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$Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$ and $Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$

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Abstract

The crystal structures of $Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$ and $Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$, which are isostructural with $SrCu_2(BO_3)_2$, have been refined from single-crystal X-ray diffraction data. The structures consist of slightly puckered layers with the composition $[CuBO_3]^-$ stacked along the c axes, with Sr, Ba or Ca atoms eight-coordinated between the layers. The interlayer separation is directly affected by the substitution of smaller Ca or larger Ba atoms in place of Sr. In both structures, each Cu atom is coordinated by four O atoms with Cu—O distances ranging from 1.91 to 1.94 Å. The borate groups are distorted from D_{3h} to C_{2v} symmetry.

Comment

The present study includes the preparation and single-crystal X-ray diffraction studies of the phases $Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$, (I), and $Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$, (II). These phases were synthesized as part of the characterization of a series of mixed alkaline earth copper(II) borates, with composition $Sr_{1-x}M_xCu_2(BO_3)_2$, where M = Ba or Ca. The phases are isotypic with the $SrCu_2(BO_3)_2$ structure (Smith & Keszler, 1991; Norrestam, Carlson, Kritikos & Sjödin, 1994). Stoichiometric mixtures of alkaline earth oxides (with BaO_2 used as a precursor to BaO), copper(II) oxide and boron oxide (10% excess of B_2O_3) were heated to 1073 K for 1 h. Then the temperature was raised at a rate of 100 K h^{-1} to 1193 K. After annealing at 1193 K for 48 h, the furnace was cooled at 100 K h^{-1} to 573 K and turned off. Blue crystalline specimens were obtained, with smaller x values than the corresponding initial compositions (Norrestam *et al.*, 1994). A limited number of attempts to prepare substituted phases by the procedure above, with higher x values, resulted in multiple phases. The major phases consisted, as judged from X-ray powder films, of $Sr_{1-x}M_xCu_2(BO_3)_2$. Analysis of ten different crystals of each phase in a scanning electron microscope (JSM-820A, equipped with a Link AN10000 EDX system) gave the compositions $Sr_{0.735(5)}Ba_{0.265(5)}Cu_2(BO_3)_2$ and $Sr_{0.661(6)}Ca_{0.339(6)}Cu_2(BO_3)_2$. Refinement of the structural models using the single-crystal diffraction intensities resulted in the compositions $Sr_{0.71(1)}Ba_{0.29(1)}Cu_2(BO_3)_2$ and $Sr_{0.69(1)}Ca_{0.31(1)}Cu_2(BO_3)_2$. The refined compositions are within three standard deviations of those obtained by the EDX analyses.

Fig. 1 shows the atomic labelling and the arrangement of coordination polyhedra around the Cu and B atoms in a layer ($0 \leq z < \frac{1}{2}$) through the crystal structure of $Sr_{1-x}M_xCu_2(BO_3)_2$. The complete crystal structure is obtained from Fig. 1 if the I-centering translation is applied to the layer. Each Cu atom is bonded to four adjacent O atoms (Tables 2, 4), in a distorted square coordination geometry (Fig. 1). A roughly planar dimeric arrangement is formed by two such coordination squares, with Cu···Cu distances of 2.912 (2) Å in the Ba-substituted phase and 2.895 (2) Å in the Ca-substituted phase. The Cu···Cu distance, along the c axes between two corresponding dimers, is considerably longer [3.654 (2) Å with Ba and 3.603 (2) Å with Ca]. By also including a very distant (about 2.93 Å) O atom in the coordination around each Cu atom, a distored square-pyramidal five-coordinate geometry is obtained. $Cu_2B_2O_8$ entities are formed when two BO_3 groups share edges with the copper–oxygen dimers.

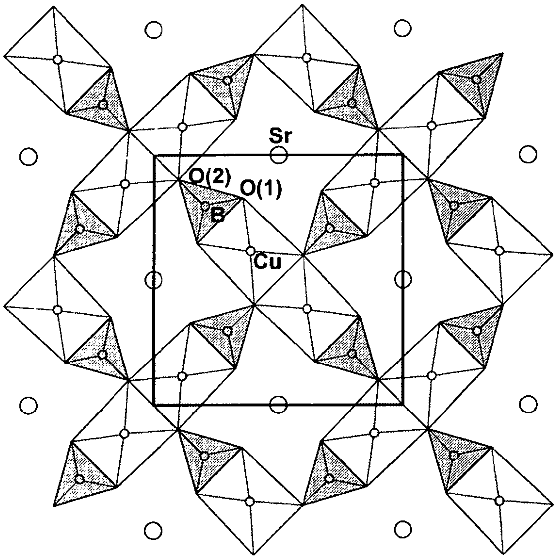

Fig. 1. Polyhedral representation of a layer ($0 \leq z < \frac{1}{2}$) through the $Sr_{1-x}M_xCu_2(BO_3)_2$ structure, viewed along the c axis. The cations and B-atom positions are drawn as circles. The Cu—O and Cu—B bonds, unit-cell and atomic labelling are also shown. The b axis is horizontal, a vertical and the origin at the upper-left corner. The coordination polyhedra around Sr atoms have been omitted.

