Ba$_2$Ti$_2$Si$_2$O$_9$F$_2$, a new titanium silicate

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Dibarium dititanium difluoride dioxide heptaoxidodisilicate, Ba$_2$Ti$_2$Si$_2$O$_9$F$_2$, is a new edge-sharing titanate with a unique titanium silicate framework. All atoms in the structure are in general positions. Titanium oxyfluoride octahedra combine with silicon tetrahedra to form a double stacked chain, which is the base unit of the layered framework. The Ba atoms lie in channels that extend along the a axis.

Comment

The number of known titanium silicate structures extends into the hundreds (Roberts *et al.*, 1996), with more naturally occuring and synthetic examples being discovered each year. Of the naturally occurring silicates, many have found a variety of technological applications and thus create a need for a synthetic growth pathway. One such material, fresnoite, was discovered in sanbornite deposits in 1965 (Alfors *et al.*, 1965). The structure was refined as Ba$_2$TiOSi$_2$O$_7$ in the *P4bm* space group (Moore, 1967). The unique titanium silicate network exhibits many desirable properties, such as piezoelectric, electrooptic, pyroelectric and nonlinear optical activities (Haussühl *et al.*, 1977). Due to these interesting properties and the fact that the material is otherwise difficult to grow, an exploration of the hydrothermal growth of fresnoite was undertaken. During the study, the title compound was synthesized as a minor product which crystallized in the *Pbca* space group.

The structure contains edge-sharing TiO$_5$F octahedra and SiO$_4$ tetrahedra (Fig. 1) which combine to form a novel titanium silicate framework. Both Ti atoms have five bonds to O, with average bond lengths of 1.93 [7] and 1.94 [8] Å for atoms Ti1 and Ti2, respectively. An F atom completes the octahedral environment for each Ti atom. The possibility of hydroxide rather than fluoride was eliminated by IR spectroscopy and differential scanning calorimetry/thermogravimetric analysis. None of the characteristic hydroxyl stretches is observed in the IR spectrum. The sample also displays thermal and gravimetric stability beyond 1073 K. Energy-dispersive X-ray analysis confirm substantial amounts of fluorine.

The F-site designation could not be unequivocally fixed by observing bond lengths. Metal–metal repulsion, similar to that observed in other edge-sharing titanium structures, causes a bond distortion (Dadachov *et al.* 1997). Therefore, bond-valence sums (Brown, 1976) were used for a preliminary assignment of the F sites. Both F1 and F2 are significantly undersaturated when refined as O, with bond-valence sums of 1.237 and 1.351 v.u., respectively. Refinements as F provide much more reasonable valence sums of 0.951 and 1.038 v.u., respectively. To confirm the fluoride designation, IR stretches for Ti—F bonds were examined. However, these are difficult to assign because of overlap with many silicate bending vibrations. Confirmation was achieved by observation of a 722 cm^{-1} band, which is characteristic of titanium and other metal oxyfluoride complexes (Laptash *et al.*, 1999). The absence of bands in the range 759–813 cm^{-1} (Clark & Errington, 1967) eliminates the possibility of any Si—F bonds. The SiO$_4$ tetrahedra share one O atom, which forms an [Si$_2$O$_7$] pyrosilicate group that is confirmed by a 662 cm^{-1} band (Farmer, 1974). The other coordinating O atoms are involved in the overall framework.

The base unit of the framework (Fig. 2) is a double stacked chain which extends along the (200) plane. It consists of alternating edge-sharing titania and [Si$_2$O$_7$] groups. This chain has two levels, with the bottom layer also alternating between the aforementioned groups. However, the lower level is staggered so that the [Si$_2$O$_7$] group is directly beneath the edge-sharing Ti. In each octahedral or tetrahedral environment,
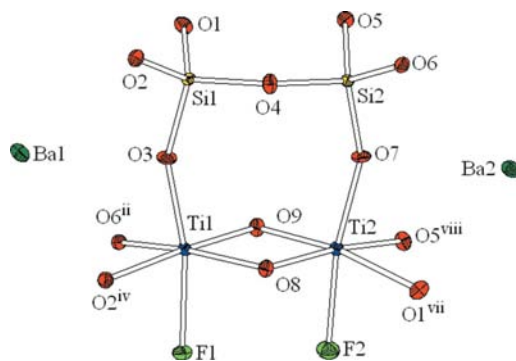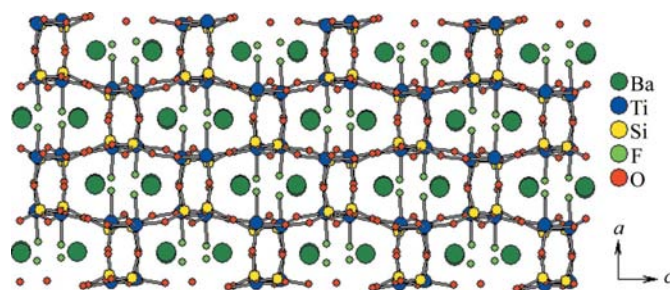

Figure 1
A view of the asymmetric unit of Ba$_2$Ti$_2$Si$_2$O$_9$F$_2$, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Symmetry-related atoms have been added to show the octahedral environments of atoms Ti1 and Ti2. [Symmetry codes: (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (iv) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$.]
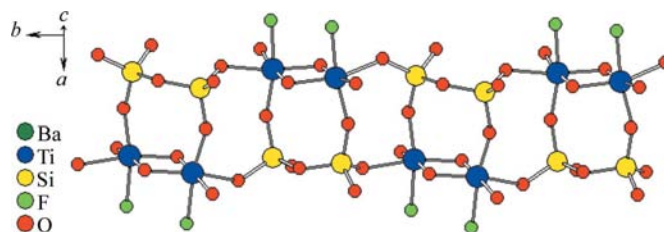
Figure 2
The base chain unit of the overall framework, projected slightly off the *ab* plane.

