Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

$Ba_2Gd_2(Si_4O_{13})$: a silicate with finite Si_4O_{13} chains

Maria Wierzbicka-Wieczorek,[a]* Uwe Kolitsch[b] and Ekkehart Tillmanns[a]

[a]Universität Wien, Institut für Mineralogie und Kristallographie, Geozentrum, Althanstrasse 14, A-1090 Wien, Austria, and [b]Mineralogisch-Petrographische Abt., Naturhistorisches Museum Wien, Burgring 7, A-1010 Wien, Austria
Correspondence e-mail: maria.wierzbicka@univie.ac.at

Received 17 December 2009
Accepted 22 January 2010
Online 3 February 2010

The title compound, dibarium digadolinium(III) tetrasilicate, crystallized from a molybdate-based flux. It represents a new structure type and contains finite zigzag-shaped C_2-symmetric Si_4O_{13} chains and Gd_2O_{12} dimers built of edge-sharing GdO_7 polyhedra. The [9+1]-coordinated Ba atoms are located in voids in the atomic arrangement. All atoms are in general positions except for one O atom, which lies on a twofold axis. The structure is compared with those of the few other known tetrasilicates.

Comment

In a comprehensive ongoing study we are focusing on the preparation, structural characterization and classification of novel microporous and small-pore mixed-framework silicates containing seven specific octahedrally coordinated M^{3+} cations (M = Sc, V, Cr, Fe, In, Y and Yb). These poorly known members of the silicate family are expected to have useful properties and interesting technical applications, similar to the related mixed-framework (SiO_4–$M^{4+}O_6$) titanosilicates and zirconosilicates. As part of our study, we have recently also included compounds containing the Gd^{3+} cation for comparison purposes, as this cation may either show octahedral coordination or have higher coordination numbers (7–8). The title compound, (I), was obtained as a by-product during the preparation of the Gd analogue of $BaY_2Si_3O_{10}$ and isotypic Sc and lanthanide representatives (Kolitsch *et al.*, 2006; Wierzbicka-Wieczorek, 2007; see also Kolitsch *et al.*, 2009). It represents a novel structure type and is a new representative of a small class of tetrasilicates with finite Si_4O_{13} chains (groups).

Additional flux-growth syntheses involving Gd^{3+} have so far yielded the following three Gd silicates: $Rb_3GdSi_8O_{19}$ and $Cs_3GdSi_8O_{19}$, both isotypic with $Cs_3ScSi_8O_{19}$ (Kolitsch & Tillmanns, 2004), and $BaKGdSi_2O_7$, isotypic with the disilicates $BaKREESi_2O_7$ (REE = Y, Yb and Sc; Kolitsch *et al.*, 2009) and $SrKScSi_2O_7$ (Wierzbicka-Wieczorek, 2007).

The asymmetric unit in monoclinic (I) contains one Ba, one Gd, two Si and seven O atoms (Fig. 1). All atoms are in general positions except O3, which lies on a twofold axis. Bond-valence sums for all atoms were calculated using the bond-valence parameters from Brese & O'Keeffe (1991): 2.01 (Ba), 3.05 (Gd), 3.99 (Si1), 3.85 (Si2), 2.06 (O1), 2.08 (O2), 2.27 (O3), 1.94 (O4), 1.84 (O5), 1.86 (O6) and 1.96 (O7) v.u. (valence units). Thus, these are all reasonably close to ideal valencies. (The oxygen ligands O3 and O4 represent bridging O atoms within the finite Si_4O_{13} chain and are expected to have slightly high bond-valence sums. However, only atom O3 shows an elevated value, while O4, bonded also to Gd, shows a normal value.)

