives $V_0 = 438.51 \pm 0.06 \text{ \AA}^3$ and $K_{T0} = 78.2 \pm 0.4$ GPa. Second-order fits of $(a/a_0)^3$ and $(c/c_0)^3$ give elastic moduli $K_{T0a} = 82.0(6)$ GPa and $K_{T0c} = 71.6(4)$ GPa: the shorter cation–cation distance is the more compressible. These values are very close to those of stottite, $\text{FeGe}(\text{OH})_6$, which has tilt system $a^+a^+c^-$. The difference in the elastic moduli K_{T0a} and K_{T0c} of bernalite and their close similarity to the stottite values support the revised *Pmnm* structure (tilt system $a^+b^+c^-$) for bernalite proposed here. The compressional anisotropy observed in bernalite may reflect its highly anisotropic and directional H-bonding topology.

KEYWORDS: bernalite, perovskite, equation of state, compression, hydrogen-bonding.

Introduction

BERNALITE, a polymorph of $\text{Fe}(\text{OH})_3$, occurs as a low-temperature mineral associated with goethite and coronadite (Birch *et al.*, 1993). It is structurally related to perovskites, ReO_3 and, specifically, to members of the schoenfliesite-soehngeite-stottite group of protonated octahedral frameworks ('POFs'). The POF minerals have structures comprising a three-dimensional framework of corner-linked cation octahedra in which all oxygens are protonated as hydroxyl groups and there is extensive hydrogen bonding between octahedra. However, unlike perovskites, the

cavity site is vacant. There are two main types of protonated octahedral framework: (1) those with a single trivalent cation and having the general formula $M^{3+}(\text{OH})_3$ with $M^{3+} = \text{Sc, Fe, Ga, In}$; (2) those with divalent and tetravalent cations and general formula $M^{2+}M^{4+}(\text{OH})_6$. In the latter, there is an alternation of M^{2+} and M^{4+} octahedra. $M^{2+} = \text{Mg, Ca, Fe, Mn, Cu, Zn}$; $M^{4+} = \text{Ge, Sn}$. Species with only trivalent cations are typically cubic with space group $Im\bar{3}$, whereas those with M^{2+}/M^{4+} cations are primitive cubic or rhombohedral, the loss of *I* centering being due to the alternation of M^{2+} and M^{4+} polyhedra. Mopungite, $\text{NaSb}(\text{OH})_6$ is the only naturally occurring 1+/5+ POF (Williams, 1985). Stottite, $\text{FeGe}(\text{OH})_6$, and mopungite have space group $P4_2/n$ and tilt system $a^+a^+c^-$ (Glazer, 1972).

* E-mail: m.welch@nhm.ac.uk
DOI: 10.1180/0026461056930252

The POF phases provide a rare opportunity to study the structural behaviour of the octahedral framework in the absence of a cavity (*A*) cation, as well as allowing H bonding to be studied in a relatively simple topology. The average cation charge on the POF framework is 3+, and as such POFs are a much closer approximation to the 3+ and 4+ charges of perovskite frameworks than is ReO_3 (6+). *M*–O bonds of POF and perovskite octahedra are very similar indeed in bond-valence terms. The $\text{Fe}^{3+}(\text{OH})_6$ octahedra of bernalite have very similar sizes and shapes to those of ferrite perovskites. For example, the Fe–O bonds in bernalite and GdFeO_3 perovskite are almost identical (2.04 and 2.05 Å, respectively) and the octahedra have nearly the same volumes. In perovskites, each oxygen forms four long bonds with the *A* cation. For trivalent *A* cations each of these bonds contributes around 0.25 v.u. to the oxygen bond-valence sum, which together with the 0.5 v.u. from each bond to adjacent octahedrally-coordinated trivalent cations amounts to the ideal 2 v.u. for the oxygen. The four *A*–O bonds, which in total contribute ~1 v.u. to the oxygen, are replaced by a single O–H bond in POFs (bond valence ~1 v.u.). As oxygen bonding needs are satisfied, no bond distortions arise; hence, cation octahedra in POFs and perovskites are of very similar sizes. On this basis, we consider that bernalite provides an exceptional chance of gaining insights into the relative importance of octahedral and cavity sites in the deformation of octahedral frameworks.

