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Barium-deficient celsian, $Ba_{1-x}Al_{2-2x}Si_{2+2x}O_8$ (x = 0.20 or 0.06)

Matthew G. Skellern, R. Alan Howie,* Eric E. Lachowski and Janet M. S. Skakle

Department of Chemistry, University of Aberdeen, Meston Walk, Aberdeen AB24 3UE, Scotland
Correspondence e-mail: r.a.howie@abdn.ac.uk

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Barium-deficient forms of celsian (barium aluminium silicate) with the formula $Ba_{1-x}Al_{2-2x}Si_{2+2x}O_8$ (x = 0.20 and 0.06) have been identified. In contrast with the celsian–orthoclase solid solutions which have been reported previously, these forms, refined in the space group *C*2/*m*, with Ba and one O atom in the 4*i* sites with *m* site symmetry, and a further O atom in a 4*g* site with twofold axial symmetry, suggest a slight solid solution with silica. The serendipitous preparation of the compounds represents a possible hazard associated with solid-state synthesis.

Comment

The mineral celsian, with the ideal formula $BaAl_2Si_2O_8$, is a barium feldspar. It is the only ternary phase within the BaO–Al_2O_3–SiO_2 phase diagram (Drummond, 1990), and is of interest due to its resistance to oxidation and reduction and its low coefficient of thermal expansion, amongst other properties (Bošković *et al.*, 1999). Originally, celsian was believed to have space group *C*2/*m*, with disorder of Al and Si over two sets of 8*j* sites (Taylor *et al.*, 1934), and indeed this provides an adequate description of the structure (Newnham & Megaw, 1960). It was shown, however, that the structure is better described by an *I*2/*c* supercell with a doubled *c* axis, although the differences are very subtle (Newnham & Megaw, 1960; Ribbe & Griffen, 1976). Similarly, in the polymorph paracelsian, small differences in the Si/Al ordering lead to a slight monoclinic distortion (space group $P2_1/a$), with a strong orthorhombic (*Pnam*) subcell (Smith, 1953; Chiari *et al.*, 1985). Finally, a hexagonal form, hexacelsian, is stable only at temperatures above 1863 K (Yoshiki & Matsumoto, 1951; Kakeuchi, 1958).

Celsian forms a continuous solid solution of formula $[K_{1-x}Ba_x][Al_{1+x}Si_{3-x}]O_8$ with orthoclase, the ideal formula of which is $KAlSi_3O_8$ (Thomas, 1950). Thus, in fact, previous reports on celsian are on the $x = 0.84$ and $x = 0.95$ members of this solid-solution series (Newnham & Megaw, 1960; Ribbe & Griffen, 1976), whereas paracelsian has been consistently reported as the stoichiometric end-member (x = 1) (Smith, 1953; Balakin & Belov, 1960; Chiari *et al.*, 1985).

The compounds studied here, (I) (with x = 0.20) and (II) (with x = 0.06), were by-products of melts of Ba-containing mixtures contained in platinum envelopes within aluminosilicate crucibles. The composition of (I) determined by EDXA (energy dispersive X-ray analysis) indicated that K was absent. However, the Ba:Al:Si ratio was non-stoichiometric and, apart from giving a range of overall compositions (Table 1), suggested either an excess of Si or a deficiency of Ba. The former is possible because of the open framework present in feldspars, and thus excess Si may easily be accommodated. Single-crystal X-ray diffraction was thus carried out, and the unit cell was determined to be comparable with the subcell of celsian (see *Experimental*). Further structure analysis was carried out in this subcell, as it adequately describes the structure and the emphasis here is primarily on the determination of the composition.

