units and may thereby perturb the chain structure. Each B—O polyanion is connected to two neighbouring Li atoms.

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Alkaline-Earth Beryllium Borate $CaBeB_2O_5$

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Abstract. Beryllium calcium diborate, $CaBeB_2O_5$, $M_r = 150.71$, monoclinic, $P2_1/n$, $a = 5.167$ (2), $b = 3.756$ (2), $c = 17.160$ (2) Å, $\beta = 98.12$ (2)°, $V = 329.7$ (2) Å^3, $Z = 4$, $D_x = 3.036$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 17.38$ cm^{-1}, $F(000) = 296$, $T = 298$ K, $R = 0.039$ for 508 reflections having $F_o^2 \geq 3\sigma(F_o^2)$. The structure is constructed from two intermingled networks – a CaO_9 polyhedral system and a beryllium borate complex constructed from four-coordinate Be and three- and four-coordinate B atoms. The extended beryllium borate complex results from the unique condensation of six-membered rings containing the triangular and distorted tetrahedral beryllate and borate groups.

Introduction. The simple pyroborate group B_2O_5 – two triangular planar BO_3 units sharing an O atom – has been found to exist in the alkaline-earth materials $AE_2B_2O_5$, where AE = Mg, Ca or Sr (Takéuchi, 1952; Schäfer, 1968; Bartl & Schuckmann, 1966) and in the mixed phase $CaMgB_2O_5$ (Yakubovich, Yamnova, Shehedrin, Simonov & Belov, 1975). No data are available in the literature on a simple pyroborate with AE = Be.

In this contribution we describe the structure of the mixed alkaline-earth compound $CaBeB_2O_5$. Although the formula indicates the structure could contain a pyroborate group, we have found instead an admixture of three- and four-coordinate B atoms in a complex beryllium borate network. So, a unique atomic arrangement is provided for addition to the small muster of known anhydrous beryllium borates: $SrBe_2(BO_3)_2$ (Schaffers & Keszler, 1990), $BaBe_2(BO_3)_2$ (Schaffers, 1992), Be_2BO_3F (Bajdina, Bakakin, Podberizskaja, Alekseev, Baconova & Pavlijucenko, 1978) and KBe_2BO_3F (Solov'eva & Bakakin, 1970).

Experimental. Crystals of $CaBeB_2O_5$ were grown in a Pt crucible from a melt consisting of 26.6 mol% CaB_2O_4 prepared from $Ca(NO_3)_2.4H_2O$ (ALFA, reagent grade) and B_2O_3 (ALFA, 99.98%), 43.2 mol% BeO made by heating BeF_2 (CERAC, 99.5%) in air, and 30.2 mol% $LiBO_2$ (AESAR, 99.9%). The melt was cooled from 1198 to 698 K at 6 K h^{-1}. The crystals were washed in hot distilled water to remove excess flux. A clear block-shaped crystal of approximate dimensions 0.25 (2) × 0.22 (2) × 0.20 (2) mm was mounted on a glass fiber with epoxy for X-ray structure analysis. Data were collected by using a Rigaku AFC-6*R* single-crystal diffractometer and Mo $K\alpha$ radiation. Sixteen automatically centered peaks in the range $30 \leq 2\theta \leq 36°$ were used for refinement of unit-cell parameters. The ω-scan technique was used to collect a total of 762 data to $\sin\theta/\lambda = 1.08$ Å^{-1} with a scan speed of 16.0° min^{-1} in ω and a scan width of $(4.50 + 0.30\tan\theta)°$; $0 \leq h \leq 6$, $0 \leq k \leq 4$ and $-20 \leq l \leq 20$. From the 683 unique reflections measured, 508 reflections had $F_o^2 \geq 3\sigma(F_o^2)$. Three standard reflections were monitored throughout the data collection and an average fluctuation of 2.0% in intensity was detected.

