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Synthetic, Structural, and Magnetic Studies of Strontium Copper(II) Borates with the Composition $Sr_{1-x}M_xCu_2(BO_3)_2$, M = Ba or Ca

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Studies of the new type of alkaline earth copper(II) borates, represented by $SrCu_2(BO_3)_2$, have been performed by high temperature techniques. In the parent structure of $SrCu_2(BO_3)_2$, the strontium content can be partially substituted by calcium or barium. A series of such phases with the composition $Sr_{1-x}M_xCu_2(BO_3)_2$ where M = Ca or Ba and $0 \leq x < 0.4$ have been prepared. X-ray powder photographs verify that these phases are isostructural to $SrCu_2(BO_3)_2$. The crystal structure of $Sr_{1-x}M_xCu_2(BO_3)_2$ can be regarded as consisting of slightly puckered layers with the composition $[CuBO_3]^-$ stacked along [001], with eight coordinated alkaline earth atoms located between the layers. Estimated bond valence sums for all atoms indicate normal bond length distributions in the structure. The structure possesses a pseudo-mirror symmetry but the deviations (<0.2 Å) from this symmetry (space group *I4/mmm*) are statistically highly significant. The substitution of strontium for smaller calcium or larger barium atoms has a pronounced effect on the interlayer separation. Measured magnetic susceptibilities of $SrCu_2(BO_3)_2$ indicate a transition to an antiferromagnetic state below 14 K.

INTRODUCTION

The present study is part of a research project (e.g., 1) aiming at the synthesis and characterization of anhydrous metal-rich borates. The stereochemistry of solid oxoborates often has close similarities to that of oxocarbonates; e.g. trivalent transition metal borates frequently adopt the calcite structure. During the last few years a new type of alkaline earth copper carbonates, with the composition $(Sr,Ba)_2CuO_2CO_3$, have been discovered (2, 3). Some of these compounds, which contain infinite copper(II)-oxygen layers, are superconductors (4). In view of these results for the oxycarbonates, we have used high temperature solid state synthetic techniques to try to prepare related oxyborate phases. In this way, the phase $LnBaCuO_2BO_3$ (Ln = La–Tb), analogous to $(Sr,Ba)_2CuO_2CO_3$, was obtained (5). Attempts were also made to prepare alkaline earth copper borates without trivalent lanthanide ions. For the initial composition $SrO + CuO + B_2O_3$, the strontium copper(II) borates, viz., $SrCu_2(BO_3)_2$, were formed as one of the major phases. After completing a structural characterisation of the $SrCu_2(BO_3)_2$ phase by single crystal X-ray diffraction techniques, the present authors were made aware of that a structural characterization of the new $SrCu_2(BO_3)_2$ phase was published in 1991 by Smith and Keszler (6). The structural results obtained by the present authors had slightly better statistical relevance, as judged by, e.g., the different R value of 0.029 (674 reflections) compared to 0.040 (604 reflections). However, the differences in the obtained structural parameters are largely negligible. In their study, Smith and Keszler used a different synthetic procedure. Accordingly, the present paper only contains a few supplementary comments on the structural study and on the different synthetic procedure applied. In the present paper some chemical substitution studies on $SrCu_2(BO_3)_2$, giving solid solutions that contain Ca or Ba, together with an investigation of the magnetic susceptibility of $SrCu_2(BO_3)_2$ in the temperature range 14–300 K, are also reported.

EXPERIMENTAL

Synthetic procedures. Blue crystalline specimens of the title compounds were obtained by heating stoichiometric mixtures of alkaline earth oxides, copper(II) oxide, and boron oxide (10% excess of B_2O_3) in open platinum crucibles at 800°C in air for 1 hr and then raising the temperature to 920°C with a speed of 100°C/hr. After annealing at 920°C for 48 hr, the furnace used was cooled down to 300°C with a speed of 200°C/hr and then turned off.