The atomic arrangement is based on finite zigzag-shaped Si_4O_{13} chains and Gd_2O_{12} dimers built of edge-sharing GdO_7 polyhedra (Fig. 2). The latter are rather irregular, although they may be described as monocapped octahedra (the capping atom being O6). The Gd_2O_{12} dimers are linked by SiO_4 tetrahedra to form a heteropolyhedral slab in the *ab* plane. These slabs are connected to adjacent slabs only *via* a bridging O3 atom of the Si_4O_{13} chain. The $Si1O_4$ tetrahedron shares the O2–O4 edge with the GdO_7 polyhedron. The [9+1]-coordinated Ba atoms are located in voids of the atomic arrangement, with Ba—O distances in the range 2.699 (3)–3.319 (3) Å.

The two non-equivalent SiO_4 tetrahedra form a tetrasilicate group (Si_4O_{13}) which can also be described as a finite chain. The bond-length distortion of the SiO_4 tetrahedra is remarkable (Table 1) and more pronounced than in comparable di- and trisilicates. The bond-angle distortion is also very strong; for the $Si1O_4$ and $Si2O_4$ tetrahedra the distortion parameters $\sigma(\text{oct})^2$ (Robinson *et al.*, 1971) are 38.60 and 22.09, respectively. The most distorted SiO_4 units are the two Si1-centred ones in the centre of the finite chain. This can be explained by the electrostatic repulsion between Si1 and the neighbouring Si1 and Si2 atoms. A similarly strong distortion of SiO_4

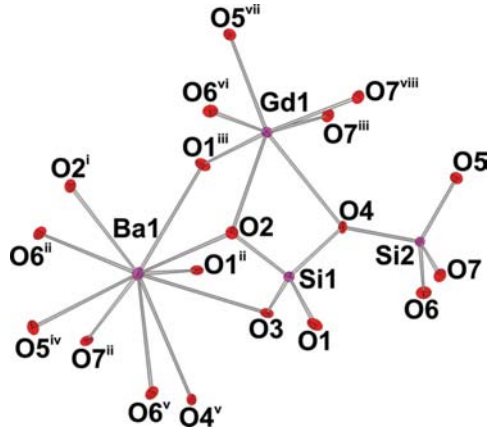

Figure 1
A view of the basic connectivity in $Ba_2Gd_2(Si_4O_{13})$, shown with displacement ellipsoids at the 50% probability level. [Symmetry codes: (i) $-x+\frac{1}{2}, y+\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y+1, -z+\frac{1}{2}$; (iii) $x, y+1, z$; (iv) $x+\frac{1}{2}, -y+\frac{1}{2}, z+\frac{1}{2}$; (v) $-x, y, -z+\frac{1}{2}$; (vi) $x+\frac{1}{2}, y+\frac{1}{2}, z$; (vii) $-x, -y+1, -z$; (viii) $-x, -y, -z$.]

 doi:10.1107/S0108270110002842

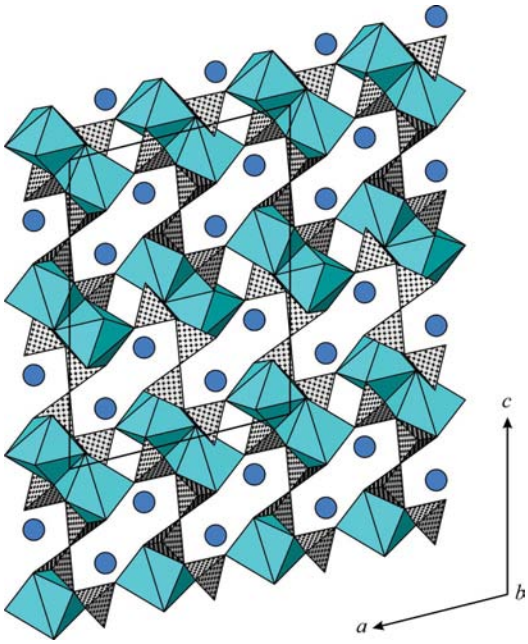

Figure 2
A view of $Ba_2Gd_2(Si_4O_{13})$ along [010]. Dimers built of edge-sharing GdO_7 polyhedra are linked *via* a zigzag-shaped finite Si_4O_{13} chain (SiO_4 tetrahedra are marked with crosses). Ba atoms are shown as spheres. The unit cell is outlined.