The structure of (I) was solved without reference to the previously determined structure of (II) and was, along with (II), found to be consistent with that of orthoclase. No evidence was found for interstitial Si, but rather the overall scattering and refined displacement parameters tended to point to Ba deficiency. Indeed, refinement of the Ba and Al/Si site occupancies in the manner noted below gave improved refinement and a final composition of $Ba_{0.80}Al_{1.60}Si_{2.40}O_8$. A second crystal from a completely different synthesis, (II), was similarly refined to give the composition $Ba_{0.94}Al_{1.88}Si_{2.12}O_8$. Thus, rather than a solid solution with orthoclase, these indicate a slight solid solution with SiO_2 and the solid-solution formula $Ba_{1-x}Al_{2-2x}Si_{2+2x}O_8$, where the two refinements give x = 0.20 and x = 0.06, with respective refined values of 0.2024 (14) and 0.062 (5).

The atoms selected for inclusion in the asymmetric unit and the labelling scheme used in the refinement of (I) can be seen in Fig. 1, along with the M—O (M is Al or Si) connectivity. Figs. 2 and 3 display the connectivity of the aluminosilicate framework more extensively. Precisely the same selection of atoms and labelling scheme were used in the final refinement of (II). In (I) and (II), Ba—O (nine-coordinate Ba) and M—O (tetrahedral M) distances [those for (II) are given in square brackets] are in the ranges 2.665 (2)–3.1212 (16) Å [2.645 (5)–3.120 (4) Å] and 1.6530 (17)–1.6830 (9) Å [1.675 (4)–1.694 (2) Å], respectively, and these are unexceptional (see also Table 2). The difference in each pair of ranges, although they overlap within the pair, is entirely consistent with the change in Ba and Al content between (I) and (II).

Previous reports have cited similar compositions. $Ba_{0.75}Al_{1.5}Si_{2.5}O_8$ was found, though, to have the hollandite structure (Zhang & Burnham, 1994). This is, perhaps, not surprising, as it has been shown that certain feldspar materials can be transformed to hollandite under high pressure (Ringwood *et al.*, 1967). $KAlSi_3O_8$ (sanidine) transforms to hollandite under 120 kbars of pressure (1 bar = 10^5 Pa) at 1173 K (Ringwood *et al.*, 1967) and celsian itself partially transforms under similar conditions (Reid & Ringwood, 1969). This is

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also consistent with the observation that the formation of celsian is more difficult in compositions with high SiO_2 content (Thomas, 1950).

Bond-valence sums (BVS; Brown & Altermatt, 1985) calculated for each composition (Table 3) provide a check on the structure solution and the assumptions made. The composition $Ba_{0.80}Al_{1.60}Si_{2.40}O_8$ gives a value of 3.60 for Al1/Si1 and 3.71 for Al2/Si2, which compare well with the expected value of 3.60 for Al:Si 0.40:0.60. The BVS for Ba is 1.65, compared with the expected value of 1.60. This is in reasonable agreement and provides further evidence for Ba deficiency. Similar results were obtained for the other composition. In both cases, slightly higher values were obtained for Al2/Si2, which might indicate more Si on this site. This, however, would have the effect of reducing the BVS on the Al1/Si1 site which, in both cases, was in very good agreement with the expected values. Therefore, the model used is perceived as giving an adequate representation of the structures.

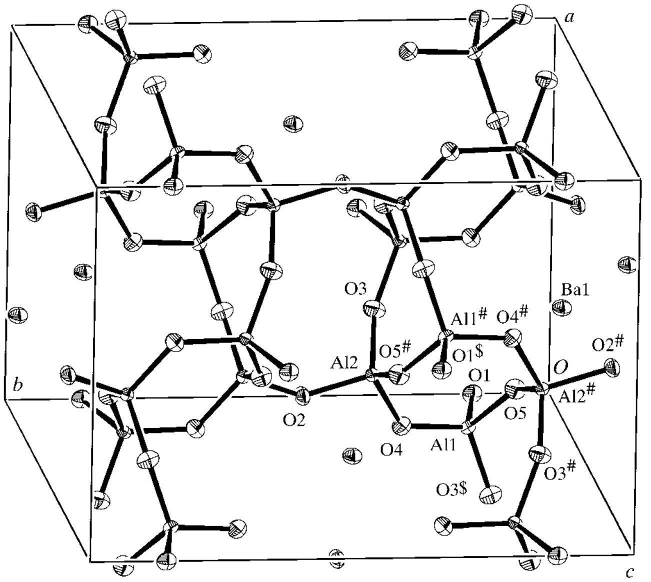

Figure 1
The cell of (I). Atoms are shown as 50% probability displacement ellipsoids. Ba···O contacts have been omitted for clarity. Atoms labelled with a hash (#) or dollar sign ($) are at the symmetry positions $(\frac{1}{2}-x, \frac{1}{2}-y, 1-z)$ and $(x-\frac{1}{2}, \frac{1}{2}-y, z)$, respectively.

