

BaY₂Si₃O₁₀: a new flux-grown trisilicate

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Received 29 September 2006

Accepted 11 October 2006

Online 10 November 2006

BaY₂Si₃O₁₀, barium diyttrium trisilicate, is a new silicate grown from a molybdate-based flux. The structure is based on zigzag chains, parallel to [010], of edge-sharing distorted YO₆ octahedra, linked by horseshoe-shaped trisilicate groups and Ba atoms in irregular eight-coordination. The layered character of the structure is caused by a succession of zigzag chains and trisilicate groups in planes parallel to ($\bar{1}01$). The Ba atoms occupy narrow channels extending parallel to [100]. The mean Y—O, Si—O and Ba—O bond lengths are 2.268, 1.626 and 1.633, and 2.872 Å, respectively. The two symmetry-equivalent terminal SiO₄ tetrahedra in the Si₃O₁₀ unit adopt an eclipsed conformation with respect to the central SiO₄ tetrahedron; the Si—O—Si and Si—Si—Si angles are 136.35 (9) and 96.12 (4)°, respectively. One Ba, one Si and two O atoms are located on mirror planes; all remaining atoms are in general positions. The geometry of isolated trisilicate groups in inorganic compounds is briefly discussed.

Comment

As part of a comprehensive study of the synthesis (by hydrothermal and flux growth methods), crystal chemistry and topologies of M^I –(M^{II})– M^{III} silicates (M^I = Na, K, Rb and Cs; M^{II} = Sr and Ba; M^{III} = Sc, V, Cr, Fe, In, Y and Yb) with mixed octahedral–tetrahedral frameworks (Wierzbicka *et al.*, 2005), the title compound, (I), was prepared from a molybdate-based flux. Further new Ba–Y and Sr–Y silicates prepared by the flux method include BaKYSi₂O₇ (Kolitsch *et al.*, 2006a), BaY₄Si₅O₁₇ (Kolitsch *et al.*, 2006b) and SrY₂Si₃O₁₀ (Kolitsch *et al.*, 2006c; Wierzbicka *et al.*, 2006). The latter trisilicate is not isostructural with (I).

The asymmetric unit of (I) contains one Ba, one Y, two Si and six O atoms. Atoms Ba, Si1, O1 and O2 are located on mirror planes ($y = \frac{1}{4}$); all remaining atoms are in general positions. The building units in the crystal structure of (I) are YO₆ octahedra, SiO₄ tetrahedra and eight-coordinated Ba atoms. The structure is based on zigzag chains, parallel to [010], of edge-sharing distorted YO₆ octahedra, linked by horseshoe-shaped trisilicate (Si₃O₁₀) groups and Ba in irre-

gular eight-coordination (Figs. 1 and 2); two further O-atom neighbours (O6) of the Ba atom, each located 3.462 (2) Å away, are too remote to be considered as ligands.

A succession of octahedral zigzag chains and trisilicate groups in planes parallel to ($\bar{1}01$) results in (I) having an octahedral–tetrahedral layered character (Fig. 1). The strong linkage of these two different polyhedral units along [100] results in a heteropolyhedral slab parallel to (001) that is linked to adjacent slabs only *via* atoms O5 and Ba; the latter occupy narrow channels extending parallel to [100] (Fig. 1a). The mean Y—O, Si—O and Ba—O bond lengths are 2.268, 1.626 and 1.633, and 2.872 Å, respectively (Table 1). The horseshoe-shaped geometry of the trisilicate unit is noteworthy. The two symmetry-equivalent terminal SiO₄ tetrahedra in this unit show an eclipsed conformation with respect to the central SiO₄ tetrahedron; the Si1—O—Si2 and Si2—Si1—Si2 angles are 136.35 (9) and 96.12 (4)°, respectively.