The *TEXSAN* crystallographic software package (Molecular Structure Corporation, 1989) was used to solve the crystal structure. The position of the Ca

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters* (Å^2) *for* $CaBeB_2O_5$

$B_{eq} = (8\pi^2/3)\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	B_{eq}
Ca	0.7915 (1)	0.6212 (2)	0.07348 (5)	1.87 (5)
Be	0.604 (1)	0.238 (2)	0.2122 (3)	1.5 (2)
B1	0.300 (1)	0.974 (1)	0.0963 (3)	1.6 (2)
B2	1.1122 (9)	0.252 (1)	0.2119 (3)	1.7 (2)
O1	0.3561 (5)	0.479 (1)	0.2236 (2)	1.7 (1)
O2	1.0854 (5)	0.0934 (8)	0.1302 (2)	1.8 (1)
O3	0.8679 (5)	0.457 (1)	0.2178 (2)	1.8 (1)
O4	0.5484 (6)	0.0793 (8)	0.1265 (2)	1.8 (1)
O5	0.2560 (6)	0.763 (1)	0.0321 (2)	2.4 (1)

atom was determined by using the direct-methods program *SHELXS*86 (Sheldrick, 1985) and the atomic positions of the remaining atoms were deduced by subsequent examination of difference electron density maps. After isotropic refinement, the data were averaged ($R_{\rm int} = 0.053$) and corrected for absorption (transmission coefficients 0.88–1.09) with the computer program *DIFABS* (Walker & Stuart, 1983). Final least-squares refinement on F_o for those 507 reflections having $F_o^2 \geq 3\sigma(F_o^2)$, and with anisotropic displacement coefficients on each atom, resulting in 82 variables, afforded the final residuals $R = 0.039$ and $wR = 0.063$ where the function $\sum w(|F_o| - |F_c|)^2$ was minimized with weights derived from $w = 1/\sigma^2(F_o)$. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). $S = 1.69$, maximum $\Delta/\sigma = 0.01$, and the maximum and minimum peaks in the final difference electron density map corresponded to 0.92 and 0.82% of a Ca atom, respectively. Atomic coordinates and isotropic thermal parameters are listed in Table 1.*

Discussion. A drawing of the unit cell of $CaBeB_2O_5$ is presented in Fig. 1. Inspection of the diagram reveals that the Ca atom is bound by nine, the Be atom by four, the B1 atom by three, and the B2 atom by four O atoms. A perspective view indicating the nature of the structure is presented in Fig. 2. Two commingled polyhedral networks extend in the *ab* plane. One of these is a Ca double layer formed from the vertex, edge, and face sharing of the CaO_9 polyhedra. The other is represented by a double layer of vertex-sharing BO_4 and BeO_4 tetrahedra that is capped on opposite surfaces by triangular BO_3 groups.

By considering the numbering scheme in Fig. 2, the CaO_9 polyhedral connections can be established. The polyhedra share faces comprised of atoms O2, O4, and O5*a* to give extension along the *b* axis, and vertices O5*b* to give extension along the *a* axis. The double layer is formed by edge sharing through atoms O5*a* and O5*b*.

The characteristics of the extended beryllium borate complex are best appreciated by considering

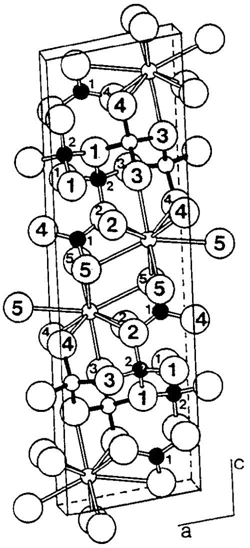

Fig. 1. Sketch of the unit cell of $CaBeB_2O_5$ viewed down the *b* axis where the small open circles with open bonds represent Ca atoms, the small open circles with shaded bonds Be atoms, the small shaded circles with open bonds B atoms, and the large shaded circles O atoms, here, and in Figs. 2 and 3.

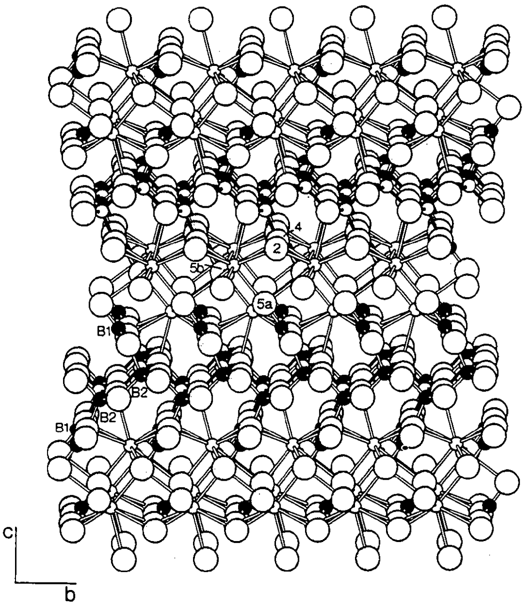

Fig. 2. Perspective view down the *a* axis of the interpenetrating CaO_9 polyhedral framework and beryllium borate framework of $CaBeB_2O_5$.