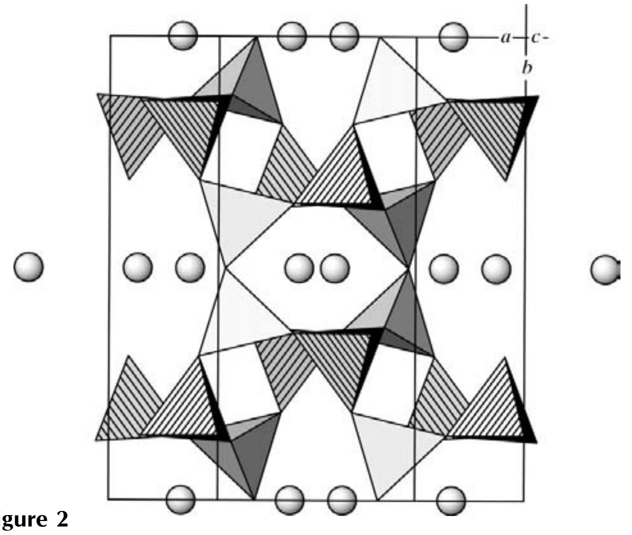

Figure 2
A portion of the structure of (I), projected on (001), with the z coordinates of the atoms confined to the range $-\frac{1}{4}$ to $\frac{5}{4}$. Al1/Si1 and Al2/S12 tetrahedra are hatched and open, respectively, and Ba atoms are shown as spheres of arbitrary radii. Ba···O contacts have been omitted for clarity.

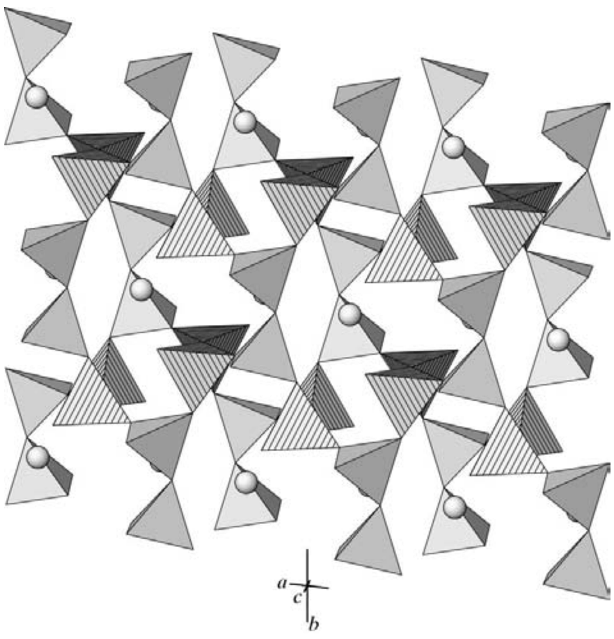

Figure 3
A more extensive view of the structure of (I), viewed along c (up out of the page). The representation is otherwise the same as that in Fig. 2.