Bond-valence sums for all atoms were calculated using the bond-valence parameters of Brese & O'Keeffe (1991). The bond-valence sums are 1.76 (Ba1), 3.05 (Y1), 3.98 (Si1), 3.91 (Si2), 2.14 (O1), 2.02 (O2), 1.96 (O3), 1.88 (O4), 1.99 (O5) and 1.92 valence units (O6), and thus are all reasonably close to ideal valencies. Although the sum calculated for Ba1 may

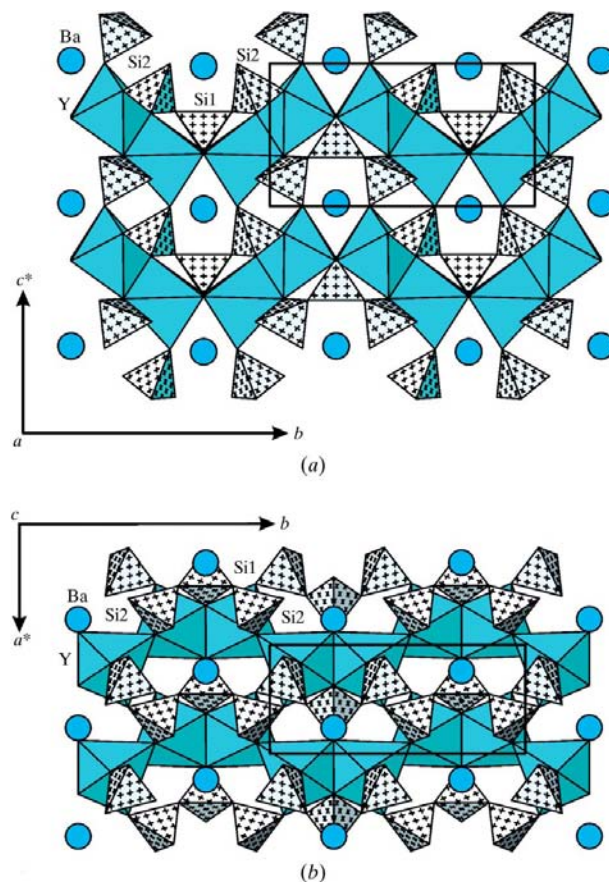


Figure 1

The crystal structure of BaY₂Si₃O₁₀, projected (a) along [100] and (b) along [001]. Zigzag chains parallel to [010] of edge-sharing distorted YO₆ octahedra are linked by horseshoe-shaped trisilicate groups and Ba atoms (shown as spheres).

appear somewhat low, it is well known that Ba compounds in general tend to give poor bond-valence sums (Brown & Wu, 1976).

Trisilicates such as (I) are uncommon representatives of the silicate family. In a first overview on natural and synthetic trisilicate compounds, Povarennykh *et al.* (1976) characterize only 17 compounds, and state 'the scarcity of the minerals is due to the difficulty in forming stoichiometric compounds with such a large silicate anion and the instability of the Si_3O_{10} group relative to Si_2O_7 and Si_3O_9 during mineral formation.' Few further examples of trisilicates have been described since then.

In the following, we provide a brief overview of silicate compounds containing isolated Si_3O_{10} units, including the protonated derivative $\text{Si}_3\text{O}_8(\text{OH})_2$, where the two terminal SiO_4 groups are protonated. Trisilicate units show a notably variable geometry: they can appear nearly linear to slightly curved, with Si—Si—Si angles between about 160 and 150° [e.g. $\text{Na}_2\text{Ca}_3[\text{Si}_3\text{O}_{10}]$ (Treushnikov *et al.*, 1971) and isotypic $\text{Na}_2\text{Cd}_3[\text{Si}_3\text{O}_{10}]$ (Simonov *et al.*, 1977); ardenite, $\text{Mn}_2(\text{Mn,Ca})_2(\text{Al,Mg})_6(\text{OH})_6 [(\text{As,V,Si})\text{O}_4][\text{SiO}_4]_2[\text{Si}_3\text{O}_{10}]$ (Donnay & Allmann, 1968; Pasero *et al.*, 1994); high-pressure L-type $\text{REE}_2\text{Si}_2\text{O}_7$, where REE is a rare earth element (Fleet & Liu, 2004); and B-type $\text{REE}_4[\text{Si}_3\text{O}_{10}][\text{SiO}_4]$ (Felsche, 1972; Fleet & Liu, 2003; Hartenbach *et al.*, 2003)].

