Syntheses and Crystal Structures of the α- and β-Forms of the Orthoborate $Sr_2Cu(BO_3)_2$

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The low-temperature α-form and the high-temperature β-form of the compound of formula Sr_2Cu $(BO_3)_2$ have been synthesized and their structures established by single-crystal X-ray methods. The α-phase crystallizes in a monoclinic cell of dimensions $a = 5.707(1)$, $b = 8.796(2)$, $c = 6.027(1)$ Å, and $\beta = 116.98(1)°$ with $Z = 2$; the space group is $P2_1/c$. The structure was determined from 1039 independent reflections and refined to the final residuals $R = 0.037$ and $R_w = 0.051$. It is composed of sheets of isolated CuO_4 square planes that are rotated out of the b–c plane and connected by BO_3 and SrO_7 units; it is isomorphous to the compound $Na_2Cu(CO_3)_2$. The β-phase crystallizes in an orthorhombic cell of dimensions $a = 7.612(3)$, $b = 10.854(7)$, $c = 13.503(4)$ Å with $Z = 8$; the space group is *Pnma*. The structure was determined from 1235 independent reflections and refined to the final residuals $R = 0.030$ and $R_w = 0.039$. This structure exhibits isolated units of stoichiometry $Cu_2(BO_3)_4$ that are built from CuO_4 distorted square planes and triangular BO_3 groups. These units are bridged by three crystallographically independent Sr atoms. The phase transition from the α-phase to the β-phase occurs at 800°C. Considerable bond scission and reformation between the two phases indicate that the transition is first order. © 1989 Academic Press, Inc.

Introduction

Only a limited number of anhydrous borates of the transition metals have been reported (*1*). Prompted, in part, by this state of underdevelopment and the characteristics of the compound $Cu_2Al_6B_4O_{17}$ we have elected to synthesize new complex copper borates and their derivatives. The aforementioned borate has been reported to catalyze oxidative dehydrogenation of a variety of organic substrates and to be effective in the conversion of synthesis gas to alcohols (*2*); the solid solutions $Cu_{2-x}M_xAl_6$ B_4O_{17} where M = Zn, Co, Ni, or Mg with $0.01 \leq x \leq 0.8$ exhibit similar characteristics.

In this report we describe the preparation, crystal structures, phase transition, and magnetic moments of the polymorphic compound $Sr_2Cu(BO_3)_2$ which is the first of a new family of alkaline earth copper(II) borates that we have discovered. Two phases, a low-temperature α-form and a high-temperature β-form, are observed between 25° and 1000°C with a first-order phase transition at 800°C.

Experimental

Syntheses

The α-phase was prepared by dissolving a stoichiometric ratio of the reagents CuO

(99.999%, Johnson Matthey) and $Sr(NO_3)_2$ (reagent grade, J. T. Baker) in dilute nitric acid and precipitating the cations with a 30% excess of oxalic acid dihydrate (reagent grade, J. T. Baker); the mixture was then dried. Powdered B_2O_3 (99.99%, Morton Thiokol) was added and the mixture ground under hexane to a fine powder. This intimate mixture was heated in an alumina crucible at 700°C for 18 hr, cooled and ground again under hexane, and finally pressed into a pellet and sintered at 740°C for an additional 18 hr. Except for a few weak lines attributable to the phase $Sr_3B_2O_6$, the powder X-ray trace of the product compares well to that calculated with the computer program LAZY-PULVERIX (3) from the results of the single-crystal structure analysis (vide infra).

Single crystals were grown with the compound $LiBO_2$ as a flux. A mixture with a sample:flux ratio by mass of 7:1 was heated in a Pt crucible to 875°C, cooled 6°/hr to 600°C, then air quenched. The resulting purple single crystals were physically separated from the crucible for the structure determination.

The β-phase was prepared by grinding a stoichiometric ratio of $Sr(NO_3)_2$, $Cu(NO_3)_2 \cdot 2.5H_2O$ (reagent grade, Mallinckrodt) and B_2O_3 under hexane to a fine powder and calcining at 600°C for 30 min. A single phase resulted from subsequent sintering at 900°C for 18 hr. The powder X-ray trace for this powder compares well to that calculated from the single-crystal X-ray data (vide infra). Lavender single crystals were obtained in a manner similar to that used for the growth of the α-phase except the sample was heated to 950°C and subsequently quenched in air after cooling to 820°C.