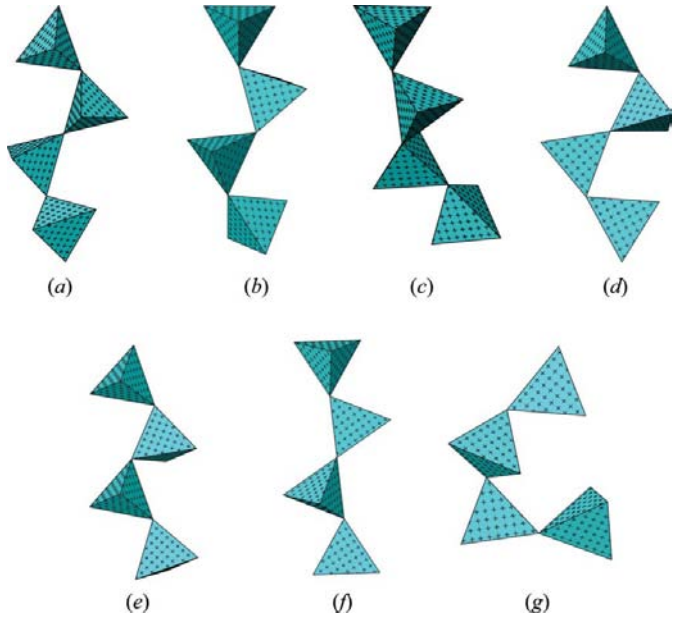

Figure 3
An overview of the configurations of the Si_4O_{13} unit in the known tetrasilicates. (*a*) $Ba_2Gd_2(Si_4O_{13})$, (*b*) $Ag_{10}(Si_4O_{13})$, (*c*) $Na_4Sc_2(Si_4O_{13})$, (*d*) $Ba_2Nd_2(Si_4O_{13})$, (*e*) $K_5Eu_2F(Si_4O_{13})$, (*f*) $Ag_{18}(SiO_4)_2(Si_4O_{13})$ and (*g*) $La_6(Si_4O_{13})(SiO_4)_2$.

tetrahedra is observed in other chemically related tetrasilicates such as $Ba_2Nd_2(Si_4O_{13})$ (range of Si—O bond lengths in the most distorted SiO_4 unit is 1.582–1.670 Å; Tamazyan & Malinovskii, 1985).

The configuration of the finite C_2-symmetric tetrasilicate group (Si_4O_{13}) in (I) has a zigzag shape, with Si···Si···Si angles of 99.88 (5)° (Table 1). The chain configuration in (I) may be compared with those in the few other tetrasilicates reported so far (Fig. 3). The first of these was only described in 1979 [$Ag_{10}(Si_4O_{13})$; Jansen & Keller, 1979]. The Si_4O_{13} unit in this compound is zigzag-shaped as well (Fig. 3*b*). A similar zigzag configuration is also shown by $Na_4Sc_2(Si_4O_{13})$ (Maksimov *et al.*, 1980; Fig. 3*c*), $Ba_2Nd_2(Si_4O_{13})$ (Tamazyan & Malinovskii, 1985; Fig. 3*d*) and $K_5Eu_2F(Si_4O_{13})$ (Chiang *et al.*, 2007; Fig. 3*e*). Two further reported tetrasilicates contain Si_4O_{13} units but also additional silicate groups. Both $Ag_{18}(SiO_4)_2(Si_4O_{13})$ (Heidebrecht & Jansen, 1991*a*,*b*) and $La_6(Si_4O_{13})(SiO_4)_2$ (Müller-Bunz & Schleid, 2002; I-type modification of $La_2Si_2O_7$) contain isolated SiO_4 groups. The Ag silicate is characterized by an Si_4O_{13} unit with a stretched zigzag configuration (Fig. 3*f*). The La silicate has an unusual horseshoe-shaped Si_4O_{13} unit (Fig. 3*g*), probably because of the additional presence of two isolated SiO_4 tetrahedra.

