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Synthesis and Structure of $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$: An Oxycarbonate Containing Infinite CuO_2 Layers

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The synthesis and structure of the layered oxycarbonate $Sr_{1.5}Ba_{0.5}CuO_2(CO)_3$ is reported here. The structure determined by time-of-flight neutron powder diffraction both at room temperature and at 4 K is tetragonal, space group $P4/mmm$, with lattice parameters $a = 3.9281(1)$ Å and $c = 7.6045(2)$ Å (room temperature). The structure of the oxycarbonate is composed of alternating carbonate and $(CuO_2)_\infty$ layers separated by layers of alkaline-earth cations; considerable orientational disorder of the carbonate groups was evident even at 4 K. Based on the detailed structural features of the new oxycarbonates, we can now discuss possible limitations on their substitutional chemistry; these will have important implications in attempts to drive the system metallic—and perhaps superconducting.

Introduction

The most significant structural feature common to all high T_c cuprate superconductors is the presence of layers of corner-sharing square CuO_4 units. For electron-doped superconductors (e.g., $Nd_{1.85}Ce_{0.15}CuO_{4-y}$ (*1*)) the copper ion has square planar coordination, whereas for hole superconductors the copper ion has a Jahn–Teller distorted square pyramidal or octahedral coordination environment. The material $Sr_2CuO_2(CO_3)$ has been reported to contain similar structural features, with initial reports suggesting that the carbonate groups have a C–O bond perpendicular to the plane of the carbon atoms but show orientational disorder with four equivalent orientations in the [110] planes (*2, 3*). A subsequent structure determination by Babu *et al.* (*4*), using time-of-flight neutron powder diffraction, revealed a somewhat different carbonate orientation. All the carbonate groups were reported to have a C–O bond along [100] or (010) and two bonds at approximately 30° to [001]. We have synthesized the isostructural phase $Sr_{2-x}Ba_xCuO_2(CO_3)$ for a range of mixed al-

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kaline-earth stoichiometry, ($0 \leq x \leq 2$). We find that the greater stability of $BaCO_3$ as compared to $SrCO_3$ imparts greater thermal stability to the Ba-containing oxycarbonates, thereby simplifying their preparation. This enhanced stability of the mixed Sr/Ba oxycarbonate phases may be important in attempts to introduce excess carriers (holes or electrons) into the system. We report here the structure of $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$, as determined from neutron diffraction experiments at room temperature and 4 K.

Experimental

$Sr_2CuO_2(CO_3)$ has been reported to occur as an intermediate in the reaction of $SrCO_3$ and CuO to form Sr_2CuO_3, decomposition to Sr_2CuO_3 occurring as soon as all the $SrCO_3$ has reacted (*2*, *3*). We ourselves discovered this material in the course of alkali doping studies on Sr_2CuO_3, using partially enclosed conditions. This particular configuration inhibits the diffusion of carbon dioxide away from the sample, thereby retarding the decomposition reaction to Sr_2CuO_3. We have exploited this technique in order to prepare a range of compounds in the solid solution series $Sr_{2-x}Ba_xCuO_2(CO_3)$ ($0 \leq x \leq 2$). For compositions with $x \leq 0.8$, barium peroxide, strontium carbonate, and copper oxide were used as starting materials, while barium carbonate was used for higher values of x. The greater stability of $BaCO_3$ as compared to that of $SrCO_3$ was found to impart an enhanced thermal stability to the barium-containing materials, thereby simplifying their preparation and study. Interestingly, $Sr_2CuO_2(CO_3)$ cannot be prepared (in single phase form) in an open furnace, presumably as a result of convection currents, but Babu *et al.* (*4*) were able to stabilize it by firing in a very slow flow of air, nitrogen or oxygen at 940°C.