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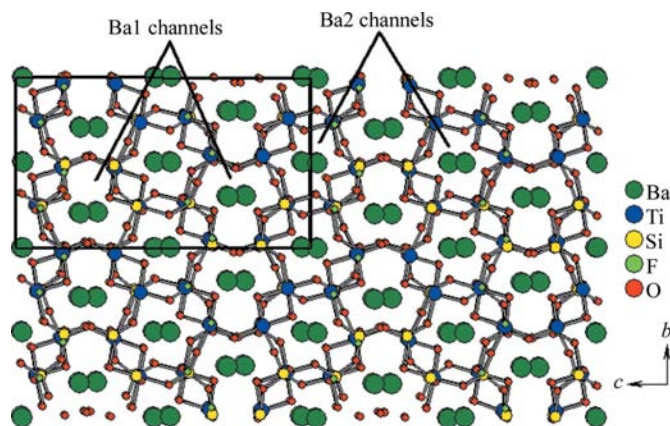
Figure 3
A view of the barium channels, which extend down the *a* axis.

Figure 4
The layered structure projected on to the *ac* plane. The titanium silicate layers occupy the (200) plane.

there is one O anion that does not participate in the propagating chain unit. This O atom serves to bridge one chain to the next to form the overall titanium silicate framework. The remaining F atoms do not participate in continuation of the framework; instead, they terminate with four bonds to both Ba1 and Ba2.

The titanium silicate network forms both channels (Fig. 3) and layers (Fig. 4), in which the Ba atoms reside. Atom Ba1 is located in a channel constructed of six-membered rings. These rings are composed of three titanium oxide and three silicon oxide environments. Each ring is bridged using three Ti—O—Si bonds. The rest of the channel is partially enclosed by Ti—F bonds. Like the Ba1 environment, the Ba2 channel also extends along the *a* axis. The ring structure, which forms the channel, is different in its composition. The first ring is a compilation of four Ti and two Si atoms bridged by O atoms, while the second ring has the exact opposite ratio, with two Ti octahedra and four Si tetrahedra. These two rings alternate as the channel descends. Similar to the Ba1 channel, the rings also connect *via* three Ti—O—Si bridges. Three Ti—F bonds complete the sheath, just as in the previous channel. Since the titanium silicate chains are constrained to the (200) plane, the fluoride bonds and Ti—O—Si bridges are oriented in between this plane. This gives the illusion of a layered structure (Fig. 4). Both Ba1 and Ba2 are located in this plane.

Table 1
Selected bond lengths (Å).

Ba1—F2^i	2.647 (3)	Ba2—O5^{vii}	3.242 (3)
Ba1—O8^{ii}	2.816 (3)	Ti1—O3	1.855 (3)
Ba1—F1^i	2.840 (3)	Ti1—O8	1.863 (3)
Ba1—O8^i	2.851 (3)	Ti1—O9	1.968 (3)
Ba1—O6^{iii}	2.863 (3)	Ti1—O2^{iv}	1.979 (3)
Ba1—O2^{iv}	2.914 (3)	Ti1—O6^{ii}	2.006 (3)
Ba1—O3	2.925 (4)	Ti1—F1	2.029 (3)
Ba1—O2	2.929 (3)	Ti2—O9	1.832 (3)
Ba1—F1^v	3.019 (3)	Ti2—O7	1.888 (3)
Ba1—O4^{ii}	3.164 (3)	Ti2—O8	1.969 (3)
Ba1—O4^{iii}	3.230 (3)	Ti2—O5^{viii}	1.973 (3)
Ba2—F1^{vi}	2.713 (3)	Ti2—F2	1.989 (3)
Ba2—O9^{vii}	2.752 (3)	Ti2—O1^{vii}	2.031 (3)
Ba2—O1^{viii}	2.773 (3)	Si1—O1	1.601 (3)
Ba2—F2^{ix}	2.783 (3)	Si1—O2	1.612 (3)
Ba2—O5^{viii}	2.810 (3)	Si1—O3	1.621 (3)
Ba2—O9^{vi}	2.854 (3)	Si1—O4	1.641 (3)
Ba2—O7	2.934 (4)	Si2—O6	1.607 (3)
Ba2—O6^x	2.945 (3)	Si2—O5	1.614 (3)
Ba2—O1^{vii}	3.100 (3)	Si2—O7	1.623 (3)
Ba2—F2^{vi}	3.178 (3)	Si2—O4	1.658 (3)

Symmetry codes: (i) $-x + 1, y - \frac{1}{2}, -z + \frac{1}{2}$; (ii) $-x + \frac{1}{2}, y - \frac{1}{2}, z$; (iii) $-x, y - \frac{1}{2}, -z + \frac{1}{2}$; (iv) $x + \frac{1}{2}, y, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, y, -z + \frac{1}{2}$; (vi) $x - \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (vii) $-x + \frac{1}{2}, y + \frac{1}{2}, z$; (viii) $x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$; (ix) $-x + 1, -y + 2, -z + 1$; (x) $-x, -y + 2, -z + 1$.

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