In the original structural study of bernalite, Birch *et al.* (1993) chose *Immm* as the likely space group despite 90 weak violators of *I*-centering. However, they also recognized *Pmnm* as a possible alternative symmetry and attempted to solve the structure in this space group. Their *Pmnm* refinement was, however, inconclusive and in the absence of good evidence for lower symmetry, Birch *et al.* (1993) chose to solve the structure as *Immm* with a resulting high $R = 0.106$ and $wR = 0.112$. McCammon *et al.* (1995) found that their electron diffraction patterns of bernalite were consistent with *Pmnm* symmetry and not space group *Immm*. Identification of the correct space group for bernalite is important because *Immm* and *Pmnm* have different tilt systems that result in very different H-bonding topologies. In terms of the notation for tilt systems in perovskite-type octahedral frameworks developed by Glazer (1972), *Immm* has tilt system $a^+b^+c^+$, whereas *Pmnm* has tilt system $a^+b^+c^-$. We shall present

evidence for bernalite having space group *Pmnm* and tilt system $a^+b^+c^-$. The tilt systems $a^+b^+c^-$ and $a^+a^+c^-$ are unusual in that there must be some distortion of the octahedra in order to construct a corner-linked framework (Woodward, 1997). This is not necessary for *Immm*. The Fe^{3+} octahedron in bernalite (*Immm*) is slightly distorted, although the oxygen positions are not tightly constrained by the structure determination of Birch *et al.* (1993).

The topologies of *Immm* and *Pmnm* POF structures, including O–H...O bridges, are shown in Fig. 1. *Pmnm* consists of alternating (002) layers of Fe(1) and Fe(2) octahedra, whereas *Immm* is unlayered with only a single Fe site. *Pmnm* has a reversed tilt along [001] and *n*-glides pass through the Fe atoms. The H-bonded configuration of *Immm* consists of (200), (020) and (002) planes of isolated rings of four O–H...O linkages and there is no significant structural anisotropy. The basic H bonding topology of *Immm* is characteristic of all POFs having +++ tilts. However, the antiphase tilt of *Pmnm* leads to a very anisotropic H-bonding topology consisting of (001) planes of isolated four-membered rings, and O–H...O crankshafts running parallel to [100] and [010] and replacing the (200) and (020) planes of four-membered rings that occur in +++ structures, resulting in a much greater density of hydrogen bonding in the *a*-*b* plane of the ++- topology. A very similar H-bonded arrangement occurs in stottite $\text{FeGe}(\text{OH})_6$, which has space group $P4_2/n$ and tilt system $a^+a^+c^-$ (Ross *et al.*, 1988), but differs from bernalite only in having intervening (002) layers of four-membered O–H...O rings due primarily to the different sizes of Fe^{2+} and Ge octahedra.

Experimental methods

Sample characterization

Small, equant, conchoidally-fractured fragments (typically <0.2 mm) of transparent bottle-green bernalite were hand-picked from a partial separate from the type specimen described by Birch *et al.* (1993). This portion of the type specimen was kindly provided by Dr Allan Pring (South Australia Museum, Adelaide). A bulk sample of 3.5 mg was obtained by hand-picking. Grains containing abundant strings of goethite inclusions or having thin goethite coatings, as described by Birch *et al.* (1993), were avoided. Preliminary screening of this bulk sample by X-ray powder diffraction (Enraf-Nonius curved PSD) indicated that it was of high purity and suitable for the

