

INORGANIC COMPOUNDS

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SrKB₅O₉

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Abstract

Strontium potassium pentaborate, SrKB₅O₉, crystallizes in the monoclinic system in space group $P2_1/c$. The structure contains both B₃O₇ and B₃O₈ rings which share a common B atom to form a complex two-dimensional network constituting the basic B₅O₉ unit in the formula. Adjacent networks are bound together by Sr and K atoms which have eight- and nine-coordinate sites, respectively.

Comment

Polyborates of the heavier alkaline earth metals can exhibit unusual and efficient emission characteristics when doped with luminescent ions (Verwey, Coronado & Blasse, 1991; Dirksen & Blasse, 1991; Meijerink, Van Heek & Blasse, 1993). As part of our continuing efforts to synthesize new examples of these materials, we have prepared the new compound SrKB₅O₉ from a study of the SrO–K₂O–B₂O₃ system. Insofar as we know, it is the first ternary borate to be discovered in this system. A powder sample is readily prepared by grinding a stoichiometric ratio of Sr(NO₃)₂ (AESAR, ACS grade), KNO₃ (JTB, ACS grade) and B₂O₃ (ALFA, 99.98%), and heating at 893 K for 2 h and 993 K for 8 h. Analysis of the product by X-ray diffraction methods indicates that it is single phase. The compound undergoes a peritectic decomposition, as an X-ray powder analysis of a solidified melt reveals only peaks attributable to the SrB₂O₄ phase. For crystal growth, KNO₃ and B₂O₃ were added to a fresh sample of SrKB₅O₉ to produce a mixture of composition SrO:K₂O:4B₂O₃. This composition was melted at 1118 K in a platinum crucible, and crystals were procured by cooling to 850 K at 6 K h⁻¹ and then to room temperature at 60 K h⁻¹. The crystals were extracted by dissolution of the flux in water.

The two-dimensional polyborate network (Fig. 1) is isotypic with that of CaNaB₅O₉ (Fayos, Howie & Glasser, 1985) and is built from a condensation of B₃O₇ (2Δ + 1T) [Δ = triangular coordination, T = tetrahedral

coordination of B] and B₃O₈ (1Δ + 2T) rings. As shown in Fig. 2, these rings share a tetrahedrally coordinated B atom to form a B₅O₁₁ group (Vegas, Cano & Garcia-Blanco, 1976). As an isolated unit, this group contains five terminal O atoms, but in the network of the title compound four of them (except atom O1) are shared with like units to give the formula $\infty[\text{B}_5\text{O}_7\text{O}_{4/2}] \equiv \infty[\text{B}_5\text{O}_9]$. As seen in Fig. 1, the thick undulating B₅O₉ sheets extend in the *ab* plane, with stacking and interdigitation of successive layers producing the sites occupied by the Sr and K atoms. The Sr sites are approximately centered in the medial planes of the polyborate networks, while the K sites are found primarily in the interlaminar spacings.

The Sr atom is bound by eight O atoms and the K atom by nine; interconnections among these polyhedra are made by sharing edges and faces. Sr–O distances are in the range 2.539 (5)–3.058 (7) Å with a mean

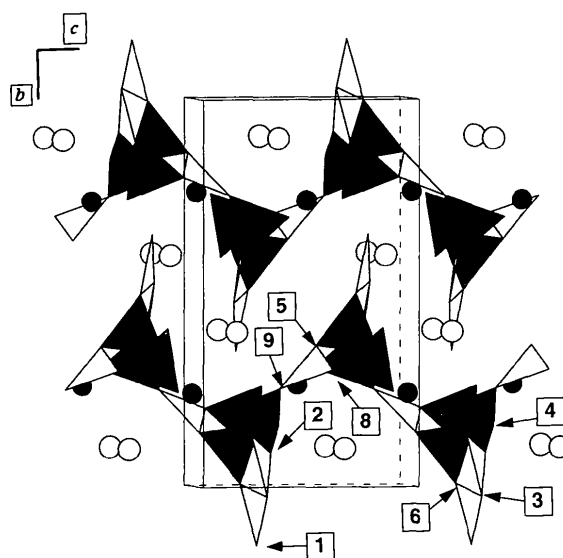


Fig. 1. Drawing of SrKB₅O₉ along [100]. Darker circles represent Sr atoms and lighter circles K atoms.