Experimental

Both compositions were by-products of melts containing barium. For composition (I) (x = 0.20), a powder sample of $Ba_2LaV_3O_{11}$ was prepared by solid-state reaction. The reagents used were $BaCO_3$ and La_2O_3 (both 99%; BDH Chemicals Ltd, Poole, England), and V_2O_5 (99.2%; Johnson Matthey, Royston, England). La_2O_3 was dried at 1173 K prior to use, and $BaCO_3$ and V_2O_5 were both dried at 573 K. Single crystals were grown according to the method of Huang *et al.* (1994). The powder was melted at 1573 K and held at this temperature for 30 min. The temperature was then decreased at a rate of 1 K min^{-1} to 1523 K, whereupon it was increased again to 1573 K in steps of 2 K min^{-1}. This was repeated three times in order to obtain, after cooling to room temperature, crystals of (I) suitable for analysis. For composition (II) (x = 0.06), the single crystal was accidentally grown during a study of the ternary phase diagram BaO–Li_2O–TiO_2 (Suckut, 1991). The target phase was in the range 10–18 mol% BaO, 12–16 mol% Li_2O and 72–77 mol% TiO_2, with an idealized formula of $BaLi_2Ti_6O_{14}$. The starting reagents were $BaCO_3$ (99.5%; May & Baker Ltd, Dagenham, England), TiO_2 (99.9%; Aldrich, USA) and

Li_2CO_3 (99%; FSA Laboratory Supplies, Loughborough, England). The composition 72 mol% TiO_2, 16.5 mol% Li_2O and 11.5 mol% BaO was used in an attempt to grow single crystals of the desired phase. The melting point of this composition was found to be 1533 K; the powder was heated to 10 K below the melting point and cooled at a rate of 0.5 K $\min^{-1}$ to 30 K below the melting point. It was then heated to 15 K below the melting point and finally cooled to room temperature. In both cases, the powder was placed in a platinum envelope in an aluminosilicate crucible. BaO is well known as a good fluxing agent in the growth of single crystals, and clearly has brought about escape of the Ba-containing melt from the envelope and reaction with the aluminosilicate crucible, to give the barium aluminosilicate phases described above. Thus, in addition to providing information on barium-deficient celsian phases, this constitutes a warning for solid-state chemists.

Compound (I)

Crystal data

$Ba_{0.80}Al_{1.60}Si_{2.40}O_8$
$M_r = 348.12$
Monoclinic, $C2/m$
$a = 8.6090 (8)$ Å
$b = 13.0658 (12)$ Å
$c = 7.2047 (7)$ Å
$\beta = 115.418 (2)°$
$V = 731.96 (12)$ Å^3
$Z = 4$

$D_x = 3.159$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 2197 reflections
$\theta = 4.8$–$32.4°$
$\mu = 4.96$ mm^{-1}
$T = 292 (2)$ K
Block, colourless
$0.20 \times 0.18 \times 0.14$ mm

Data collection

Bruker SMART 1000 CCD area-detector diffractometer
φ/ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{\min} = 0.349$, $T_{\max} = 0.500$
3542 measured reflections

1366 independent reflections
1223 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.022$
$\theta_{\max} = 32.5°$
$h = -12 \rightarrow 13$
$k = -16 \rightarrow 19$
$l = -10 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.056$
$S = 1.07$
1366 reflections
64 parameters

$w = 1/[\sigma^2(F_o^2) + (0.0302P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.73$ e Å^{-3}
$\Delta\rho_{\min} = -0.82$ e Å^{-3}

Compound (II)

Crystal data

$Ba_{0.94}Al_{1.88}Si_{2.12}O_8$
$M_r = 367.03$
Monoclinic, $C2/m$
$a = 8.633 (6)$ Å
$b = 13.063 (8)$ Å
$c = 7.214 (5)$ Å
$\beta = 115.17 (5)°$
$V = 736.3 (9)$ Å^3
$Z = 4$

$D_x = 3.311$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 14 reflections
$\theta = 12.3$–$14.2°$
$\mu = 5.65$ mm^{-1}
$T = 298 (2)$ K
Block, colourless
$0.6 \times 0.6 \times 0.3$ mm

Data collection

Nicolet *P*3 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.127$, $T_{\max} = 0.551$
1169 measured reflections
1112 independent reflections
1111 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.049$
$\theta_{\max} = 30°$
$h = 0 \rightarrow 12$
$k = 0 \rightarrow 18$
$l = -10 \rightarrow 9$
2 standard reflections every 50 reflections
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.095$
$S = 1.36$
1112 reflections
65 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0373P)^2 + 6.7094P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 1.31$ e Å^{-3}
$\Delta\rho_{\min} = -1.03$ e Å^{-3}
Extinction correction: *SHELXL*97 (Sheldrick, 1997)
Extinction coefficient: 0.0261 (16)

Al/Si and Ba site occupancies were initially refined, but were constrained so as to ensure charge balance, while assuming full occupancy but complete disorder of the Al/Si sites.