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* Lists of anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55645 (8 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST0579]

Fig. 2 and the representation in Fig. 3. The Be-centered distorted tetrahedra share vertices to form chains extending along the *b* axis. In like manner, the B2-centered tetrahedra form similar chains that also extend along the same axis. These chains are alternately conjoined along the *a* axis by sharing vertices O1 and O3. Apices of neighboring Be- and B-centered tetrahedra are also bridged along this axis by the triangular $B(1)O_3$ group. With this connection, the fundamental six-membered ring BeB_2O_8 (*cf.* inset Fig. 3) is readily identified. The two-dimensional beryllium borate matrix results from fusing these rings through the O atoms of the tetrahedral B and Be sites. The corresponding homoatomic ring B_3O_8 $(1\Delta + 2T)$ (Δ = triangular coordination, T = tetrahedral coordination of B) is rather uncommon in borate systems, but is has been observed in the materials BaB_4O_7 (Block & Perloff, 1965), $LaMgB_5O_{10}$ (Saubat, Vlasse & Fouassier, 1980) and $Ba_2LiB_5O_{10}$ (Smith & Keszler, 1989*a*), and the heteroatomic ring BZn_2O_8 $(1\Delta + 2T)$ has been identified in the compound $BaZn_2(BO_3)_2$ (Smith & Keszler, 1992). In each of these phases, however, said rings are interconnected by other types of rings or borate groups. Insofar as we know, the structure of the title compound is the first example of an extended system formed from the exclusive condensation of the $1\Delta + 2T$ ring.

Selected interatomic distances and angles are listed in Table 2. The average Ca—O distance is 2.6 (2) Å which can be compared to Ca—O distances of 2.5 (1) Å for six-coordinate Ca in $CaCO_3$ (De Villiers, 1971), 2.5 (2) Å for eight-coordinate Ca in $Ca_3(BO_3)_2$ (Vegas, Cano & García-Blanco, 1975), 2.5 (2) Å for nine-coordinate Ca in CaB_4O_7 (Zayakina & Brovkin, 1977), and 2.56 Å calculated from Shannon (1976) radii.

The average Be—O length of 1.59 (1) Å compares to 1.63 (4) Å in $SrBe_2(BO_3)_2$, 1.63 (4) Å in $BaBe_2(BO_3)_2$, and 1.65 Å calculated from crystal radii.

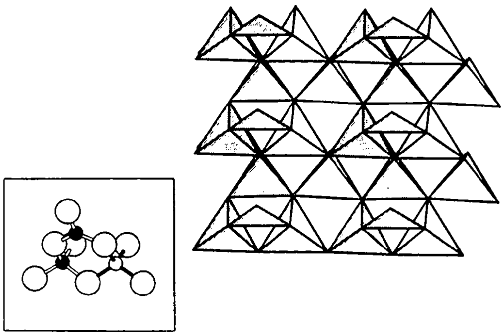

Fig. 3. A polyhedral sketch of the two-dimensional connectivity of the BeO_4 and BO_4 tetrahedra and BO_3 triangles. The BeB_2O_8 ring is inset.

Table 2. *Selected interatomic distances* (Å) *and angles* (°) *for* $CaBeB_2O_5$

Ca—O2	2.601 (3)	O2—Ca—O2	96.1 (1)
—O2	2.446 (3)	O2—Ca—O3	56.3 (1)
—O3	2.529 (3)	O2—Ca—O4	64.0 (1)
—O4	2.621 (3)	O2—Ca—O5	70.5 (1)
—O4	2.385 (3)	O3—Ca—O4	59.1 (1)
—O5	2.809 (4)	O3—Ca—O5	106.8 (1)
—O5	2.651 (4)	O4—Ca—O4	97.1 (1)
—O5	2.301 (3)	O5—Ca—O5	85.8 (1)
—O5	2.928 (4)	O5—Ca—O5	91.0 (1)
		O5—Ca—O5	72.6 (1)
Be—O1	1.600 (6)	O1—Be—O3	113.3 (4)
—O3	1.586 (6)	O1—Be—O3	105.9 (3)
—O3	1.590 (6)	O1—Be—O4	106.6 (3)
—O4	1.576 (6)	O3—Be—O3	108.2 (3)
		O3—Be—O4	116.0 (4)
		O3—Be—O4	107.0 (3)
B1—O2	1.395 (6)	O2—B1—O4	120.3 (4)
—O4	1.374 (6)	O2—B1—O5	118.6 (4)
—O5	1.352 (6)	O4—B1—O5	121.0 (4)
B2—O1	1.502 (6)	O1—B2—O1	106.6 (3)
—O1	1.511 (6)	O1—B2—O2	113.6 (4)
—O2	1.511 (6)	O1—B2—O2	108.1 (3)
—O3	1.494 (6)	O1—B2—O3	108.0 (3)
		O1—B2—O3	113.4 (4)
		O2—B2—O3	107.4 (3)