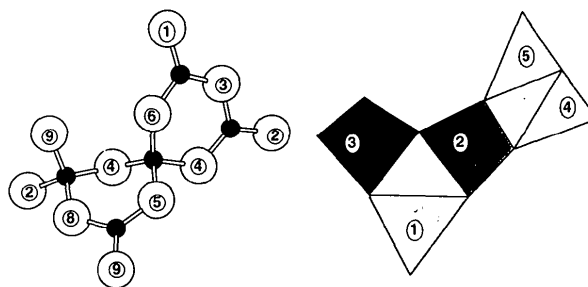


Fig. 2. Labeled drawings of a single B₅O₁₁ unit.

of $2.67 \pm 17 \text{ \AA}$, and K—O distances are in the range $2.633(4)$ – $3.265(4) \text{ \AA}$ with an average of $2.87 \pm 19 \text{ \AA}$. Atoms B1, B4 and B5 bind to O atoms in a triangular mode and the remaining B atoms occupy distorted tetrahedral sites.

B1	0.383 (1)	−0.007 (1)	0.1942 (4)	0.014 (3)
B2	0.807 (1)	−0.2799 (9)	0.3975 (5)	0.014 (3)
B3	0.463 (1)	0.215 (1)	0.3270 (5)	0.013 (4)
B4	0.833 (1)	−0.1979 (9)	0.5644 (5)	0.015 (4)
B5	0.062 (1)	−0.217 (1)	0.4387 (5)	0.015 (4)

Experimental

Crystal data

SrKB₅O₉

$M_r = 324.76$

Monoclinic

$P2_1/c$

$a = 6.676(1) \text{ \AA}$

$b = 7.969(2) \text{ \AA}$

$c = 14.259(2) \text{ \AA}$

$\beta = 93.00(1)^\circ$

$V = 757.6(2) \text{ \AA}^3$

$Z = 4$

$D_x = 2.847 \text{ Mg m}^{-3}$

Mo $K\alpha$ radiation

$\lambda = 0.71069 \text{ \AA}$

Cell parameters from 19

reflections

$\theta = 15$ – 18°

$\mu = 7.479 \text{ mm}^{-1}$

$T = 296 \text{ K}$

Plate

$0.10(2) \times 0.06(2) \times$

$0.03(2) \text{ mm}$

Colorless

Data collection

Rigaku AFC-6R diffractometer

ω - 2θ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker &

Stuart, 1983)

2544 measured reflections

2364 independent reflections

1471 observed reflections

$[F_o^2 \geq 3\sigma(F_o^2)]$

$R_{\text{int}} = 0.058$

$\theta_{\text{max}} = 37.5^\circ$

$h = 0 \rightarrow 9$

$k = 0 \rightarrow 11$

$l = -20 \rightarrow 20$

3 standard reflections

monitored every 200

reflections

intensity decay:

$\sim 5.0\%$

Refinement

Refinement on F

$R = 0.044$

$wR = 0.048$

$S = 1.27$

1471 reflections

145 parameters

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} = 0.03$

$\Delta\rho_{\text{max}} = 0.87 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.71 \text{ e \AA}^{-3}$

Extinction correction:

Zachariasen (1967)

Extinction coefficient:

$0.78(3) \times 10^{-7}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	U_{eq}
Sr	0.9218 (1)	0.0151 (9)	0.2392 (4)	0.0095 (3)
K	0.5022 (2)	−0.1540 (2)	0.4007 (1)	0.0175 (6)
O1	0.0917 (6)	−0.2020 (6)	0.3467 (3)	0.015 (3)
O2	0.3608 (6)	0.1784 (6)	0.4131 (3)	0.014 (3)
O3	0.8729 (6)	−0.1729 (6)	0.4726 (3)	0.017 (3)
O4	0.6717 (6)	0.1674 (6)	0.3420 (3)	0.013 (3)
O5	0.2223 (6)	−0.0468 (6)	0.1353 (3)	0.013 (3)
O6	0.2089 (6)	−0.2678 (6)	0.5026 (3)	0.017 (3)
O7	0.0191 (6)	0.2366 (6)	0.3690 (3)	0.014 (3)
O8	0.5547 (6)	−0.0999 (6)	0.1974 (3)	0.017 (3)
O9	0.3591 (6)	0.1312 (6)	0.2470 (3)	0.015 (3)