X-Ray Work

Powder X-ray diffractograms were obtained from an automated Philips powder diffractometer equipped with a diffracted-beam monochromator set for $CuK\alpha$ radiation.

A crystal of the α-phase with dimensions $0.32 \times 0.18 \times 0.08$ mm was chosen for the structure determination. Unit cell parameters were derived from a least-squares analysis of 22 reflections in the range $19° < 2\theta < 31°$ that were automatically centered on a Rigaku AFC6R diffractometer using monochromatic $MoK\alpha$ radiation. Intensity data in the range of indices $0 \leq h \leq 9$, $0 \leq k \leq 15$, $-10 \leq l \leq 9$ were collected with the ω-2θ scan technique at a scan speed of $16°/min$ in ω and a scan width $\Delta\omega = (1.25 + 0.3 \tan \theta)°$. From the 1504 reflections measured to $2\theta = 75°$, 1039 unique data having $F_0^2 \geq 3\sigma(F_0^2)$ were obtained.

Likewise, a crystal of the β-phase with dimensions $0.30 \times 0.16 \times 0.06$ mm was studied. Lattice parameters were refined from 18 reflections in the range $30° < 2\theta < 40°$. From 1900 reflections measured in the range of indices $0 \leq h \leq 10$, $-14 \leq k \leq 15$, $0 \leq l \leq 18$ to $2\theta = 60°$, 1235 unique data having $F_0^2 \geq 3\sigma(F_0^2)$ were obtained.

All calculations were performed on a microVax II computer with programs from the TEXRAY crystallographic software package. The systematic absences $h0l$, $l = 2n + 1$ and $0k0$, $k = 2n + 1$ unambiguously define the space group $P2_1/c$ for the α-phase. The systematic absences $0kl$, $k + l = 2n + 1$ and $hk0$, $h = 2n + 1$ indicate that the β-phase crystallizes in the centric group $Pnma$ or the acentric group $Pn2_1a$. We favor the centric group on the basis of the statistical analyses of the intensities (4) as well as the successful solution and refinement of the structure in this group. For each structure, the positional parameters for the Sr and Cu atoms were determined from the direct methods program MITHRIL (5) with the remaining atomic positions determined from analysis of subsequent difference electron density syntheses. Following refinement with isotropic thermal parameters the data were corrected

TABLE I

CRYSTAL DATA AND EXPERIMENTAL CONDITIONS
FOR α- AND β-$Sr_2Cu(BO_3)_2$

Crystal data	Experimental conditions	
	α-phase	β-phase
Diffractometer	Rigaku AFC6R	
Radiation	Graphite monochromated MoKα ($\lambda(K\alpha_1)$ = 0.70926 Å)	
Formula wt. (amu)	356.40	
a (Å)	5.707(1)	7.612(3)
b (Å)	8.796(2)	10.854(7)
c (Å)	6.027(1)	13.503(4)
β (degrees)	116.98(1)	
V (Å³)	269.6(2)	1116(1)
Space group	$P2_1/c$	$Pnma$
D_{calc} (g cm⁻³)	4.39	4.24
Crystal vol. (mm³)	0.005	0.003
$F(000)$	326	1304
Z	2	8
Linear abs. coeff. (cm⁻¹)	230.07	222.44
P factor	0.05	0.05
No. unique data with $F_o^2 > 3\sigma(F_o^2)$	1039	1235
R_{int}		0.027
R (on F for $F_o^2 > 3\sigma(F_o^2)$)	0.037	0.030
$R_w(F)$	0.051	0.039
Error in observation of unit wt. (e²)	1.38	1.01

for absorption with the computer program DIFABS (6); equivalent reflections were then averaged. Final least-squares refinement on F_o with data having $F_o^2 \geq 3\sigma(F_o^2)$ and anisotropic thermal factors for each atom resulted in the residuals $R = 0.037$ and $R_w = 0.051$ for the α-phase and $R = 0.030$ and $R_w = 0.039$ for the β-phase. The largest peaks in the final difference maps for the α- and β-phases have heights of 0.742% and 0.628% of a Sr atom, respectively. Additional crystal data and experimental conditions are summarized in Table I.