More or less strongly curved units, with Si—Si—Si angles between about 134 and 103°, occur in $\text{SrY}_2[\text{Si}_3\text{O}_{10}]$ (Kolitsch *et al.*, 2006c; Wierzbicka *et al.*, 2006), in rosenhahnite, $\text{Ca}_3[\text{Si}_3\text{O}_8(\text{OH})_2]$ (Jeffery & Lindley, 1973; Wan *et al.*, 1977), in $\text{Na}_4\text{Cd}_2[\text{Si}_3\text{O}_{10}]$ (Simonov *et al.*, 1968, 1978), and in the microporous compound MCV-2, $\text{Ba}_2\text{Na}[\text{Na}_{0.5}(\text{H}_2\text{O})_{0.5}]_2\text{Zr}_2\text{Si}_6\text{O}_{19} \cdot 3\text{H}_2\text{O}$ (Si—Si—Si = 103.4°; Ferdov *et al.*, 2005).

Finally, Si_3O_{10} units with horseshoe-shaped geometries and Si—Si—Si angles ranging between 98.1 and 76.2° are encountered in kilchoanite, $\text{Ca}_6[\text{SiO}_4][\text{Si}_3\text{O}_{10}]$ (Taylor, 1971), in the title compound, in kinoite, $\text{Ca}_2\text{Cu}_2(\text{H}_2\text{O})_2[\text{Si}_3\text{O}_{10}]$ (Laughon, 1971), in fluorthalenite-(Y)-type $\text{M}_3\text{F}[\text{Si}_3\text{O}_{10}]$,

where $M = \text{Y, Dy, Ho}$ and Er (Yakubovich *et al.*, 1988; Schleid & Müller-Bunz, 1998; Müller-Bunz & Schleid, 2000), in $\text{K}_3\text{Y}[\text{Si}_3\text{O}_8(\text{OH})_2]$ (Maksimov *et al.*, 1968), and in isotypic $\text{K}_3\text{Ho}[\text{Si}_3\text{O}_8(\text{OH})_2]$ (Ponomarev *et al.*, 1988) and $\text{K}_3\text{Yb}[\text{Si}_3\text{O}_8(\text{OH})_2]$ (Filipenko *et al.*, 1999).

It is conspicuous that the narrowest Si—Si—Si angles are predominantly shown by silicates containing either F atoms or OH groups (not bonded to Si) or $[\text{Si}_3\text{O}_8(\text{OH})_2]$ groups. Preliminary studies of the several possible influences on the unusually variable geometry of Si_3O_{10} groups in the mentioned compounds indicate that very narrow Si—Si—Si angles preferentially occur in structures where larger metal cations are octahedrally coordinated. A more detailed discussion, including a comparison with compounds containing Ge_3O_{10} and Al_3O_{10} groups, will be presented as part of the description of the crystal structure of $\text{SrY}_2\text{Si}_3\text{O}_{10}$ (Wierzbicka *et al.*, 2006).

Experimental

The title compound was grown from a $\text{BaO-Rb}_2\text{O-MoO}_3$ flux containing dissolved precursor compounds of Ba, Rb, Y and Si (experimental parameters: 1 g BaCO_3 , 0.6 g Rb_2CO_3 , 1 g MoO_3 , 0.1614 g Y_2O_3 , 0.1718 g SiO_2 ; Pt crucible covered with a lid, $T_{\text{max}} = 1423 \text{ K}$, holding time 3 h, cooling rate 2 K h^{-1} , $T_{\text{min}} = 1173 \text{ K}$, slow cooling to room temperature after switching off the furnace). The reaction products were recovered by dissolving the flux in distilled water. $\text{BaY}_2\text{Si}_3\text{O}_{10}$ formed small (up to about 0.10 mm) pseudo-hexagonal plates, accompanied by rectangular plates to thick tabular crystals of a silicate with the tentative chemical formula $\text{Rb}_3\text{YSi}_8\text{O}_{19}$, which, according to preliminary results, appears to be a superstructure variant of $\text{Cs}_3\text{ScSi}_8\text{O}_{19}$ (MCV-1; Kolitsch & Tillmanns, 2004) and isotypic $\text{Cs}_3\text{YSi}_8\text{O}_{19}$ (Kolitsch *et al.*, 2006a). Preliminary results from single-crystal X-ray diffraction studies prove that an isotypic Yb analogue of the title compound can also be synthesized; this analogue has the following unit-cell parameters: $a = 5.377 (1) \text{ \AA}$, $b = 12.117 (2) \text{ \AA}$, $c = 6.790 (1) \text{ \AA}$, $\beta = 106.50 (3)^\circ$ and $V = 424.17 (12) \text{ \AA}^3$.