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sr—O1 ⁱ	2.539 (5)	K—O1	2.833 (4)
Sr—O1 ⁱⁱ	2.564 (5)	K—O2	2.821 (5)
Sr—O4	2.581 (4)	K—O2 ^{iv}	2.770 (4)
Sr—O5 ⁱ	2.602 (4)	K—O3	2.633 (4)
Sr—O7 ⁱ	2.614 (5)	K—O4	2.940 (5)
Sr—O7 ⁱⁱⁱ	2.744 (4)	K—O6	2.658 (4)
Sr—O8	2.655 (4)	K—O8	2.970 (5)
Sr—O9 ⁱ	3.058 (4)	K—O9	2.965 (4)
B1—O5	1.366 (7)	K—O9 ⁱⁱⁱ	2.902 (5)
B1—O8	1.363 (8)	B1—O9	1.347 (8)
B2—O4	1.472 (8)	B2—O5 ⁱⁱ	1.467 (8)
B2—O6 ^{iv}	1.436 (8)	B2—O7 ⁱ	1.535 (7)
B3—O2	1.464 (8)	B3—O4	1.449 (7)
B3—O8 ⁱⁱ	1.518 (8)	B3—O9	1.466 (8)
B4—O2 ^{iv}	1.361 (8)	B4—O3	1.364 (8)
B4—O7 ^{iv}	1.367 (8)	B5—O1	1.341 (8)
B5—O3 ^v	1.419 (8)	B5—O6	1.365 (8)
O1 ⁱ —Sr—O4	105.9 (9)	O1—K—O2	79.7 (1)
O1 ⁱ —Sr—O5 ⁱ	83.1 (2)	O2—K—O3	109.9 (1)
O1 ⁱ —Sr—O7 ⁱ	86.9 (1)	O2—K—O6	91.6 (1)
O1 ⁱ —Sr—O8	106.1 (1)	O2—K—O8	89.0 (1)
O4—Sr—O5 ⁱ	162.4 (1)	O3—K—O4	78.0 (1)
O4—Sr—O7 ⁱ	54.9 (1)	O3—K—O6	118.1 (1)
O5 ⁱ —Sr—O7 ⁱ	111.1 (1)	O3—K—O8	103.4 (1)
O5 ⁱ —Sr—O8	122.4 (1)	O4—K—O6	139.3 (1)
O7 ⁱ —Sr—O8	125.8 (1)	O6—K—O8	135.4 (1)
O7 ⁱⁱⁱ —Sr—O9 ^v	94.6 (2)	O5—B1—O9	114.9 (6)
O5—B1—O8	121.7 (6)	O4—B2—O5 ⁱⁱ	109.6 (5)
O8—B1—O9	123.4 (5)	O4—B2—O7 ⁱ	105.6 (5)
O4—B2—O6 ^{iv}	114.7 (5)	O5 ⁱⁱ —B2—O7 ⁱ	103.6 (5)
O5 ⁱⁱ —B2—O6 ^{iv}	111.4 (5)	O2—B3—O4	108.1 (5)
O6 ^{iv} —B2—O7 ⁱ	111.2 (5)	O2—B3—O9	109.8 (5)
O2—B3—O8	116.1 (4)	O4—B3—O9	114.0 (5)
O4—B3—O8 ⁱⁱ	110.6 (5)	O2 ^{iv} —B4—O3	116.4 (5)
O8 ⁱⁱ —B3—O9	103.7 (5)	O3—B4—O7 ^{iv}	122.1 (6)
O2 ^{iv} —B4—O7 ^{iv}	121.5 (6)	O1—B5—O6	122.8 (6)
O1—B5—O3 ^v	119.4 (6)	O3 ^v —B5—O6	117.7 (5)

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

TEXSAN (Molecular Structure Corporation, 1985) was used for structure solution and refinement.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: BR1081). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Co₁₀Ge₃O₁₆

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Abstract

The structure of a new cobalt germanate, Co₁₀Ge₃O₁₆, has been determined using X-ray diffraction data collected on a single crystal grown by slow cooling of a stoichiometric melt at atmospheric pressure. Co₁₀Ge₃O₁₆ is isostructural with (Ni,Mg)₁₀Ge₃O₁₆ and is also structurally related to the mineral aerugite, Ni_{8.5}As₃O₁₆. Its crystal structure is based on a cubic close-packing of O atoms with octahedral (Co and Ge) and tetrahedral (Ge) metal-atom sites. It can be described as an intergrowth of {111} spinel triple layers with {111} rock-salt single layers along the [001]_{hex} direction of the rhombohedral cell.