Measurements

A Harrop model DT-726 differential thermal analyzer interfaced to a PC via a Metrabyte DAS-8 A/D converter and Series M1000 signal conditioner was used to obtain DTA data. The sample and reference (Al_2O_3) were enclosed in Pt cups. A strong signal was observed with a heating rate of 10°C/min.

The effective magnetic moments were obtained at room temperature by the Gouy method. Measurements were made at a field strength of 5 kG, using an Alpha Model AL 7500 water-cooled magnet with 4-in. pole faces and a 1.5-in. air gap. The Gouy tube was calibrated with HgCo (SCN)₄. Diamagnetic corrections to molar susceptibilities were made from reported values (7) except for the Sr^{2+} ion whose correction was determined by interpolation.

Results

Structure of α-$Sr_2Cu(BO_3)_2$

Final atomic coordinates and thermal parameters of the α-form of the title compound are listed in Table IIa. Selected interatomic distances and angles are given in Table IIIa. A drawing of the contents of the unit cell is given in Fig. 1.

The structural features are square-planar CuO_4 units, trigonal-planar BO_3 groups, and tetragonal-base, trigonal-base SrO_7 units. The square and trigonal planes share vertices to form a two-dimensional sheet $^2_\infty[Cu(BO_3)_2]$ extending parallel to the b–c plane. The CuO_4 planes of the sheet are rotated about the O(2)–Cu–O(2) axes by ap-
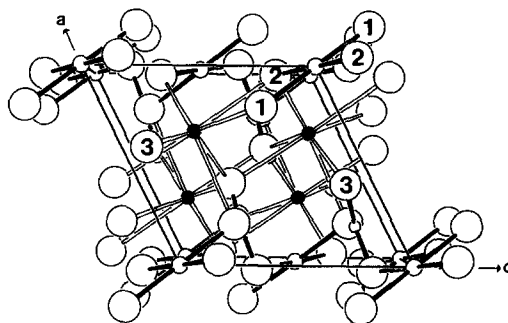

FIG. 1. Sketch of the unit cell of the structure of α-$Sr_2Cu(BO_3)_2$ viewed along the b axis. The large open circles represent O atoms, the smallest circles represent B atoms, and the small solid circles represent Sr atoms, here, and in all figures following.

TABLE IIa

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR α-Sr$_2$Cu(BO$_3$)$_2$

Atom	x	y	z	$B_{eq}{}^a$
Sr	0.3285(1)	0.1049(1)	0.6591(1)	0.66(1)
Cu	0	0	0	0.53(2)
B	0.805(1)	0.2521(6)	0.6597(8)	0.5(1)
O(1)	0.7950(7)	0.4068(4)	0.1813(6)	0.8(1)
O(2)	0.0375(7)	0.1863(4)	0.1850(6)	0.8(1)
O(3)	0.5909(9)	0.3388(4)	0.6146(6)	0.8(1)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr	0.0080(1)	0.0084(2)	0.0084(2)	−0.0004(1)	0.0036(1)	−0.0008(1)
Cu	0.0077(3)	0.0065(3)	0.0062(3)	0.0005(3)	0.0033(2)	0.0002(2)
B	0.010(2)	0.009(2)	0.002(1)	0.001(2)	0.002(1)	0.001(1)
O(1)	0.012(2)	0.006(1)	0.010(1)	0.000(1)	0.003(1)	−0.001(1)
O(2)	0.011(1)	0.011(2)	0.011(1)	−0.002(1)	0.007(1)	−0.002(1)
O(3)	0.012(2)	0.011(2)	0.010(1)	0.004(1)	0.006(1)	0.002(1)

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

TABLE IIb

FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS FOR β-Sr$_2$Cu(BO$_3$)$_2$