In the present study, $SrCu_2(BO_3)_2$ was first prepared and studied by X-ray investigations. With similar synthetic techniques, the attempts to prepare the pure Ca and Ba analogues (with BaO_2 used as precursor to BaO) failed. However, it was possible to prepare phases where the Sr content in $SrCu_2(BO_3)_2$ was partially replaced with Ca or Ba. The present study thus includes the preparations and characterization of the phases with the formal composition $Sr_{1-x}M_xCu_2(BO_3)_2$, with M = Ca or Ba. Although the initial compositions of the mixtures were $x \leq 0.5$,

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TABLE 1

Unit Cell Parameters from Indexed Powder Photographs for the Synthesized Compounds with Formal Composition $Sr_{1-x}M_xCu_2(BO_3)_2$, Isostructural to $SrCu_2(BO_3)_2$

	x_{Calc}	x_{Obs}	a (Å)	c (Å)	V (Å^3)
$Sr_{1-x}Ca_xCu_2(BO_3)_2$	0.15	0.11(1)	8.9850(4)	6.6055(5)	533.26(5)
	0.25	0.165(8)	8.9795(5)	6.5871(4)	531.13(6)
	0.50	0.339(6)	8.9692(9)	6.540(2)	526.1(2)
$Sr_{1-x}Ba_xCu_2(BO_3)_2$	0.15	0.11(1)	9.0001(4)	6.7141(7)	543.85(7)
	0.25	0.200(6)	9.0054(3)	6.7516(6)	547.54(6)
	0.50	0.265(5)	9.010(2)	6.779(3)	550.3(3)

Note. x_{Calc} denote the initial composition of the synthesis mixture and x_{Obs} that found by SEM analysis on the obtained crystalline specimens. The e.s.d.'s are given in parentheses.

subsequent analyses showed that the specimens obtained after the synthetic reactions, had x values considerably smaller than the initial compositions (cf. Table 1). For the mixtures with higher x, the specimens obtained by the applied synthetic procedure contained multiple phases, but the major phases as judged from X-ray powder photographs were $Sr_{1-x}M_xCu_2(BO_3)_2$.

EDX, X-ray, and magnetic measurements. The synthesized $Sr_{1-x}M_xCu_2(BO_3)_2$ phases (M = Ca or Ba) were analyzed in a scanning electron microscope (SEM), model JSM-840A, equipped with a Link AN10000 EDX system. EDX spectra were collected for 10 different crystals of each phase. Unit cell dimensions of the phases (Table 1) were determined from index Guinier photographs, taken with Cu$K\alpha_1$ radiation and using silicon as internal standard.

The magnetic susceptibility of a powder sample of $SrCu_2(BO_3)_2$ in the temperature range 14–300 K was measured with a Lake Shore AC Susceptometer model 7130 equipped with a helium cryostat. Measurements on tetramethylethylenediammonium tetrachlorocuprate(II), $[(CH_3)_2NHCH_2CH_2NH(CH_3)_2]CuCl_4$, were used (7) to check the performance of the susceptometer. The measured susceptibilities were corrected for diamagnetic contributions ($<0.2 \times 10^{-8}$ m$^3 \cdot$ mol^{-1}) from the sample holder. A frequency of 500 Hz and a magnetic field strength of 125 A $\cdot$ m^{-1} were used.

DISCUSSION

The structure (6) of the $Sr_{1-x}M_xCu_2(BO_3)_2$ phases (Fig. 1) consists of slightly puckered layers at $z \approx \pm\frac{1}{4}$, with the overall composition $[CuBO_3]^-$. Such layers are stacked along [001], giving a separation of ≈3.3 Å. From the absence of stronger bonds between the layers, the strontium atoms (located at $z = 0, \frac{1}{2}$) can be anticipated to play a crucial role in linking the layers together in the [001] direction of the crystal structure. The strontium atoms are coordinated by four oxygen atoms from each adjacent layer, and thus become eight-coordinated. It can be noted that the atoms within the $[CuBO_3]^-$ layers have a pronounced freedom to move out of the layers, as is evident from their relatively large thermal displacement components along [001]. Empirical bond valences estimated (9) for the different atoms in $SrCu_2(BO_3)_2$ are within 3% of their formal valences, suggesting normal bond length distributions around each of the atoms in the structure.