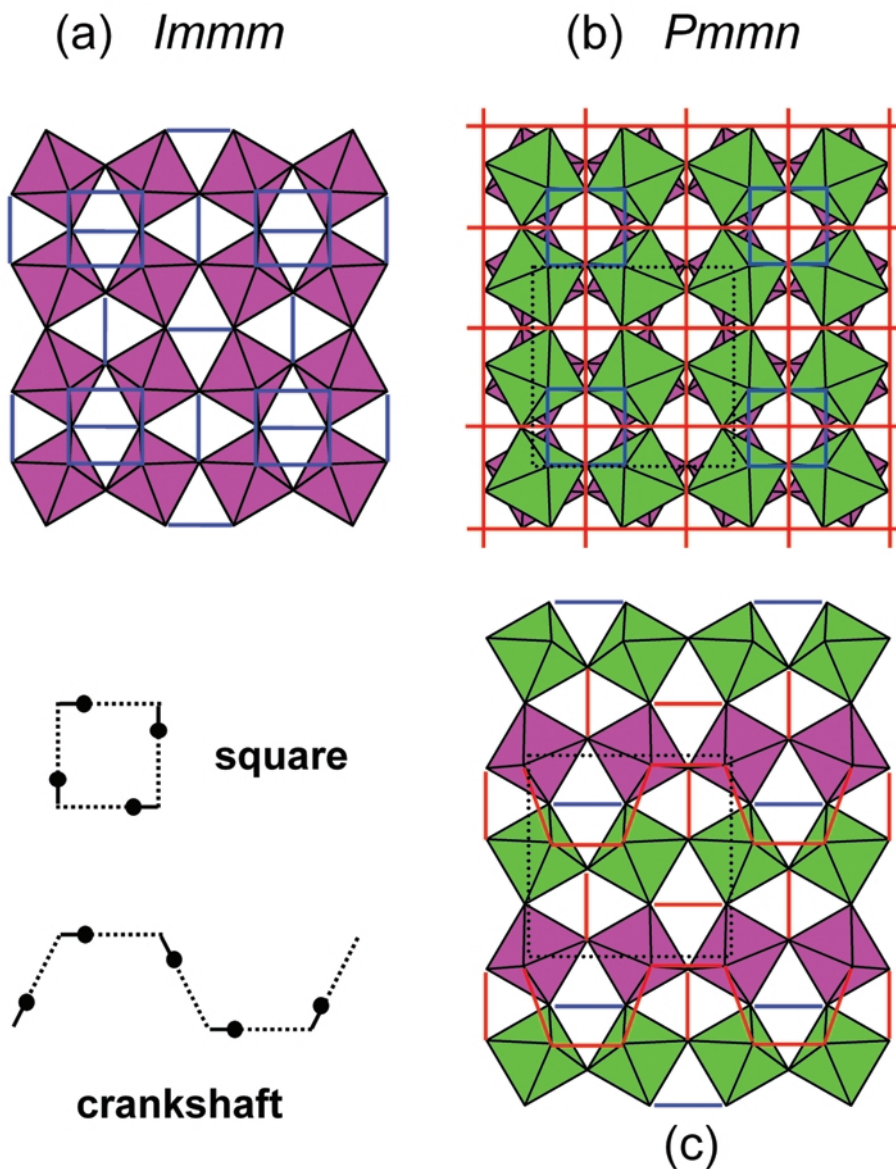


FIG. 1. The octahedral and H-bonded topologies of bernalite for (a) *Immm* and (b,c) *Pmmn* structures with tilt systems $a^+b^+c^+$ and $a^+b^+c^-$, with structures projected onto (001) for (a), (b) and onto (100) for (c). Four-membered rings of O-H...O bridges are shown in blue and crankshafts are shown in red. The *Immm* structure contains only four-membered rings occurring in (200), (020) and (002) layers, whereas the *Pmmn* structure has crankshafts running parallel to [200], [020] and [002], and (001) layers of four-membered rings. The *Pmmn* structure is a slight orthorhombic distortion of the $P4_2/n$ structure of stottite ($a^+a^+c^-$) which, apart from having an ordered M^{2+}/M^{4+} cation arrangement, differs only in having extra (002) layers of four-membered rings.

intended high-pressure, synchrotron X-ray powder diffraction study.