Atom	x	y	z	B_{eq}
Sr(1)	0	0	0	1.05(3)
Sr(2)	0.3839(1)	$\frac{1}{4}$	0.95434(6)	0.75(3)
Sr(3)	0.16218(7)	0.02423(5)	0.71699(4)	0.74(2)
Cu(1)	0.3120(1)	$\frac{1}{4}$	0.57219(8)	0.81(4)
Cu(2)	0.0280(1)	$\frac{1}{4}$	0.29959(7)	0.84(4)
B(1)	0.066(1)	$\frac{1}{4}$	0.1276(7)	0.9(3)
B(2)	0.491(1)	$\frac{1}{4}$	0.7125(7)	0.7(3)
B(3)	0.1271(8)	0.4355(6)	0.4329(5)	0.8(2)
O(1)	0.0764(8)	$\frac{1}{4}$	0.6997(4)	0.9(2)
O(2)	0.0766(8)	$\frac{1}{4}$	0.0275(4)	1.1(2)
O(3)	0.4416(5)	0.1415(4)	0.6657(3)	0.8(1)
O(4)	0.3015(5)	0.4649(4)	0.8867(3)	1.1(2)
O(5)	0.0604(6)	0.1430(4)	0.1846(3)	1.3(2)
O(6)	0.4825(5)	0.1260(4)	0.1048(3)	0.8(1)
O(7)	0.1961(5)	0.1059(4)	0.5219(3)	1.0(1)

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr(1)	0.0100(4)	0.0146(4)	0.0154(4)	0.0025(3)	0.0002(3)	0.0029(3)
Sr(2)	0.0105(3)	0.0102(3)	0.0079(3)	0	0.0005(3)	0
Sr(3)	0.0095(2)	0.0096(2)	0.0092(2)	−0.0005(2)	−0.0001(2)	−0.0003(2)
Cu(1)	0.0112(4)	0.0092(4)	0.0105(5)	0	−0.0035(4)	0
Cu(2)	0.0144(5)	0.0089(4)	0.0084(5)	0	0.0003(4)	0
B(1)	0.014(4)	0.008(4)	0.012(4)	0	−0.001(3)	0
B(2)	0.011(4)	0.006(4)	0.008(4)	0	0.000(3)	0
B(3)	0.011(3)	0.010(3)	0.010(3)	0.004(2)	0.004(2)	0.000(2)

TABLE IIb—*Continued*

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	0.014(3)	0.018(3)	0.004(2)	0	0.002(2)	0
O(2)	0.014(3)	0.020(3)	0.010(3)	0	0.000(2)	0
O(3)	0.009(2)	0.012(2)	0.011(2)	0.000(1)	0.001(1)	0.001(2)
O(4)	0.016(2)	0.012(2)	0.014(2)	−0.001(2)	−0.005(2)	−0.001(2)
O(5)	0.028(2)	0.012(2)	0.011(2)	0.002(2)	0.002(2)	0.001(2)
O(6)	0.012(2)	0.009(2)	0.011(2)	0.000(1)	−0.003(1)	0.001(2)
O(7)	0.012(2)	0.013(2)	0.010(2)	−0.003(2)	−0.004(2)	−0.001(2)

proximately 35° out of the *b–c* plane, affording the herringbone pattern, Scheme **1**, when viewed along the *c* axis. The B atoms bridge the isolated square planes, Scheme **2**. The structure is completed by joining successive sheets of Scheme **2** by interleaving Sr atoms.

The average Cu–O distance of 1.930(6) Å is similar to values observed in other copper borates, e.g., 1.95(1) Å for $Cu_3B_2O_6$ (*8*) and 1.968 Å for CuB_2O_4 (*9*). The square planes distort slightly to afford the angle O(1)–Cu–O(2) of 85.2(2)°. The edge O(1) · · · O(2) of this acute angle is shared by the Sr atom. The Sr atom is sevenfold coordinate, centering approximately a distorted tetragonal-base, trigonal-base polyhedron. An additional O atom O(1) is located 3.110(4) Å from the Sr atom. If this long distance were considered to be a weak bonding interaction, the environment could be described as a distorted square antiprism. A similar coordination environment without the additional O atom exists in the compound $Sr_2ScLi(B_2O_5)_2$ where the Sr atom occupies an irregular heptacoordinate site between two layers of O atoms (*10*). The Sr–O distances vary from 2.509(4) Å to 2.670(4) Å with an average value of 2.59(3)

Å. This compares well with the average Sr–O distances of 2.61 Å in $SrCuO_2$ (*11*), 2.59 Å in Sr_2CuO_3 (*12*), and 2.69 Å in SrB_4O_7 (*13*). The BO_3 groups are metrically quite regular. The average B–O distance, 1.38(2) Å, compares to similar interactions observed in a variety of other simple orthoborates discovered in this lab (*10, 14*) and by others (*1*). All O atoms are bonded to four cations.