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The $Cu_2B_2O_8$ entities form puckered layers by corner sharing, with the overall composition $[CuBO_3]^-$. The separation of such layers along the *c* axes is 3.389 Å in $Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$ and 3.270 Å in $Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$. Owing to the displacement of adjacent $[CuBO_3]^-$ layers (at $z \simeq \pm\frac{1}{4}$), channels are formed along the *c* axes. These channels are occupied by the alkaline earth atoms. These metal atoms are, as a result of the absence of stronger bonds between the layers, responsible for the major binding forces that hold the layers together along the *c* axes. Each alkaline earth atom is eight-coordinated by four O atoms (Tables 2, 4) from each adjacent $[CuBO_3]^-$ layer. The cubic coordination geometry is distorted towards a square prism by an elongation along the *c* axes.

From Fig. 2 (and Tables 1, 3) it can be seen that the *z* coordinates of all atoms deviate from 0 modulo $\frac{1}{4}$ by less than 0.3 Å. This might indicate that the structure could have mirror symmetry perpendicular to [001]. After an origin shift of $(0,\frac{1}{2},\frac{1}{4})$ the structure can, at least approximately, be described with the minimal non-isomorphic supergroup symmetry *I4/mmm*. However, refinements of the derived *I4/mmm* models yielded *R* values in the range 0.24–0.26 and unreasonable oscillating shifts on several of the structural parameters. The lack of convergence and the high *R* values obtained indicate that the higher symmetry can only be regarded as pseudosymmetry.

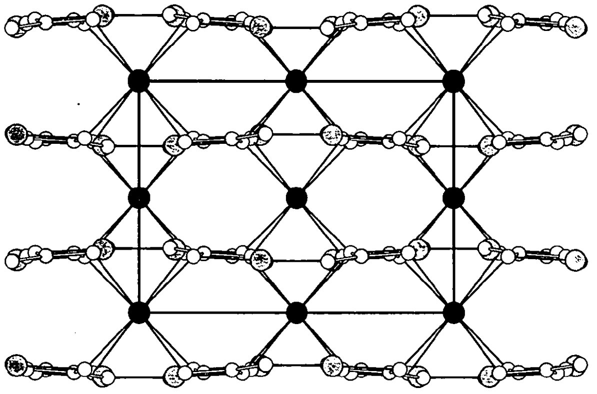

Fig. 2. Ball-and-stick representation along the *a* axis of the $Sr_{1-x}M_xCu_2(BO_3)_2$ structure. The metal atoms are represented by larger circles, B and O by smaller circles. Cu and B are grey, Sr is black, and O white. The *b* axis is horizontal, *c* vertical and the origin is at the upper-left corner.

Experimental

Compound (I)

Crystal data

$Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$
$M_r = 345.5$ (3)
Tetragonal
$I\bar{4}2m$
$a = 9.010$ (2) Å
$c = 6.779$ (2) Å
$V = 550.3$ (3) Å^3
$Z = 4$
$D_x = 4.185$ (4) Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 14 reflections
$\theta = 12.8–28.9°$
$\mu = 16.34$ mm^{-1}
$T = 293$ (1) K
Prismatic
0.30 × 0.20 × 0.05 mm
Blue

Data collection

Stoe Siemens AED 2 diffractometer
ω–θ scans
Absorption correction: by integration from crystal shape
$T_{min} = 0.09$, $T_{max} = 0.36$
683 measured reflections
263 independent reflections
240 observed reflections $[I > 5\sigma(I)]$

$R_{int} = 0.016$
$\theta_{max} = 30.0°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 10$
3 standard reflections frequency: 360 min intensity variation: 1.7%

Refinement

Refinement on *F*
$R = 0.027$
$wR = 0.035$
$S = 1.00$
240 reflections
29 parameters
$w = 1/[\sigma^2(F) + 0.0007F^2]$
$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 1.6$ e Å^{-3}
$\Delta\rho_{min} = -1.5$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (I)

$$U_{eq} = (1/3)\Sigma_i\Sigma_jU_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	*y*	*z*	U_{eq}
Sr	0	1/2	0	0.0106 (2)
Ba	0	1/2	0	0.0106 (2)
Cu	0.3857 (1)	*x*	0.2226 (2)	0.0135 (3)
O(1)	0.1727 (4)	0.3554 (4)	0.2408 (12)	0.0152 (10)
O(2)	0.0992 (4)	*x*	0.2924 (12)	0.019 (2)
B	0.2049 (6)	*x*	0.2609 (19)	0.0133 (16)

Table 2. *Selected geometric parameters* (Å, °) *for* (I)

Sr—O(1)	× 4	2.604 (6)	Cu—O(2)		2.923 (8)
Sr—O(1)	× 4	2.684 (6)	B—O(1)	× 2	1.393 (7)
Cu—O(1)	× 2	1.943 (4)	B—O(2)		1.364 (7)
Cu—O(2)	× 2	1.931 (4)			
O(1)—Cu—O(1)		73.62 (15)	O(1^{i})—Cu—O(2^{ii})	× 2	102.30 (15)
O(2)—Cu—O(2)		81.79 (15)	O(1)—B—O(2)	× 2	123.3 (5)
O(2)—Cu—O(2)	× 2	84.1 (3)	O(1)—B—O(1^{i})		113.3 (4)