The range of O—Be—O angles from 105.9 (3) to 116.0 (4)° demonstrates the deviations from tetrahedral values.

Atom B1 is coordinated to three O atoms - O2, O4 and O5 - at distances of 1.395 (6), 1.374 (6), and 1.352 (6) Å, respectively. These lengths are typical when compared to average B—O bond lengths for BO_3 triangles in $Sr_2Cu(BO_3)_2$ [1.38 (2) Å (Smith & Keszler, 1989*b*)], $Sr_5(BO_3)Cl$ [1.37 (3) Å (Alekel & Keszler, 1992)] and $Sr_3Sc(BO_3)_3$ [1.38 (1) Å (Thompson, 1991)]. The triangles reside in layers orthogonal to (001) (Fig. 2), sharing edges with the CaO_9 polyhedra and vertices with the CaO_9, BeO_4, and $B2O_4$ polyhedra. Atom B2 is four-coordinate to atoms O1 (× 2), O2, and O3 with an average length of 1.505 (8) Å that compares to 1.49 (4) Å for CaB_4O_7 (Zayakina & Brovkin, 1977) and 1.49 Å calculated from crystal radii and a four-coordinate B atom.

The O atoms occupy three-, four-, and five-coordinate sites where O1 is three-coordinate, O2, O3, and O4 are four-coordinate, and O(5) is five-coordinate. The connectivity may be discerned by considering Table 2 and the various cations bound to each O atom.

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Redetermination of Tristrontium Uranate(VI). A Rietveld Refinement of Neutron Powder Diffraction Data

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Abstract. Sr_3UO_6, $M_r = 596.89$, monoclinic, $P2_1/n$. At room temperature, $a = 6.0126$ (2), $b = 6.2138$ (2), $c = 8.6139$ (3) Å, $\beta = 90.239$ (2)°, $V = 321.82$ (3) Å^3, $Z = 2$, $D_x = 6.160$ (1) Mg m^{-3}, $\mu R = 0.12$, $\lambda = 2.57155$ (3) Å, $R_{wp} = 3.19\%$. The structure has been refined by Rietveld analysis of neutron powder diffraction data for 147 reflections. The structure is of a monoclinic $GdFeO_3$-type perovskite. The octahedra are in complete order.

Introduction. Since strontium is an important fission product in nuclear technology the compounds and phase relations in the system Sr–U–O are a common subject of research. The crystal structures of β-$SrUO_4$, Sr_2UO_5 and Sr_3UO_6 have been reported (Loopstra & Rietveld, 1969) and recently the structure of $Sr_3U_{11}O_{36}$ was determined (Cordfunke, van Vlaanderen, Onink & IJdo, 1991). Sr_3UO_6 is reported by Loopstra & Rietveld (1969) to adopt a monoclinic deformed perovskite-like structure with space group $P2_1$. In relation to other substituted perovskites, this space group seems improbable (van Duivenboden & IJdo, 1986) and a redetermination of the structure is reported here.

Experimental. Sr_3UO_6 was prepared from a stoichiometric mixture of SrO and U_3O_8 which was kept in a gold crucible at 1250 K in oxygen for a week, with repeated grindings and then annealed for one week at 1073 K. X-ray powder diffraction patterns were obtained with a Guinier camera; no other phases were observed. Systematic absences suggest the space group $P2_1/n$. Since no single crystals were available, Rietveld's (1969) method was used for refinement of the neutron powder diffraction data. Experimental details were given earlier in the paper describing the structure determination of Sr_2CaUO_6 (Groen & IJdo, 1987). This structure was used as a trial model and refinement used the program *DBW*3.2*S* version 8802, with correction for multiplicities of Laue group

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