The z coordinates of all atoms are within 0.2 Å from 0 modulo $\frac{1}{4}$ for all atoms. This might indicate that the structure could have a mirror symmetry perpendicular to [001]. The structure can be approximately described with the minimal non-isomorphic supergroup symmetry $I4/mmm$ after a shift of $(0, \frac{1}{2}, \frac{1}{4})$ is applied to the coordinates. However, refinements of the derived $I4/mmm$ models for $SrCu_2(BO_3)_2$ vs collected single crystal data yielded R

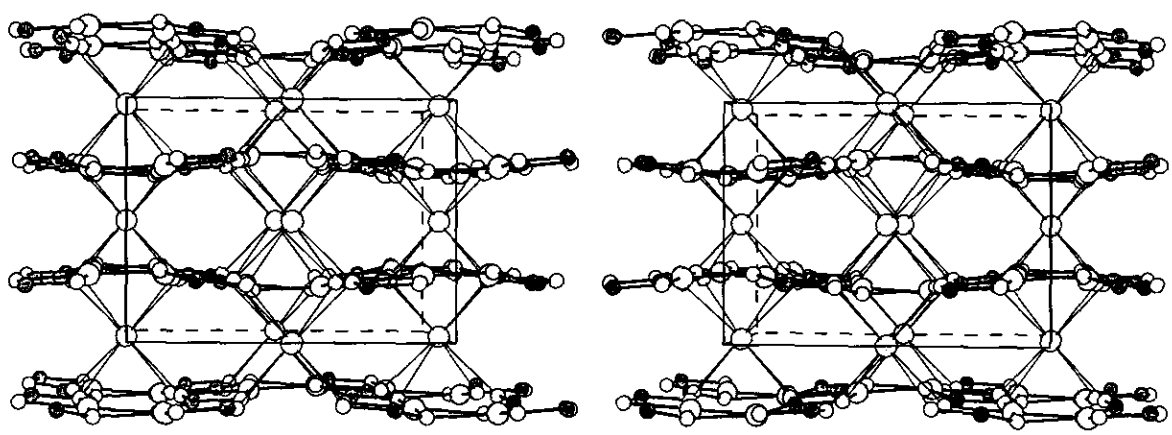

FIG. 1. Stereoview along [100] of a ball-and-stick representation of the $SrCu_2(BO_3)_2$ structure obtained by the program *ATOMS* (8). The metal atoms are represented by larger circles and boron and oxygen by smaller ones. Copper and boron atoms are dark grey, while strontium is light grey and oxygen white.

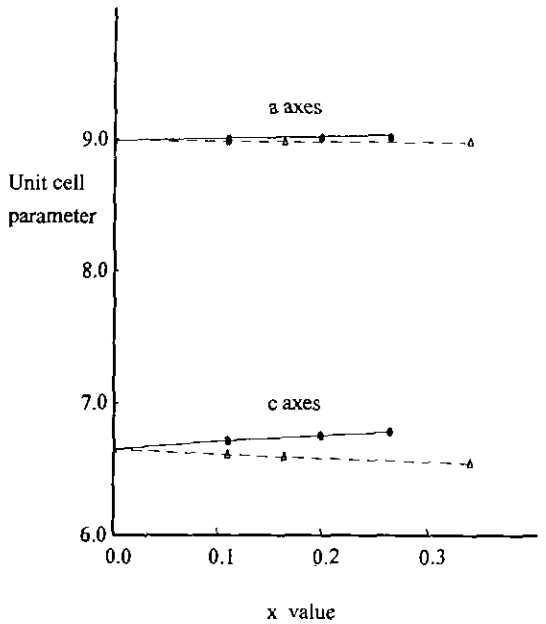

FIG. 2. The variation of unit cell volume (Å^3) with the composition parameter x for $Sr_{1-x}M_xCu_2(BO_3)_2$. The filled ellipses represent M = Ba and the unfilled triangles M = Ca. The correlation coefficients of the two (solid and dashed) least-squares lines are above 0.996.

values of about 0.24. The refinements lead to unreasonable large oscillating shifts on several structural parameters. The lack of convergence and the high R value obtained indicate that the higher symmetry can only be regarded as a pseudo-symmetry, in agreement with the characteristics of calculated X-ray data intensity distributions.

The synthetic studies (cf. above) showed that the strontium content can partially be replaced by both smaller divalent ions such as Ca^{2+} and larger ones such as Ba^{2+}. X-ray powder photographs on calcium- and barium-substituted phases (Table 1) suggest that they are isostructural to $SrCu_2(BO_3)_2$. This is also verified by the results (10) from single crystal X-ray diffraction studies of the two phases $Sr_{0.735}Ba_{0.265}Cu_2(BO_3)_2$ and $Sr_{0.661}Ca_{0.339}Cu_2(BO_3)_2$. Figure 2 shows that the changes in cell parameters on substitution follow Vegard's law of linear variation. As can be anticipated from the structural features, the variations of the c axis which determine the interlayer separations are considerably larger than those of the a axis. A limited number of attempts to prepare substituted phases with higher calcium and barium content were not successful.