For compound (I), data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990);

Table 1
Results of EDXA analysis of a range of crystals from the preparation of (I) (atom%).

	Al	Si	Ba
1	35.6 (5)	48.5 (6)	15.9 (2)
2	34.9 (6)	49.5 (7)	15.6 (2)
3	33.5 (6)	51.8 (7)	14.7 (2)
4	34.4 (4)	49.6 (5)	16.09 (13)
5	35.6 (5)	48.4 (6)	16.01 (16)
6	35.9 (6)	47.6 (7)	16.6 (2)
7	34.3 (9)	49.3 (10)	16.3 (3)
Mean	34.9	49.2	15.9
σ_{n-1}	0.9	1.3	0.6

Table 2
Selected bond lengths and angles (Å, °) for compositions (I) and (II).

	(I) ($x = 0.20$)	(II) ($x = 0.06$)
Ba1—O2$^{\rm i}$	2.665 (2)	2.645 (2)
Ba1—O1	2.8689 (14)	2.853 (3)
Ba1—O5	2.9307 (17)	2.910 (4)
Ba1—O3$^{\rm ii}$	2.9599 (17)	2.933 (4)
Ba1—O4$^{\rm i}$	3.1212 (16)	3.120 (4)
*M*1—O3$^{\rm iii}$	1.6653 (17)	1.676 (4)
*M*1—O4	1.6692 (16)	1.675 (4)
*M*1—O5	1.6784 (16)	1.682 (4)
*M*1—O1	1.6830 (9)	1.694 (2)
*M*2—O3	1.6530 (17)	1.669 (4)
*M*2—O5$^{\rm iv}$	1.6615 (16)	1.683 (4)
*M*2—O4	1.6656 (16)	1.675 (4)
*M*2—O2	1.6710 (10)	1.681 (2)
O4—*M*1—O3$^{\rm iii}$	112.34 (9)	112.64 (19)
O5—*M*1—O3$^{\rm iii}$	112.99 (9)	114.1 (2)
O1—*M*1—O3$^{\rm iii}$	103.65 (7)	102.58 (16)
O5—*M*1—O4	109.76 (9)	109.97 (19)
O1—*M*1—O4	114.57 (9)	114.9 (2)
O1—*M*1—O5	103.15 (7)	102.13 (17)
O3—*M*2—O5$^{\rm iv}$	112.15 (8)	112.49 (19)
O4—*M*2—O5$^{\rm iv}$	113.39 (9)	114.1 (2)
O2—*M*2—O5$^{\rm iv}$	108.40 (10)	108.4 (2)
O4—*M*2—O3	112.17 (9)	112.5 (2)
O2—*M*2—O3	107.93 (10)	107.3 (2)
O2—*M*2—O4	102.11 (9)	101.2 (2)
*M*1—O1—*M*1$^{\rm v}$	140.97 (14)	139.7 (3)
*M*2—O2—*M*2$^{\rm vi}$	135.57 (14)	134.2 (3)
*M*2—O3—*M*1$^{\rm vii}$	150.59 (12)	149.3 (2)
*M*1—O4—*M*2	128.89 (10)	128.3 (2)
*M*1—O5—*M*2$^{\rm iv}$	139.61 (11)	138.7 (2)

Notes: *M*1 and *M*2 represent the Al1/Si1 and Al2/Si2 sites, respectively. Symmetry codes: (i) $\frac{1}{2} + x, y - \frac{1}{2}, z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, -z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z$; (iv) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$; (v) $-x, y, -z$; (vi) $x, 1 - y, z$; (vii) $\frac{1}{2} + x, \frac{1}{2} - y, z$.