Structure of β-$Sr_2Cu(BO_3)_2$

Final atomic coordinates and thermal factors are listed in Table IIb with selected interatomic distances and angles appearing in Table IIIb. A drawing of the contents of the unit cell is given in Fig. 2.

Because of the presence of three crystallographically independent Sr atoms this structure appears to be more complicated than the α-phase. Rather than an extended copper borate network, this structure is composed of isolated units, Scheme **3**, of stoichiometry $Cu_2(BO_3)_4$. Two highly distorted square planes occupied by the Cu atoms are bridged by two BO_3 groups by sharing O vertices. The terminal edges are completed by the sharing of two *cis* O atoms of the square plane with planar BO_3
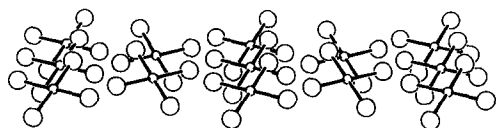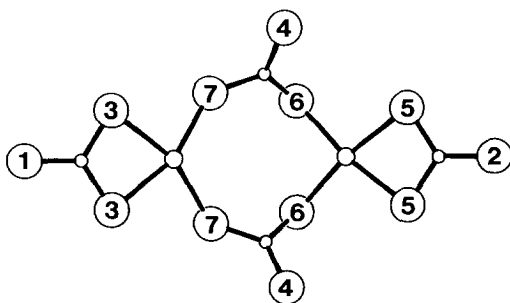

SCHEME 1

SCHEME 2

<table>
<tr><th colspan="3">TABLE IIIa</th></tr>
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	TABLE IIIa				TABLE IIIb		
	SELECTED DISTANCES (Å) AND ANGLES (°) FOR α-Sr$_2$Cu(BO$_3$)$_2$				SELECTED DISTANCES (Å) AND ANGLES (°) FOR β-Sr$_2$Cu(BO$_3$)$_2$		

Combined tables:

TABLE IIIa — SELECTED DISTANCES (Å) AND ANGLES (°) FOR α-Sr$_2$Cu(BO$_3$)$_2$

Atoms	Distance		Angle
Cu–O(1)	1.921(3) ×2	O(1)–Cu–O(2)	85.8(2)
Cu–O(2)	1.938(3) ×2		
B–O(1)	1.407(6)	O(1)–B–O(2)	117.2(4)
B–O(2)	1.378(6)	O(2)–B–O(3)	122.4(4)
B–O(3)	1.358(6)	O(3)–B–O(1)	120.4(4)
Sr–O(3)	2.509(4)	O(1)–Sr–O(1)	95.4(1)
Sr–O(2)	2.528(4)	O(2)–Sr–O(2)	76.4(1)
Sr–O(1)	2.536(3)	O(3)–Sr–O(3)	74.5(1)
Sr–O(1)	2.606(4)	O(3)–Sr–O(3)	82.7(1)
Sr–O(3)	2.629(4)	O(2)–Sr–O(3)	81.8(1)
Sr–O(3)	2.642(4)	O(2)–Sr–O(3)	125.3(1)
Sr–O(2)	2.670(4)		