Electron-microprobe analysis (a total of 12 spot analyses of three grains) gave the composition for

the cation site (all Fe as Fe^{3+}) as $\text{Fe}_{0.89(4)}\text{Si}_{0.07(1)}\text{Pb}_{0.02(1)}\text{Zn}_{0.02(1)}$. This composition is very similar to that reported by Birch *et al.* (1993) for the type material for which the cation content is

$\text{Fe}_{0.92}\text{Si}_{0.06}\text{Pb}_{0.01}\text{Zn}_{0.01}$. No chemical or optical zoning was evident.

Synchrotron X-ray powder diffraction to 9 GPa

Diffraction patterns were collected on beamline ID30 at the European Synchrotron Radiation Facility (ESRF), Grenoble at 17 pressures from 10^{-4} to 7.81 GPa at 298 K, of which nine collections were made on decompression. Pressure was determined by the ruby-fluorescence method and in our experiments it is considered accurate to within 0.04 GPa. The powder sample and a ruby crystal were held in a membrane-driven diamond-anvil cell (600 μm diamond culet) fitted with a pre-indented Inconel steel gasket with a 250 μm hole in it. Dry methanol-ethanol (4:1) was used as the pressure-transmitting medium. After reaching the set pressure, the DAC was allowed to relax for ~ 30 min before data collection commenced. Pressure was determined before and immediately after each 5 min data collection and the pressures quoted in Table 1 are the post-run values, as the time interval between extracting the cell from the beam-line and measuring the pressure was 10 min less than that between measuring the initial set pressure, aligning the sample in the X-ray beam

and commencing data collection. Differences between ‘before’ and ‘after’ pressures were typically < 0.1 GPa.

X-rays from two phased undulators were monochromated to $\lambda = 0.3738$ \AA using a channel-cut Si crystal (NBS 640a Si standard, $a = 5.43088$ \AA) under vacuum, giving a d -spacing range of 0.9–24 \AA ($1-24^{\circ}2\theta$). A MAR image-plate detector was used and images of diffraction patterns were corrected for spatial distortion and non-linear background features using the Fit2D software package (Hammersley *et al.*, 1996). Calibration of the sample-to-detector distance and plate displacement was done using a NBS Si powder. In order to obtain good sample averaging in the beam, multiple collections at seven 0.1° intervals of ω between $\pm 0.3^{\circ}\omega$, for each of which the sample was translated to nine different positions and a diffraction pattern collected. About half of the data collections were made during decompression. Integrated diffraction patterns were corrected for background (Compton scattering from diamonds) using a polynomial function in the Fit2D program. Lattice parameters were obtained by the Le Bail method (Le Bail *et al.*, 1988) using the GSAS program (Larson and Von Dreele, 1994).

TABLE 1. Variation of the cell parameters of bernalite with pressure for a tetragonal metric.

P (GPa)*	a (\AA)	c (\AA)	V (\AA^3)
0.0001	7.6191(2)	7.5534(4)	438.48(3)
0.97	7.5923(2)	7.5168(4)	433.27(3)
1.53 ⁺	7.5827(2)	7.5016(5)	431.32(3)
1.84 ⁺	7.5724(2)	7.4899(5)	429.48(3)
2.44 ⁺	7.5536(2)	7.4702(5)	426.22(3)
3.04	7.5301(2)	7.4491(5)	422.38(3)
3.22 ⁺	7.5306(2)	7.4469(4)	422.32(3)
3.96	7.5067(2)	7.4264(5)	418.48(3)
4.61 ⁺	7.4929(2)	7.4091(5)	415.98(3)
5.47 ⁺	7.4723(2)	7.3880(5)	412.51(3)
6.32	7.4488(2)	7.3615(6)	408.45(3)
6.48 ⁺	7.4486(2)	7.3606(5)	408.37(3)
6.92 ⁺	7.4363(2)	7.3498(5)	406.43(3)
7.48 ⁺	7.4230(2)	7.3352(6)	404.18(3)
8.15	7.4066(2)	7.3186(6)	401.48(4)
8.47	7.4025(2)	7.3135(6)	400.76(3)
9.35	7.3829(2)	7.2942(7)	397.59(4)