Table 3
Bond-valence sums for $Ba_{1-x}Al_{2-2x}Si_{2+2x}O_8$.

	Composition (I) (x = 0.20)		Composition (II) (x = 0.06)	
	Expected	Calculated	Expected	Calculated
Ba1	1.60	1.65	1.88	1.74
Al1/Si1	3.60	3.60	3.53	3.55
Al2/Si2	3.60	3.71	3.53	3.59

program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* in *OSCAIL* (McArdle, 1994, 2000) and *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

For compound (II), data collection: *P*3/*R*3 (Nicolet, 1980); cell refinement: *P*3/*R*3; data reduction: *RDNIC* (Howie, 1980); program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); software used to prepare material for publication: *SHELXL*97.

We acknowledge the use of the EPSRC Chemical Database Service at Daresbury (Fletcher *et al.*, 1996).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1678). Services for accessing these data are described at the back of the journal.

References

Balakin, V. V. & Belov, N. V. (1960). *Kristallografiya*, **5**, 864–868.

Bošković, S., Kosanović, D., Bahloul-Hourlier, Dj., Thomas, P. & Kiss, S. J. (1999). *J. Alloys Compd*, **290**, 230–235.

Brown, I. D. & Altermatt, D. (1985). *Acta Cryst.* B**41**, 244–247.

Bruker (1998). *SMART*. Version 5.054. Bruker AXS Inc., Madison, Wisconsin, USA.

Bruker (2000). *SADABS* (Version 2.03) and *SAINT* (Version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Chiari, G., Gazzoni, G. G., Craig, J. R., Gibbs, G. V. & Louisnathan, S. J. (1985). *Am. Mineral.* **70**, 969–974.

Dowty, E. (1999). *ATOMS for Windows*. Version 5.0.7. Shape Software, 521 Hidden Valley Road, Kingsport, TN 37663, USA.

Drummond, C. H. (1990). *J. Non-Cryst. Solids*, **123**, 114–128.

Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.

Howie, R. A. (1980). *RDNIC*. University of Aberdeen, Scotland.

Huang, J., Gu, Q. & Sleight, A. W. (1994). *J. Solid State Chem.* **110**, 226–233.

Kakeuchi, Y. (1958). *Mineral. J.* **2**, 311–332.

McArdle, P. (1994). *J. Appl. Cryst.* **27**, 438–439.

McArdle, P. (2000). *OSCAIL for Windows*. National University of Ireland, Galway, Ireland.

Newnham, R. E. & Megaw, H. D. (1960). *Acta Cryst.* **13**, 303–312.

Nicolet (1980). *P3/R3 Data Collection Operator's Manual*. Nicolet XRD Corporation, Cupertino, California, USA.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Reid, A. F. & Ringwood, A. E. (1969). *J. Solid State Chem.* **1**, 6–9.

Ribbe, P. H. & Griffen, D. A. (1976). *Am. Mineral.* **61**, 414–418.

Ringwood, A. E., Reid, A. F. & Wadsley, A. D. (1967). *Acta Cryst.* **23**, 1093–1095.

Sheldrick, G. M. (1990). *Acta Cryst.* A**46**, 467–473.

Sheldrick, G. M. (1997). *SHELXL*97. University of Göttingen, Germany.

Smith, J. V. (1953). *Acta Cryst.* **6**, 613–620.

Suckut, C. A.-K. (1991). MSc thesis, University of Aberdeen, Scotland.

Taylor, W. H., Darbyshire, J. A. & Strunz, H. (1934). *Z. Kristallogr.* **87**, 464–466.

Thomas, R. H. (1950). *J. Am. Ceram. Soc.* **33**, 34–44.

Yoshiki, B. & Matsumoto, K. (1951). *J. Am. Ceram. Soc.* **34**, 283–286.

Zhang, J. & Burnham, C. W. (1994). *Am. Mineral.* **79**, 168–174.