TABLE IIIb — SELECTED DISTANCES (Å) AND ANGLES (°) FOR β-Sr$_2$Cu(BO$_3$)$_2$

Atoms	Distance		Angle
Cu(1)–O(3)	1.988(4) ×2	O(3)–Cu(1)–O(3)	72.7(2)
Cu(1)–O(7)	1.920(4) ×2	O(7)–Cu(1)–O(7)	109.1(2)
Cu(2)–O(5)	1.955(4) ×2	O(5)–Cu(2)–O(5)	72.9(3)
Cu(2)–O(6)	1.897(4) ×2	O(6)–Cu(2)–O(6)	90.4(2)
B(1)–O(2)	1.35(1)	O(2)–B(1)–O(5)	123.5(4)
B(1)–O(5)	1.394(7) ×2	O(5)–B(1)–O(5)	112.9(7)
B(2)–O(1)	1.35(1)	O(1)–B(2)–O(3)	121.9(3)
B(2)–O(3)	1.388(6) ×2	O(3)–B(2)–O(3)	116.1(7)
B(3)–O(4)	1.361(7)	O(4)–B(3)–O(6)	122.1(5)
B(3)–O(6)	1.385(7)	O(6)–B(3)–O(7)	117.6(5)
B(3)–O(7)	1.386(7)	O(7)–B(3)–O(4)	120.2(5)
Sr(1)–O(7)	2.600(4) ×2	O(7)–Sr(1)–O(3)	61.1(1)
Sr(1)–O(3)	2.750(4) ×2	O(3)–Sr(1)–O(4)	67.0(1)
Sr(1)–O(4)	2.785(4) ×2	O(4)–Sr(1)–O(7)	52.4(1)
Sr(1)–O(2)	2.800(2) ×2	O(2)–Sr(1)–O(3)	66.4(1)
Sr(1)–O(5)	2.972(4) ×2	O(5)–Sr(1)–O(2)	49.5(1)
Sr(2)–O(2)	2.539(6)	O(2)–Sr(2)–O(1)	148.1(2)
Sr(2)–O(1)	2.544(6)	O(1)–Sr(2)–O(4)	81.4(1)
Sr(2)–O(6)	2.550(4) ×2	O(6)–Sr(2)–O(6)	63.7(2)
Sr(2)–O(4)	2.582(4) ×2	O(4)–Sr(2)–O(6)	82.9(1)
Sr(2)–O(7)	2.863(4) ×2	O(7)–Sr(2)–O(7)	66.2(2)
Sr(3)–O(6)	2.483(4)	O(6)–Sr(3)–O(5)	66.3(1)
Sr(3)–O(4)	2.527(4)	O(4)–Sr(3)–O(3)	72.5(1)
Sr(3)–O(1)	2.547(2)	O(1)–Sr(3)–O(7)	68.4(2)
Sr(3)–O(3)	2.574(4)	O(3)–Sr(3)–O(5)	70.0(1)
Sr(3)–O(3)	2.636(4)	O(3)–Sr(3)–O(3)	116.7(2)
Sr(3)–O(7)	2.792(4)	O(7)–Sr(3)–O(6)	71.0(1)
Sr(3)–O(5)	2.816(4)	O(5)–Sr(3)–O(6)	66.3(1)
Sr(3)–O(5)	2.819(5)	O(5)–Sr(3)–O(5)	96.3(1)

groups. These edges are pinched by the BO$_3$ groups to afford the angles 72.7(2)° and 72.9(3)° for O(3)–Cu(1)–O(3) and O(5)–Cu(2)–O(5), respectively. The planarity of the CuO$_4$ groups is also perturbed as evidenced by the angles O(3)–Cu(1)–O(7), 159.2(2)°, and O(5)–Cu(2)–O(6), 170.2(2)°. As seen in Scheme **4**, there is a substantial deviation from planarity of the Cu$_2$(BO$_3$)$_4$ unit with a bend at the atom O(6). The angle B(3)–O(6)–Cu(2), 116.6(4)°, contrasts to that observed for B(3)–O(7)–Cu(1), 138.2(4)°. These angles are consistent with the chemically distinct nature of these atoms; atom O(6) is four-coordinate, binding to atoms B(3), Cu(2), and Sr(2, 3), while
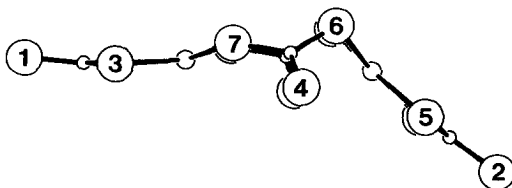
atom O(7) is five-coordinate, binding to atoms B(3), Cu(1), and Sr(1-3). The Cu–O and B–O distances are similar to those observed in the α-phase.