* Uncertainty on P is ± 0.04 GPa

⁺ data collection on decompression

Results

Figure 2 shows the initial ambient in-cell synchrotron X-ray powder diffraction pattern of bernalite. Numerous, mostly weak, reflections are present that violate the I -centering: (201), (221), (311), (302) and (401). The (311) reflection at $9.36^{\circ}2\theta$ has a relative intensity I/I_0 of 10% and is the strongest I violator. Several peaks at higher angles are split in a $\sim 2:1$ intensity ratio that is characteristic of tetragonal metric symmetry. Simulations of these split peaks as triplets, as orthorhombic ($Pm\bar{m}n$) symmetry would allow, did not result in statistically significant deviations from tetragonal metric symmetry. Consequently, the lattice parameters for a primitive tetragonal unit-cell were refined using the Le Bail method (Le Bail *et al.*, 1988). All refinements converged and had final χ^2 values between 2.8 and 10.1. The compression data for bernalite are given in Table 1 and shown in Figs 3 and 4. No discontinuities in the compression of lattice parameters occur and the volume reduction is 9.5% at 9.35 GPa. The zero-pressure room-temperature bulk modulus, K_{70} , was obtained by fitting the 17 unit-cell volumes to a Birch-

COMPRESSION OF BERNALITE

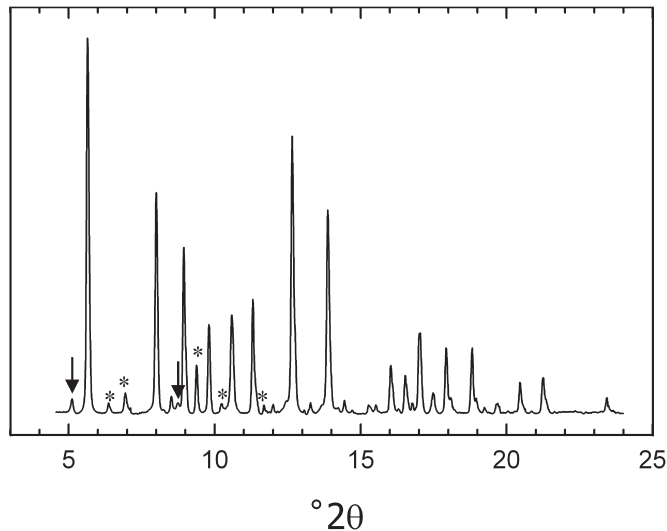


FIG. 2. The ambient in-cell XRD pattern of bernalite showing five obvious reflections (asterisks) violating the I centering. From low to high angle these violators are (201), (221), (311), (302) and (401). None of these violates the n -glide of $Pmmn$. Two peaks due to a goethite impurity are arrowed.

Murnaghan equation-of-state using the program EOSFIT52 (Angel, 2000). F - f analysis of the data indicated that only a second-order fit was justified, for which

$$P = \frac{3}{2} K_{T0} [(V_0/V_P)^{7/3} - (V_0/V_P)^{5/3}]$$

Data were weighted (σ^{-2}) by the error on V . The K_{T0} value obtained from this fit is

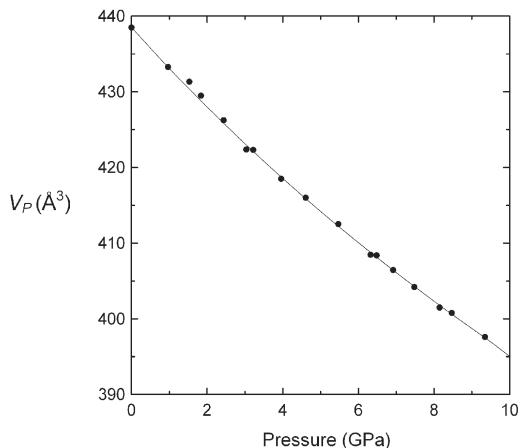


FIG. 3. Volume compression of bernalite to 9.35 GPa refined as metrically tetragonal. The curve is calculated for a second-order Birch-Murnaghan equation-of-state with $K_{T0} = 79$ GPa ($K_{T0}' = 4$). Standard errors (1σ) on volume data are smaller than the symbols.