Comment

The original determination of phase relations in the NiO–MgO–GeO₂ and CoO–MgO–GeO₂ systems (Navrotsky, 1973) showed strong similarities between both systems as well as the existence of unidentified intermediate phases in the Co system. The recent discovery of the compound (Ni,Mg)₁₀Ge₃O₁₆ (Barbier, 1987; Fleet & Barbier, 1988) prompted a re-investigation of the CoO–MgO–GeO₂ system, which is currently in progress. Initial results have indeed confirmed the existence of the phase (Co_{1-x}Mg_x)₁₀Ge₃O₁₆, which, unlike the Ni analog, includes the $x = 0$ end-member, Co₁₀Ge₃O₁₆. This new cobalt germanate melts congruently at temperatures between 1573 and 1673 K, which made it possible to grow single crystals from a stoichiometric melt (sealed in a Pt tube to prevent loss of GeO₂ by evaporation). Although no chemical analysis of the crystals has been carried out, their chemical composition is confirmed by the structure refinement.

The Co₁₀Ge₃O₁₆ structure is based on a 12-layer close-packing of O atoms with a c/a ratio of 4.85, close to the ideal value of $6\sqrt{2}/\sqrt{3} = 4.90$. The Co atoms occupy octahedral sites only, whereas the Ge atoms are found in both octahedral and tetrahedral sites (Table 2). No evidence of mixed Co/Ge site occupancy has been shown by the refinement and the displacement parameters of all atoms are nearly isotropic. The atomic distribution has also been confirmed by bond-valence sum calculations (Brown & Altermatt, 1985), which yielded the following values: O1 1.98 (1), O2 1.84 (1), O3 1.94 (1), O4 1.92 (1), Co1 1.89 (1), Co2 1.90 (1), Co3 1.95 (1), Ge1 4.09 (2) and Ge2 3.70 (4). This last value indicates that the tetrahedral Ge2—O bonds are stretched, as is also observed in the isostructural compound (Ni,Mg)₁₀Ge₃O₁₆ (Fleet & Barbier, 1988) and in Mg₂GeO₄ spinel (Von Dreele, Navrotsky & Bowman, 1977). As shown in Fig. 1, the Co1O₆, Co3O₆ and Ge2O₄ polyhedra make up a spinel-like triple layer, while the Co2O₆ and Ge1O₆ octahedra make up a rock-salt type single layer. Exactly the same spinel–rock salt intergrowth also occurs in (Ni,Mg)₁₀Ge₃O₁₆ (Fleet & Barbier, 1988), while related cation-deficient structures are formed by the arsenate mineral aerugite, Ni_{8.5}As₃O₁₆ (Fleet & Barbier, 1989), its Mg analog (Bless & Kostiner, 1973) and its Co analog (formulated as Co₈As₃O₁₆; Krishnamachari & Calvo, 1970).

Co₁₀Ge₃O₁₆ forms as part of a (Co,Mg)₁₀Ge₃O₁₆ solid solution which exists on the Co-rich side of the CoO–MgO–GeO₂ system together with a

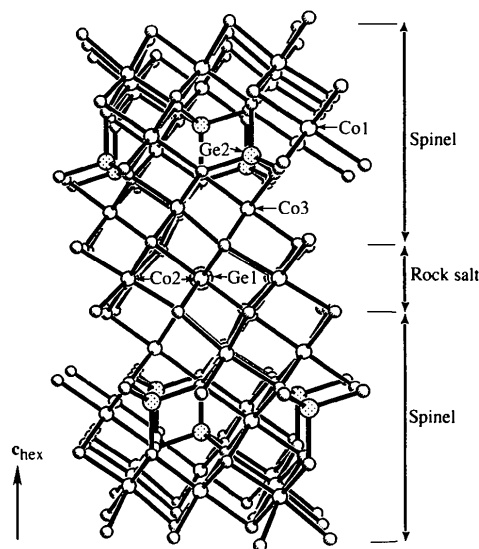


Fig. 1. Perspective view of the Co₁₀Ge₃O₁₆ structure along the [210] direction. The structure consists of an intergrowth of spinel slabs and rock-salt layers along the c_{hex} direction of the rhombohedral unit cell. Large, medium and small circles represent Ge, Co and O atoms, respectively. Note that the Ge atoms occupy tetrahedral sites (Ge2) in the spinel slabs, and octahedral sites (Ge1) in the rock-salt layers.