The copper borate units are bridged by Sr atoms occupying sites of high coordination
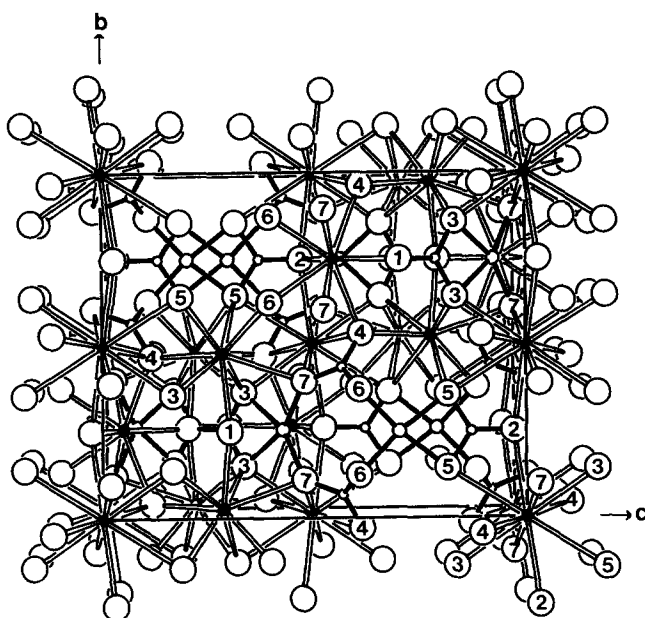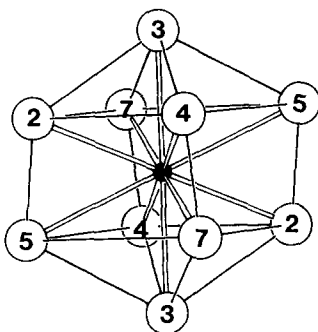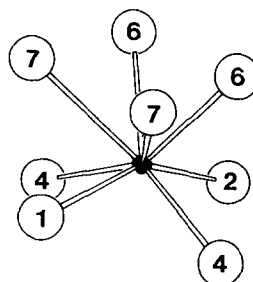

SCHEME 3

SCHEME 4

FIG. 2. Sketch of the unit cell of the structure of β-Sr₂Cu(BO₃)₂ viewed along the *a* axis.

numbers. The atom Sr(1) occupies a site, Scheme **5**, with 10 O atoms that are located at distances ranging from 2.600(4) to 2.972(4) Å. Its environment may be described as a highly distorted capped cube. Atom Sr(2) occupies an irregular square antiprismatic site, Scheme **6**, with the Sr atom depressed toward the plane formed by atoms O(1), O(2), and O(4); representative angles include O(1)–Sr(2)–O(4), 81.4(1)°, and O(6)–Sr(2)–O(6), 63.7(2)°. The Sr(2)–

O(7) distance, 2.863(4) Å, is considerably longer than the remaining Sr(2)–O distances (mean = 2.56(1) Å). Atom Sr(3) occupies an irregular eightfold dodecahedral site, Scheme **7**, with distances ranging from 2.483(4) to 2.819(5) Å. From these descriptions for the environments of the cations, atoms O(1), O(2), O(4), and O(6) are each observed to bond to four cations and the atoms O(3), O(5), and O(7) each bond to five cations.

SCHEME 5

SCHEME 6
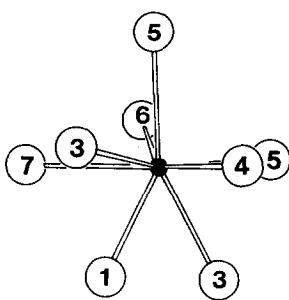
SCHEME 7

We note that we have prepared the Ba analog (*15*) of the title compound and find it to crystallize only in the β-form, consistent with the larger crystal radius of the Ba atom relative to the Sr atom.

Discussion

The effective magnetic moments at 23°C of the α- and β-forms are 1.70(2) and 1.72(2) BM, respectively. These values are consistent with the d^9 electronic configuration for isolated Cu(II) ions and spin-only contributions to the magnetic moment. Values of μ_{eff} for Cu(II) molecular complexes typically range from 1.7–1.9 BM (*16*) and average 1.63 BM for $ACuO_2$ where A = Ca, Sr, or Ba (*17*).