78.3(4) GPa ($\chi^2 = 4.5$) with a refined V_0 value of 438.51(6) \AA^3 , the latter being almost identical to that determined experimentally, 438.48(3) \AA^3 . Using EOSFIT52, axial moduli of bernalite were obtained by fitting the pressure variations of

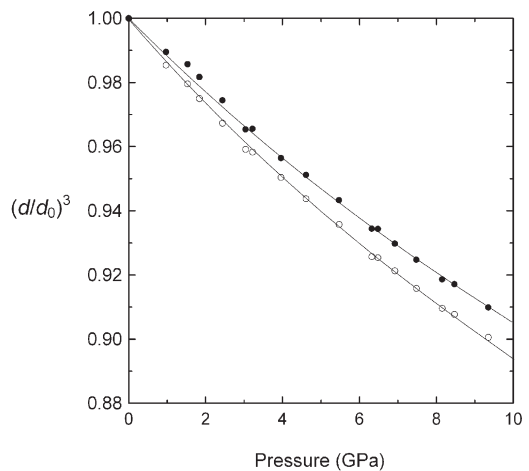


FIG. 4. Relative compression curves for a and c parameters of bernalite refined as metrically tetragonal. The two curves are for second-order Birch-Murnaghan equations of state with $K_{Ta0} = 82$ GPa and $K_{Tc0} = 72$ GPa ($K_{Ta0}' = K_{Tc0}' = 4$) fitted to the pressure variation of the parameters $(a/a_0)^3$ and $(c/c_0)^3$ used in data fitting. Standard errors (1σ) on lattice parameters are comparable to the sizes of the symbols.

$(a/a_0)^3$ and $(c/c_0)^3$ to second-order BM EoSs: $K_{T0a} = 82.0(6)$ GPa ($\chi^2 = 10.6$) and $K_{T0c} = 71.6(4)$ GPa ($\chi^2 = 3.5$).

Discussion

The value of the bulk modulus of bernalite is close to those of vismirmovite $\text{ZnSn}(\text{OH})_6$, schoenfliesite $\text{MgSn}(\text{OH})_6$, dzahlindite $\text{In}(\text{OH})_3$, ($K_{T0} = 72, 78$ and 80 GPa, respectively: Welch *et al.*, in prep.) and stottite ($K_{T0} = 78$ GPa: Ross *et al.*, 2002). K_{T0} near 80 GPa appears to be characteristic of perovskite-like octahedral frameworks with vacant A sites, and appears to be largely independent of V_0 and tilt system. The A cation has a major effect upon the compressibility of perovskites, and stiffens the structure by a factor of ~ 2 relative to the framework. The bulk modulus of GdFeO_3 perovskite is $182(1)$ GPa (Ross *et al.*, 2004) in comparison with $K_{T0} = 78.3(4)$ GPa for bernalite, thus demonstrating the marked stiffening effect of the A cation in perovskites. Burtite, $\text{CaSn}(\text{OH})_6$ (cubic $Pn\bar{3}$) is unusual among the six POFs studied here in being exceptionally compressible, having $K_{T0} = 47$ GPa (Welch and Crichton, 2002a). CaSnO_3 perovskite, on the other hand, has $K_{T0} = 163(1)$ GPa (Kung *et al.*, 2001) that is greater (less compressible) than that predicted by a linear trend of K_{T0} with V_0^{-1} of Ca-oxide perovskites. The anomalously high compressibility of burtite is not yet fully understood. Ross (2000) observed that the compressional behaviour of perovskites is highly variable and controlled by the relative compressibilities of the A and B sites. Zhao *et al.* (2004) developed a model based on bond valence theory (Brown and Altermatt 1985) that successfully predicts the high-pressure behaviour of many oxide perovskites. Work is underway to see if values of K_{T0} for perovskite-like octahedral frameworks with vacant A sites can be predicted from the model, but high-pressure structural studies of POFs will be needed to correlate structural distortions in POFs and perovskites.