Fig. 3 clearly demonstrates that the configuration in (I) (Fig. 3*a*) is most similar to that in $Ag_{10}(Si_4O_{13})$ (Fig. 3*b*) and least similar to those in $La_6(Si_4O_{13})(SiO_4)_2$ (Fig. 3*g*; horseshoe-shaped unit) and $Na_4Sc_2Si_4O_{13}$ (Fig. 3*c*; twisted unit). This similarity is also reflected in the Si···Si···Si angles in these silicates: the angle in (I), 99.88 (5)° (×2), is fairly similar to the Si···Si···Si angles in $Ag_{10}(Si_4O_{13})$ (101.0 and 110.2°) and $K_5Eu_2F(Si_4O_{13})$ (102.8 and 104.3°), whereas the values in $Ba_2Nd_2(Si_4O_{13})$ are distinctly smaller (85.1 and 85.3°), and those in $Na_4Sc_2(Si_4O_{13})$ (125.7 and 126.0°) and $Ag_{18}(SiO_4)_2(Si_4O_{13})$ (2 × 125.9°) are distinctly larger. The unusual horseshoe-shaped unit in $La_6(Si_4O_{13})(SiO_4)_2$ shows fairly small Si···Si···Si angles, 91.0 and 100.7°. The cation radii of the non-Si cations in these silicates appear to be negatively correlated with the Si···Si···Si angle: the silicate with the largest cations [$Ba_2Nd_2(Si_4O_{13})$] is characterized by the smallest Si···Si···Si angles, whereas the silicate with the smallest cations [$Na_4Sc_2(Si_4O_{13})$] exhibits the largest Si···Si···Si angles. Compound (I) and $K_5Eu_2F(Si_4O_{13})$ show an intermediate behaviour.

The connectivities in the crystal structures of $Na_4Sc_2(Si_4O_{13})$, $K_5Eu_2F(Si_4O_{13})$ and $Ba_2Nd_2(Si_4O_{13})$ are slightly similar to that in (I). The first silicate contains Sc_2O_{10} dimers (composed of two ScO_6 octahedra sharing one common edge), comparable with the Gd_2O_{12} dimers in (I). In contrast with (I), no edge is shared between an Sc-centred polyhedron and an SiO_4 tetrahedron. $K_5Eu_2F(Si_4O_{13})$ contains $Eu_2O_{10}F$ dimers composed of two corner-sharing EuO_5F octahedra (the F atom is the shared atom). In $Ba_2Nd_2(Si_4O_{13})$, NdO_8 polyhedra are edge-linked to each other, thereby forming an incomplete polyhedral layer parallel to (011). Despite the strong similarity of the respective chain units, the connectivity in $Ag_{10}(Si_4O_{13})$ bears no similarity to that in (I), and this is most likely due to the irregular coordination environments of the Ag atoms and a much higher metal:Si ratio.

Although the structural formula of the complex silicate $NaBa_3Nd_3(Si_2O_7)(Si_4O_{13})$ (Malinovskii *et al.*, 1983) again suggests that this compound also contains finite chains, the

Si_4O_{13} unit is in fact a branched finite Si_3O_{10} chain (insular tetramer). The finite chain anion $(Si_4O_{13})^{10-}$ has not only been found in silicates, but also in acid aqueous solutions during the trimethylsilylation of $Ag_{10}(Si_4O_{13})$ (Calhoun *et al.*, 1980).

