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Tetragonal form of barium cobalt disilicate, $Ba_2CoSi_2O_7$

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(Si–O) = 0.006 Å
R factor = 0.025
wR factor = 0.064
Data-to-parameter ratio = 16.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of $Ba_2CoSi_2O_7$ consists of layers made from corner-sharing of $[SiO_4]$ and $[CoO_4]$ polyhedra. These layers, lying parallel to (001), are linked by Ba···O interactions. Co^{2+} forms flattened CoO_4 tetrahedra (point symmetry $\overline{4}$), which are isolated in the structure. The blue color of the solid might be explained by the coordination mode of the Co atoms.

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Comment

In the mixed-silicate system MO–TO–SiO_2, where M is an alkaline earth metal and T is a divalent 3d metal atom, many compounds of type $(M,T)_3Si_2O_7$ have been reported in the literature: $Ca_2CoSi_2O_7$ (Kimata, 1982, 1983; Hagiya *et al.*, 1993), $Ca_{2.33}Mn_{0.67}Si_2O_7$ (Kimata, 1989), $Ca_2ZnSi_2O_7$ (Warren & Trautz, 1930; Louisnathan, 1969), $Sr_2CuSi_2O_7$ (Tovar *et al.*, 1998), $BaCo_2Si_2O_7$ (Adams *et al.*, 1993), $Ba_2CoSi_2O_7$ (Adams *et al.*, 1996), $Ba_2CuSi_2O_7$ (Malinovskii, 1984), $BaCu_2Si_2O_7$ (Janczak *et al.*, 1990), $BaZn_2Si_2O_7$ (Lin *et al.*, 1999). Adams *et al.* (1996) did not mention any structure transformation when they reported the monoclinic form of $Ba_2CoSi_2O_7$. The present paper deals with a new tetragonal form of this mixed silicate, which is isostructural with $Ca_2MSi_2O_7$ (M = Co and Zn). Crystals of the new phase were obtained quite by chance during the melting of a phosphate powder in a crucible made of quartz. The structure of $Ba_2CoSi_2O_7$ can de described as a two-dimensional framework of $[SiO_4]$ and $[CoO_4]$ tetrahedra sharing corners. These layers, lying parallel to the (001) plane at around x = 0.5, are interconnected by barium ions, as shown in Fig. 1. Alternatively, the structure can be described as being composed of BaO_8 polyhedra sharing edges and faces to form a sheet. These Ba sheets share corners with Si_2O_7 moieties to

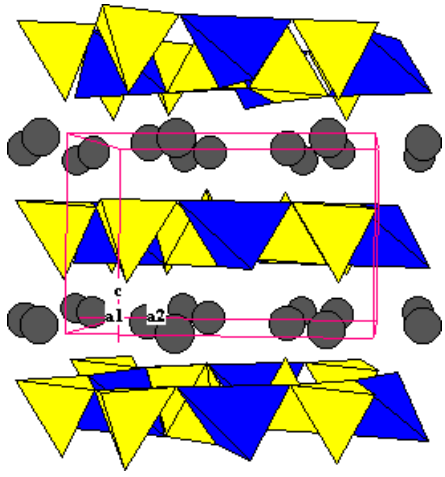

Figure 1
Perspective view of the crystal structure of $Ba_2CoSi_2O_7$. Yellow polyhedra $[Si_2O_7]$, blue polyhedra $[CoO_4]$ and grey spheres Ba^{2+}.