ReO_3 possesses the same arrangement of corner-linked octahedra as cubic perovskites but without the A cation. At room temperature the structure remains cubic up to 0.5 GPa and the octahedra undergo compression. Above 0.5 GPa, cubic symmetry is broken, the octahedra tilt, and further compression is primarily achieved by increasing the tilt angle (Jorgensen *et al.*, 1986). The presence of an A cation in perovskites, absent from ReO_3 , clearly plays a role in determining the

behaviour of the octahedral framework upon compression. The absence of an A cation in the POFs is similar to ReO_3 but different from the ABO_3 perovskites. Unlike ReO_3 , POFs are highly tilted at ambient conditions (e.g. bernalite has $\angle \text{B-O-B} = 144^\circ$). The extent to which compression can be achieved by tilting *vs.* bond-length compression is unknown and raises the interesting question: is the compression mechanism in POFs primarily tilting or compression of octahedra, and do they switch with increasing pressure? We are planning to undertake high-pressure, single-crystal X-ray studies of POFs in the near future with the aim of understanding the compressional mechanisms involved.

Compressional anisotropy in bernalite

The compressional anisotropy observed in bernalite is very similar to that of stottite $\text{FeGe}(\text{OH})_6$ (tilt system $a^+a^+c^-$). In a study of the compression of stottite to 8 GPa, Ross *et al.* (2002) found that the c axis, the shorter cell dimension, was 10% more compressible than the a axis: $K_{T0a} = 81.39(3)$ GPa with $K_{T0a}' = 6.4(1)$, $K_{T0c} = 73.3(6)$ GPa with $K_{T0c}' = 5.7(2)$. It is relevant to note that bernalite has a very similar H-bonded arrangement to that of stottite. The marked difference in the elastic moduli K_{T0a} and K_{T0c} of bernalite and their close similarity to the stottite values supports the revised $Pm\bar{m}n$ structure (tilt system $a^+b^+c^-$) for bernalite described above. Ross *et al.* (2003) attributed the different elastic moduli of stottite to the highly anisotropic H-bonding topology of stottite. It is known that highly directional H-bonded topologies can stiffen structures significantly. For example, in the sheet silicate chlorite (Welch and Marshall, 2001; Welch and Crichton, 2002b), the interlayer H bonding reduces the compressibility of this mineral by 30% relative to micas, which have no interlayer H bonding, but interlayer cations. Hydrogen bonding can, therefore, have a significant physical presence and so the very similar compressional anisotropies of bernalite and stottite probably reflect the highly anisotropic and directional hydrogen bonding topologies associated with their $++-$ tilt systems.

Acknowledgements

We thank Dr Allan Pring (South Australian Museum, Adelaide) for providing the bernalite specimen used in this study, and the ESRF for

beamtime for in-house research. NLR acknowledges support from National Science Foundation grants EAR-01058864 and EAR-0408460. Dr Andrew Christy is acknowledged for his constructive and insightful review.