The molar magnetic susceptibility, χ_M ($m^3 \cdot mol^{-1}$), in the range 14–302 K, together with the inverse molar magnetic susceptibility, χ_M^{-1}, are shown in Fig. 3a. A linear least-squares fit (correlation 0.9995) through the χ_M^{-1} data of the high temperature region ($170 < T < 273$ K) gives a Curie constant $C = 9.43(14) \times 10^{-6}$ $m^3 \cdot K \cdot mol^{-1}$ and a Weiss temperature $\theta = -52(2)$ K. The negative sign of θ, together with a continuous decrease (upon cooling) of $\chi_M \cdot T$ as a function of T (Fig. 3b), indicates a probable antiferromagnetic ordering. The spin-only formula ($C \propto g\sqrt{S(S+1)}$, with $g \approx 2.0$) suggests 1.65(1) unpaired electrons per dimer unit $Cu_2B_2O_8$. This value is significantly below the expected 2 unpaired electrons in the dimer unit,

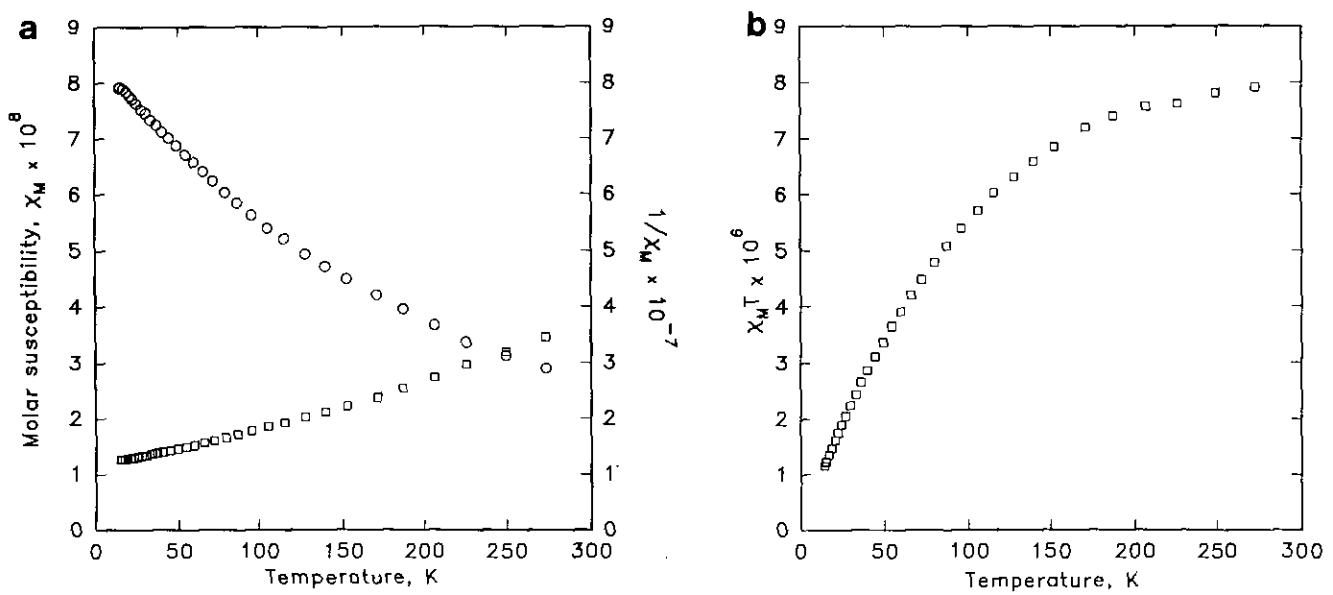

FIG. 3. Temperature dependence (14–300 K) of the magnetic behavior of $SrCu_2(BO_3)_2$. (a) The molar magnetic susceptibility (circles), χ_M ($m^3 \cdot mol^{-1}$), together with the inverse molar magnetic susceptibility (squares), χ_M^{-1}. (b) $\chi_M \cdot T$ vs T plot, indicating the possible antiferromagnetic ordering at low temperatures.

possibly due to the relatively short Cu ··· Cu distance (2.91 Å), suggesting weak antiferromagnetic coupling effects between the copper ions.

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