Interestingly, tetrasilicates containing finite Si_4O_{13} chains have not been reported yet in nature. Futhermore, only one germanate is known that contains finite Ge_4O_{13} chains, namely $Cu_2Fe_2(Ge_4O_{13})$ (Masuda *et al.*, 2003); it is characterized by a slightly curved chain (with all GeO_4 tetrahedra in an eclipsed orientation), a geometry completely different from those of the above silicates. A larger number of phosphates with finite P_4O_{13} chains are known (see references cited in Alekseev *et al.*, 2009), but only a single arsenate with a finite As_4O_{13} chain was described very recently $\{Ag_6[(UO_2)_2(As_2O_7)(As_4O_{13})]$, with a zigzag configuration of the As_4O_{13} unit; Alekseev *et al.*, 2009}. Among vanadates, there are only three known examples containing finite V_4O_{13} chains. All of these are characterized by a horseshoe-shaped configuration $\{Ba_3[V_4O_{13}]$ (Gatehouse *et al.*, 1987), $Fe_2[V_4O_{13}]$ (Permer & Laligant, 1997) and $([\{NH_3(CH_2)_3NH_2\}Zn]_2^{3+}[V_4O_{13}]^{6-}$ (Natarajan, 2003)}. If chromates are considered, one finds again a larger number of examples, such as $K_2[Cr_4O_{13}]$ (Casari & Langer, 2005) and $Cs_2[Cr_4O_{13}]$ (Kolitsch, 2004), all with a zigzag configuration.

Experimental

The title compound was crystallized from a $BaO–Rb_2O–MoO_3$ flux containing dissolved precursor compounds of Ba, Rb, Gd and Si. The experimental parameters were: $BaCO_3$ (1.0022 g), Rb_2CO_3 (0.5997 g), MoO_3 (1.0020 g), Gd_2O_3 (0.1727 g) and SiO_2 (0.1611 g); Pt crucible covered with a lid, T_{max} = 1423 K, holding time = 3 h, cooling rate = 2 K h^{-1}, T_{min} = 1173 K, slow cooling to room temperature after switching off the furnace. The reaction products were recovered by dissolving the Rb–molybdate flux solvent in distilled water. $Ba_2Gd_2(Si_4O_{13})$ formed small colourless pseudotetragonal prisms, which were accompanied by tiny prisms of $BaY_2Si_3O_{10}$ type (Kolitsch *et al.*, 2006) and $BaREE_2^{3+}Si_3O_{10}$ (REE = Gd, Er, Yb and Sc; Wierzbicka-Wieczorek, 2007).

Crystal data

$Ba_2Gd_2(Si_4O_{13})$
M_r = 909.52
Monoclinic, $C2/c$
a = 12.896 (3) Å
b = 5.212 (1) Å
c = 17.549 (4) Å
β = 104.08 (3)°
V = 1144.1 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 18.73 mm^{-1}
T = 293 K
0.08 × 0.08 × 0.02 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2006)
T_{min} = 0.316, T_{max} = 0.706
11887 measured reflections
2625 independent reflections
1910 reflections with $I > 2\sigma(I)$
R_{int} = 0.032

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.046
S = 1.04
2625 reflections
97 parameters
$\Delta\rho_{max}$ = 1.30 e Å^{-3}
$\Delta\rho_{min}$ = −1.65 e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Ba1—O2^{i}	2.669 (3)	Gd1—O1^{iii}	2.331 (3)
Ba1—O6^{ii}	2.710 (3)	Gd1—O2	2.382 (3)
Ba1—O1^{iii}	2.802 (3)	Gd1—O7^{iii}	2.485 (3)
Ba1—O2	2.827 (3)	Gd1—O4	2.625 (3)
Ba1—O5^{iv}	2.841 (3)	Si1—O1	1.589 (3)
Ba1—O3	2.890 (2)	Si1—O2	1.602 (3)
Ba1—O7^{ii}	2.947 (3)	Si1—O3	1.6481 (15)
Ba1—O4^{v}	3.041 (3)	Si1—O4	1.667 (3)
Ba1—O6^{v}	3.055 (3)	Si2—O5	1.595 (3)
Ba1—O1^{ii}	3.319 (3)	Si2—O6	1.625 (3)
Gd1—O6^{vi}	2.294 (3)	Si2—O7	1.646 (3)
Gd1—O5^{vii}	2.299 (3)	Si2—O4	1.692 (3)
Gd1—O7^{viii}	2.302 (3)		
Si1^{v}—O3—Si1	143.2 (2)	Si2—Si1—Si1^{v}	99.88 (5)
Si1—O4—Si2	125.18 (16)		

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

The highest residual electron-density peak is 0.75 Å from the Gd1 site and the deepest hole is 1.24 Å from the Ba1 site.