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

Compound (II)

Crystal data

$Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$
$M_r = 316.2$ (6)
Tetragonal
$I\bar{4}2m$
$a = 8.9692$ (9) Å
$c = 6.540$ (1) Å
$V = 526.1$ (2) Å^3
$Z = 4$
$D_x = 3.992$ (8) Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 15 reflections
$\theta = 12.9–29.1°$
$\mu = 15.17$ mm^{-1}
$T = 293$ (1) K
Prismatic
0.1 × 0.1 × 0.02 mm
Blue

Data collection

Stoe Siemens AED 2 diffractometer
ω–θ scans
Absorption correction: by integration from crystal shape
$T_{\min} = 0.29$, $T_{\max} = 0.66$
654 measured reflections
250 independent reflections
198 observed reflections $[I > 5\sigma(I)]$

$R_{\text{int}} = 0.034$
$\theta_{\max} = 29.9°$
$h = -1 \rightarrow 13$
$k = -1 \rightarrow 13$
$l = -1 \rightarrow 9$
3 standard reflections
frequency: 360 min
intensity variation: 2.0%

Refinement

Refinement on F
$R = 0.024$
$wR = 0.030$
$S = 1.27$
198 reflections
29 parameters
$w = 1/[\sigma^2(F) + 0.0007F^2]$
$(\Delta/\sigma)_{\max} = 0.004$

$\Delta\rho_{\max} = 0.6$ e Å^{-3}
$\Delta\rho_{\min} = -1.0$ e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2) *for* (II)

$$U_{\text{eq}} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Sr	0	1/2	0	0.0103 (4)
Ca	0	1/2	0	0.0103 (4)
Cu	0.3859 (1)	x	0.2267 (2)	0.0134 (3)
O(1)	0.1720 (4)	0.3549 (4)	0.2419 (12)	0.0138 (10)
O(2)	0.0986 (5)	x	0.2785 (19)	0.031 (3)
B	0.2053 (6)	x	0.256 (2)	0.0127 (19)

Table 4. *Selected geometric parameters* (Å, °) *for* (II)

Sr—O(1)	× 4	2.565 (6)	Cu—O(2)		2.938 (12)
Sr—O(1)	× 4	2.631 (6)	B—O(1)	× 2	1.378 (7)
Cu—O(1)	× 2	1.940 (4)	B—O(2)		1.361 (7)
Cu—O(2)	× 2	1.913 (5)			
O(1)—Cu—O(1)		73.45 (15)	O(2)—Cu—O(2)	× 2	86.1 (4)
O(1)—Cu—O(2)	× 2	102.43 (17)	O(1)—B—O(2)		122.7 (5)
O(2)—Cu—O(2)		81.64 (19)	O(1)—B—O(1$^{\text{i}}$)	× 2	114.6 (4)

Symmetry code: (i) y, x, z.

The structural refinement was performed with the *SHELX*76 program package (Sheldrick, 1976). The program *ATOMS* (Dowty, 1989) was used to obtain the structure diagram. Cell parameters were obtained from scanned Guinier X-ray powder photographs, using Cu $K\alpha_1$ radiation with silicon as an internal standard. Data were collected at room temperature and corrected for background, Lorentz and polarization effects.

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: BR1074). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Octasodium Hydrogen Decatungstogadolinate Triacontahydrate

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Abstract

The decatungstogadolinate anion in the title compound, $Na_8H[GdW_{10}O_{36}].30H_2O$, has approximately D_{4d} symmetry, with Gd—O and W—O distances of 2.39 (2)–2.42 (2) Å and 1.69 (2)–2.34 (2) Å, respectively.

Comment

In our survey of the structures of decatungstolanthanoate anions (Ozeki, Takahashi & Yamase, 1992; Ozeki & Yamase, 1993, 1994*a*,*b*; Sugeta & Yamase, 1993; Yamase, Ozeki & Ueda, 1993; Yamase & Ozeki, 1993), the lanthanide atoms of the $[LnW_{10}O_{36}]^{9-}$ (Ln = Pr, Nd, Sm, Gd, Tb, Dy) anions in their tripotassium tetrasodium salts were found to deform to C_{4v} symmetry from their highest possible symmetry of D_{4d}. This structural distortion originates from the attachment of the K$^+$ cations to the LnO_8 square antiprism in the $[LnW_{10}O_{36}]^{9-}$ anion (Ozeki & Yamase, 1994*a*). We report here the structure of the title compound, (1), and compare it with that of $K_3Na_4H_2[GdW_{10}O_{36}].21H_2O$, (2) (Yamase & Ozeki, 1993) to illustrate the effect of crystal packing on the structures of the decatungstolanthanoate anions.

As shown in Fig. 1, the decatungstogadolinate anion in compound (1) possesses the same metal–oxygen framework structure as found in compound (2). Unlike the $[GdW_{10}O_{36}]^{9-}$ anion in (2), where the Gd—W distances are asymmetric for the two $[W_5O_{18}]^{6-}$