Crystal data

$\text{BaY}_2\text{Si}_3\text{O}_{10}$
 $M_r = 559.43$
 Monoclinic, $P2_1/m$
 $a = 5.399 (1) \text{ \AA}$
 $b = 12.179 (2) \text{ \AA}$
 $c = 6.852 (1) \text{ \AA}$
 $\beta = 106.37 (3)^\circ$
 $V = 432.28 (14) \text{ \AA}^3$

$Z = 2$
 $D_x = 4.298 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 $\mu = 18.28 \text{ mm}^{-1}$
 $T = 293 (2) \text{ K}$
 Fragment, colourless
 $0.11 \times 0.10 \times 0.02 \text{ mm}$

Data collection

Nonius KappaCCD diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SCALEPACK; Otwinowski *et al.*, 2003)
 $T_{\text{min}} = 0.238$, $T_{\text{max}} = 0.711$

3139 measured reflections
 1636 independent reflections
 1578 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.013$
 $\theta_{\text{max}} = 32.6^\circ$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.016$
 $wR(F^2) = 0.040$
 $S = 1.10$
 1636 reflections
 80 parameters

$w = 1/[\sigma^2(F_o^2) + (0.02P)^2 + 0.43P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.97 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -1.29 \text{ e \AA}^{-3}$
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0116 (5)

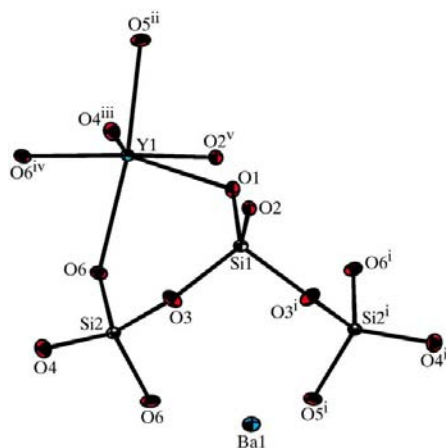


Table 1

Selected geometric parameters (Å, °).

Si1—O1	1.611 (2)	Y1—O6 ^{iv}	2.2769 (14)
Si1—O2	1.619 (2)	Y1—O6	2.2883 (14)
Si1—O3	1.6368 (14)	Y1—O1	2.2920 (11)
Si2—O4	1.6037 (15)	Y1—O2 ^v	2.3497 (12)
Si2—O5	1.6096 (15)	Ba1—O5 ^{vi}	2.7013 (14)
Si2—O6	1.6421 (14)	Ba1—O4 ^{vii}	2.8245 (14)
Si2—O3	1.6781 (15)	Ba1—O2 ^{viii}	2.881 (2)
Y1—O5 ⁱⁱ	2.1935 (14)	Ba1—O1 ^{viii}	2.965 (2)
Y1—O4 ⁱⁱⁱ	2.2092 (15)	Ba1—O3 ⁱ	3.0392 (15)
Si1—O3—Si2	136.35 (9)	Si2—Si1—Si2 ⁱ	96.12 (4)

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

The highest electron-density peak in (I) is located 0.98 Å from the O5 site and the deepest hole in the difference map is located 0.99 Å from the Ba site.

Data collection: *COLLECT* (Nonius, 2005); cell refinement: *SCALEPACK* (Otwinowski *et al.*, 2003); data reduction: *DENZO* (Otwinowski *et al.*, 2003) and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

Financial support by the Austrian Science Foundation (FWF) (grant No. P17623-N10) and the International Centre for Diffraction Data (grant No. 90-03 ET) are gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3015). Services for accessing these data are described at the back of the journal.

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