Data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ATOMS* (Shape Software, 1999); software used to prepare material for publication: *SHELXL97*.

Financial support from the Austrian Science Foundation (FWF) (grant No. P15220-N06) is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: LG3027). Services for accessing these data are described at the back of the journal.

References

Alekseev, E. V., Krivovichev, S. V. & Depmeier, W. (2009). *J. Mater. Chem.* **19**, 2583–2587.
Brese, N. E. & O'Keeffe, M. (1991). *Acta Cryst.* B**47**, 192–197.
Bruker (2006). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2008). *APEX2* and *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
Calhoun, H. P., Masson, C. R. & Jansen, M. (1980). *J. Chem. Soc. Chem. Commun.* pp. 576–577.
Casari, B. M. & Langer, V. (2005). *Acta Cryst.* C**61**, i117–i119.
Chiang, P.-Y., Lin, T.-W., Dai, J.-H., Chang, B.-C. & Lii, K.-H. (2007). *Inorg. Chem.* **46**, 3619–3622.
Gatehouse, B. M., Guddat, L. W. & Roth, R. S. (1987). *J. Solid State Chem.* **71**, 390–395.
Heidebrecht, K. & Jansen, M. (1991*a*). *Z. Anorg. Allg. Chem.* **597**, 79–86.
Heidebrecht, K. & Jansen, M. (1991*b*). *Z. Anorg. Allg. Chem.* **606**, 242.
Jansen, M. & Keller, H. L. (1979). *Angew. Chem.* **91**, 500.
Kolitsch, U. (2004). *Acta Cryst.* C**60**, i17–i19.
Kolitsch, U. & Tillmanns, E. (2004). *Mineral. Mag.* **68**, 677–686.
Kolitsch, U., Wierzbicka, M. & Tillmanns, E. (2006). *Acta Cryst.* C**62**, i97–i99.
Kolitsch, U., Wierzbicka-Wieczorek, M. & Tillmanns, E. (2009). *Can. Mineral.* **47**, 421–431.
Maksimov, B. A., Mel'nikov, O. K., Zhdanova, T. A. & Ilyukhin, V. V. (1980). *Dokl. Akad. Nauk SSSR*, **251**, 98–102.
Malinovskii, Yu. A., Baturin, S. V. & Bondareva, O. S. (1983). *Dokl. Akad. Nauk SSSR*, **272**, 865–869.
Masuda, T., Chakoumakos, B. C., Nygren, C. L., Imai, S. & Uchinokura, K. (2003). *J. Solid State Chem.* **176**, 175–179.

Müller-Bunz, H. & Schleid, T. (2002). *Z. Anorg. Allg. Chem.* **628**, 564–569.
Natarajan, S. (2003). *Inorg. Chim. Acta*, **348**, 233–236.
Permer, L. & Laligant, Y. (1997). *Eur. J. Solid State Inorg. Chem.* **34**, 41–52.
Robinson, K., Gibbs, G. V. & Ribbe, P. H. (1971). *Science*, **172**, 567–570.
Shape Software (1999). *ATOMS for Windows and Macintosh*. Version 5.0.4. Shape Software, Kingsport, Tennessee, USA.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Tamazyan, R. A. & Malinovskii, Yu. A. (1985). *Dokl. Akad. Nauk SSSR*, **285**, 124–183.
Wierzbicka-Wieczorek, M. (2007). PhD thesis, University of Vienna, Austria.