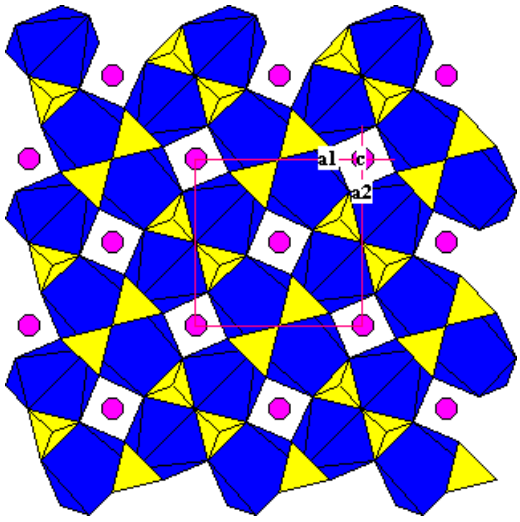

Figure 2
Projection of the structure on to the *ab* plane. Blue polyhedra [BaO_8], yellow polyhedra [Si_2O_7] and pink spheres Co^{2+}.

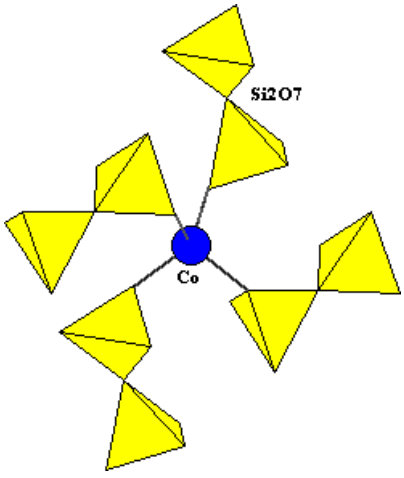

Figure 3
Coordination of Co^{2+} in $Ba_2CoSi_2O_7$. Colors as in Fig. 2.

delimit tunnels, parallel to [001], which contain Co^{2+} cations. Fig. 2 depicts the projection of the structure on to the *ab* plane.

Co^{2+} forms flattened CoO_4 tetrahedra (point symmetry $\overline{4}$), the four apices of the tetrahedron belonging to four $Si_2O_7^{4-}$ groups, as shown in Fig. 3. The average Co—O distance of 1.964 Å can be compared with the value of 1.926 Å in $Ca_2CoSi_2O_7$. Co^{2+} polyhedra are isolated in the structure, the shortest Co···Co distance being 5.778 Å, larger than that reported in $Ca_2CoSi_2O_7$ (5.015 Å; Kimata, 1982). The blue color is a consequence of the geometry of Co^{2+}. In general, for many compounds containing this metal in the 2+ oxidation state, the rose color points to an octahedral configuration, while a blue color indicates tetrahedral geometry.

Ba^{2+} occupies an eight-coordinated site. The average Ba···O distance is 2.763 Å, a value close to the value of 2.814 Å reported for $Ba_2CuSi_2O_7$, but it is shorter than the value of 2.927 Å in monoclinic $Ba_2CoSi_2O_7$. Such a value has also been reported for phosphates such as $Ba_2Ni(PO_4)_2$ (2.765 Å; El Bali *et al.*, 1994).

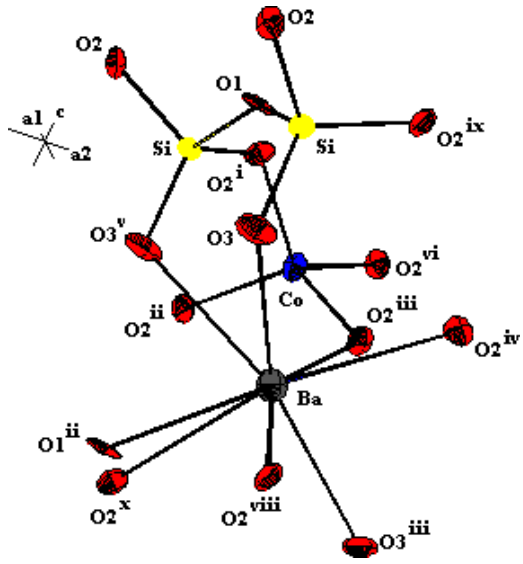

Figure 4
Perspective view of a fragment of $Ba_2CoSi_2O_7$, showing the atomic connectivity, with the atom labeling. Displacement ellipsoids are drawn at the 50% probability level. Symmetry codes for equivalent atoms: (i) $x-1, y, z$; (ii) $x, y, z-1$; (iii) $1-x, -y, z$; (iv) $1-x, -y, z-1$; (v) $y, 1-x, -z$; (vi) $y, 1-x, 1-z$; (vii) $-y, x-1, 1-z$; (viii) $x-\frac{1}{2}, -y+\frac{1}{2}, 1-z$; (ix) $y+\frac{1}{2}, x-\frac{1}{2}, z$; (x) $y+\frac{1}{2}, x-\frac{1}{2}, z-1$.