References

- Angel, R.J. (2000) Equations of state. Pp. 35–60 in: *High-pressure, High-temperature Crystal Chemistry* (R.M. Hazen and R.T. Downs, editors). Reviews in Mineralogy and Geochemistry, **41**. Mineralogical Society of America and the Geochemical Society, Washington, D.C.
- Birch, W.D., Pring, A., Reller, A. and Schmalle, H.W. (1993) Bernalite, $\text{Fe}(\text{OH})_3$, a new mineral from Broken Hill, New South Wales: Description and structure. *American Mineralogist*, **78**, 827–834.
- Brown, I.D. and Altermatt, D. (1985) Bond-valence parameters obtained from a systematic analysis of the Inorganic Crystal Structure Database. *Acta Crystallographica*, **B41**, 244–247.
- Glazer, A.M. (1972) The classification of tilted octahedra in perovskites. *Acta Crystallographica*, **B53**, 32–43.
- Hammersley, A.P., Svensson, S.O., Hanfland, M., Fitch, A.N. and Häusermann, D. (1996) Two-dimensional detector software: From real detector to idealised image or two-theta scan. *High-Pressure Research*, **14**, 235–248.
- Jorgensen, J.E., Jorgensen, J.D., Batlogg, B., Remeika, J.P. and Axe, J.D. (1986) Order parameter and critical exponent for the pressure-induced phase transitions in ReO_3 . *Physical Review B*, **33**, 4793–4798.
- Kung, J., Angel, R.J. and Ross, N.L. (2001) Elasticity of CaSnO_3 perovskite. *Physics and Chemistry of Minerals*, **28**, 35–43.
- Larson, A.C. and Von Dreele, R.B. (1994) *General Structure Analysis System (GSAS)*. Los Alamos National Laboratory, LAUR 86–748, New Mexico, USA.
- Le Bail, A., Duroy, H. and Fourquet, J.L. (1988) *Ab-initio* structure determination of LiSbWO_6 by X-ray powder diffraction. *Materials Research Bulletin*, **23**, 447–452.
- McCammon, C.A., Pring, A., Keppler, H. and Sharp, T. (1995) A study of bernalite, $\text{Fe}(\text{OH})_3$, using Mössbauer spectroscopy, optical spectroscopy and transmission electron microscopy. *Physics and Chemistry of Minerals*, **22**, 11–20.
- Ross, C.R., II, Bernstein, L.R. and Waychunas, G.A. (1988) Crystal-structure refinement of stottite, $\text{FeGe}(\text{OH})_6$. *American Mineralogist*, **73**, 657–661.
- Ross, N.L. (2000) Framework structures. Pp. 257–287 in: *High-temperature and High-pressure Crystal Chemistry* (R.M. Hazen and R.T. Downes, editors). Reviews in Mineralogy and Geochemistry, **41**. Mineralogical Society of America and the Geochemical Society, Washington, D.C.
- Ross, N.L., Chaplin, T.D. and Welch, M.D. (2002) Compressibility of stottite, $\text{FeGe}(\text{OH})_6$: an octahedral framework with protonated oxygens. *American Mineralogist*, **87**, 1410–1414.
- Ross, N.L., Zhao, J. and Angel, R.J. (2004) Equations of state of GdAlO_3 and GdFeO_3 perovskites. *Journal of Physics: Condensed Matter*, **16**, 5721–5730.
- Welch, M.D. and Crichton, W.A. (2002a) Compressibility to 8 GPa at 298 K of the protonated octahedral framework mineral burtite, $\text{CaSn}(\text{OH})_6$. *Mineralogical Magazine*, **66**, 433–442.
- Welch, M.D. and Crichton, W.A. (2002b) Compressibility of clinocllore to 8 GPa at 298 K and a comparison with micas. *European Journal of Mineralogy*, **14**, 561–565.
- Welch, M.D. and Marshall, W.G. (2001) High-pressure behavior of clinocllore. *American Mineralogist*, **86**, 1380–1386.
- Williams, S.A. (1985) Mopungite, a new mineral from Nevada. *Mineralogical Record*, **16**, 73–74.
- Woodward, P.M. (1997) Octahedral tilting in perovskites I: Geometrical constraints. *Acta Crystallographica*, **B53**, 32–43.
- Zhao, J., Ross, N.L. and Angel, R.J. (2004) A new view of the high-pressure behaviour of GdFeO_3 -type perovskites. *Acta Crystallographica*, **B60**, 263–271.

[Manuscript received 15 August 2004;
revised 12 March 2005]