Four other borates with a similar formula $A_2^{2+}B^{2+}(BO_3)_2$ have been reported. The compound $Ba_2Mg(BO_3)_2$ is isomorphous to the trigonal mineral buetschliite, $K_2Ca(CO_3)_2$ (*18*), the compound $Ca_2Mg(BO_3)_2$ is tetragonal, and the compounds $Ba_2Ca(BO_3)_2$ and $Sr_2Mg(BO_3)_2$ are related to buetschliite (*19*). These materials all appear to crystallize in structures that are similar to calcite and dolomite, containing discreet layers of trigonal borate or carbonate groups with the cations located between these layers. The title compound exists in structures of lower symmetry with structural motifs that are different from these reported borates.

Borates and carbonates are often iso-

structural, and the compounds $M_2Cu(CO_3)_2$ with M = alkali metal could be expected to be isomorphous to the title compound. Three such carbonates have been reported; they are the potassium compound $K_2Cu(CO_3)_2$ (*20*), the sodium compound $Na_2Cu(CO_3)_2$ (*21*), and the mineral chalconatronite, $Na_2Cu(CO_3)_2 \cdot 3H_2O$ (*22*). The compound $K_2Cu(CO_3)_2$ is face-centered orthorhombic (*Fdd2*) with square-planar coordination of the Cu atom, chalconatronite is monoclinic ($P2_1/n$) with square-pyramidal coordination of the Cu atom, while the compound $Na_2Cu(CO_3)_2$ is isomorphous to the α-phase of the title compound. Structural differences between the two isomorphs are a substantial elongation of the unique axis, b, (8.19(2) Å in the carbonate versus 8.796(2) Å in the borate) and a six-coordinate Na atom (*23*) instead of the seven-coordination of the Sr atom. The larger coordination number results from displacement and distortion of the CuO_4 square planes in the borate relative to those in the carbonate. Specifically, the Sr–O(2) interaction of 2.670(1) Å does not find a counterpart in the carbonate. As a Sr atom shares the edge O(1) · · · O(2) of the square plane, a more acute angle, 85.8(2)°, occurs in comparison with that (88.7(5)°) observed in the carbonate. The atom O(2) is three-coordinate in the carbonate whereas it is four-coordinate in the borate.

The discreet unit $Cu_2(BO_3)_4$ of the unique β-phase has not previously been observed. The large coordination numbers for the Sr atom, however, are common in borates. A coordination number of 9 has been observed in the compounds $Sr_3(BO_3)_2$ (*24*), SrB_4O_7 (*13*), $Sr_3Sc(BO_3)_3$ (*25*), and $SrNaBO_3$ (*26*). Of course, such high coordination numbers should be anticipated since a substantial proportion of the available bonding electron density is locked into the covalent BO_3 units, forcing the Sr atom to bind to a greater number of O atoms to satisfy its bonding requirements.

The transition from the α-phase to the β-phase occurs at 800 ± 10°C as determined by differential thermal analysis. On heating a sample of the α-phase a strong endothermic response is observed while on cooling no signal is observed. X-ray powder diffractograms of samples of the α-phase that have been heated and rapidly cooled through the transition temperature reveal the presence of the β-phase only. Thus it is easy to quench the β-phase in place. The technique of slowly cooling the solute/flux solution at 6°C/hr through the transition temperature affords a solubility of the α-phase that is great enough for the growth of single crystals at lower temperatures.

From consideration of the DTA data and the results of the structure determinations it is clear that the phase transition is first-order. The structure of the α-phase exhibits one crystallographically independent Sr atom with a coordination number of 7 while the structure of the β-phase exhibits larger coordination numbers for the three crystallographically independent Sr atoms. Moreover, 50% of the O atoms exhibit a higher coordination number in the β-phase with a substantial reorganization of the copper borate substructure. The transformation from the α-phase to the β-phase is thus characterized by the extensive bond scission and reformation of a first-order transition.

Acknowledgments

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