Tetrahedral Si^{4+} in two neighboring SiO_4 units share O1 to form the pyrosilicate $[Si_2O_7]^{4-}$ group. Si—O distances range from 1.592 (6) to 1.664 (3) Å, with an average of 1.633 Å, similar to other mixed pyrosilicates; *e.g.* 1.636 Å in $Ca_2ZnSi_2O_7$ and 1.628 Å in $Ba_2CuSi_2O_7$. Si_2O_7 can be also characterized by its almost eclipsed conformation and the bridging angle φ(Si,O,Si) of 142.8 (5)°, a value close to those reported in the homologous phases; *e.g.* 142.2° in monoclinic $Ba_2CoSi_2O_7$, 142° in $Ba_2CuSi_2O_7$ and 141.5° in $Ba_2ZnSi_2O_7$. Fig. 4 shows a fragment of $Ba_2CoSi_2O_7$ with the atomic connectivity.

Experimental

A mixture of $BaCO_3$, $CoCO_3$ and $(NH_4)_2HPO_4$, in a 2:1:2 molar ratio, was ground and heated progressively to 1173 K. The resulting powder was then melted at 1423 K in a crucible made of quartz. Two materials were obtained, *viz*. blue crystals of the title compound and an unknown amorphous substance.

Crystal data

$Ba_2CoSi_2O_7$
M_r = 501.79
Tetragonal, $P\overline{4}2_1m$
a = 8.1709 (7) Å
c = 5.3374 (7) Å
V = 356.34 (6) Å^3
Z = 2
D_x = 4.677 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 922 reflections
θ = 3.6–30.3°
μ = 13.56 mm^{-1}
T = 293 (2) K
Prism, intense blue
0.13 × 0.05 × 0.05 mm

Data collection

Bruker SMART CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.392, T_{max} = 0.522
1383 measured reflections
575 independent reflections
536 reflections with $I > 2\sigma(I)$
R_{int} = 0.026
θ_{max} = 30.5°
$h = -11 \rightarrow 6$
$k = -8 \rightarrow 11$
$l = -7 \rightarrow 7$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.025$
$wR(F^2) = 0.064$
$S = 1.18$
575 reflections
34 parameters
$w = 1/[\sigma^2(F_o^2) + (0.0223P)^2 + 0.683P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 1.04$ e Å^{-3}
$\Delta\rho_{min} = -0.87$ e Å^{-3}
Absolute structure: Flack (1983), 216 Friedel pairs
Flack parameter = −0.12 (7)

Table 1
Selected geometric parameters (Å).

Ba1—O3^{v}	2.628 (6)	Co1—O2^{vii}	1.964 (4)
Ba1—O2^{xi}	2.681 (4)	Si1—O3	1.592 (6)
Ba1—O1^{ii}	2.738 (6)	Si1—O2	1.637 (5)
Ba1—O3	2.800 (5)	Si1—O1	1.664 (3)
Ba1—O2^{iv}	2.888 (4)		

Symmetry codes: (v) $y, 1-x, -z$; (xi) $x-\frac{1}{2}, \frac{1}{2}-y, 1-z$; (ii) $x, y, z-1$; (iv) $1-x, -y, z-1$; (vii) $-y, x-1, 1-z$.

The maximum electron-density peak is 0.87 Å from Ba1.

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINT* (Bruker, 1999); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ATOMS* (Dowty, 1999); software used to prepare material for publication: *SHELXL*97.

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