Samples of nominal stoichiometry $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$ were prepared by a number of routes using $SrCO_3$, BaO_2, and CuO as starting materials. A typical sample enclosure consisted of an alumina crucible with a loose fitting lid. Samples were fired at 920°C, with reaction times governed by the sample volume (larger volumes requiring longer times). Several firings and intermediate grindings were found necessary to form single phase material. The firing times decreased progressively as the reaction neared completion. All samples contained a small quantity of $(Sr,Ba)CO_3$ with the barium concentration, as gauged by changes in lattice parameter, increasing with time. This increase in the barium content of the unreacted carbonate effectively reduced the reactivity of the remaining alkaline-earth carbonate, thus slowing the reaction down. X-ray Diffraction Powder patterns were taken on a Phillips PW1710 X-ray diffractometer with Cu$K\alpha$ radiation.

An 8-g powder sample of $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$ was prepared for characterisation by powder neutron diffraction on the diffractometer POLARIS at the Rutherford Appleton Laboratory, U.K. Data were collected both at room temperature and at 4 K. Rietveld refinement of the structure used the least squares program TF14LS based on the Cambridge Crystallographic Subroutine Library (*5*, *6*). Scattering Lengths for Sr, Ba, Cu, O, and C of 0.702, 0.525, 0.7718, 0.5805, and 0.6648 (all $\times$ 10^{-12} cm), respectively, were used.

Results and Discussion

X-ray powder diffraction patterns for $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$ could be indexed to a tetragonal unit cell, with derived lattice constants $a = 3.924(1)$ Å and $c = 7.597(1)$ Å. Both X-ray and neutron diffraction patterns revealed the presence of trace amounts of $(Sr,Ba)CO_3$, the peaks of which were excluded from the subsequent refinement, wherever possible. Initial refinement used the model proposed by Babu *et al.* (*4*) for the isostructural $Sr_2CuO_2(CO_3)$, except that

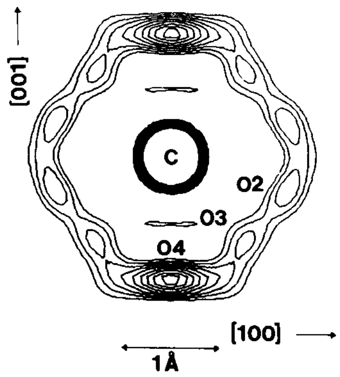

FIG. 1. Fourier cross-section in the *ac* plane showing the scattering density about a carbon atom. (Data recorded at room temperature.)

we included anisotropic temperature factors for all atoms. In view of the longer data collection time and good statistics at 4 K, various structural models were tested using these data. Fourier maps were obtained for the *ac* and *ab* planes for various cross sections around the level of the carbon atoms in order to obtain information on the position of the carbonate oxygen atoms. In Fig. 1 we show the observed Fourier map in the *ac* plane around the carbon atom at room temperature. Large anisotropic temperature factors were obtained for these oxygen atoms, even for the data obtained at 4 K. The Fourier maps suggest a shift along the z axis of the oxygens reported by Babu *et al.* (*4*) to lie along the [010] and [100] directions. For the remaining oxygens the scattering density was found to be centred at $(0,0,z)$ but was very diffuse perpendicular to [001], with the suggestion of another site at $(x,0,z')$. A variety of models for the carbonate group orientation were tested in the initial structure refinement and these are summarized in Fig. 2. Values of χ^2[1] obtained from the various orientations A–F for the carbonate anion are also shown.

Models A and B, containing 90° bond angles, gave rather poor fits (χ^2 of 16.17 and 15.91, respectively). Substantial improvements were obtained for the remaining models C–F, which have bond angles closer to the ideal value of 120°. Model C represents that proposed by Babu *et al.* (*4*). Models D, E, and F, with the oxygens in the plane of the carbons shifted along z, all show a slightly better fit than that for model C. In view of the close similarity in χ^2 obtained for each of models D, E, and F, a disordered mode for the carbonate anion was devised. This model attempted to fit the oxygen atoms close to the z axis by using a split site, with one position at $(0,0,z)$ and another at $(x,0,z')$, the relative occupancies of this split site being refined. Models with either two of the three carbonate oxygen atoms spread over this split site (as in models, A, C, and E) or one (as in models B, D, and F) were subsequently tested. These are referred to as the first and second disordered models, respectively. The first model gave a markedly better fit. Refined structural parameters for both models are shown in Table I, and

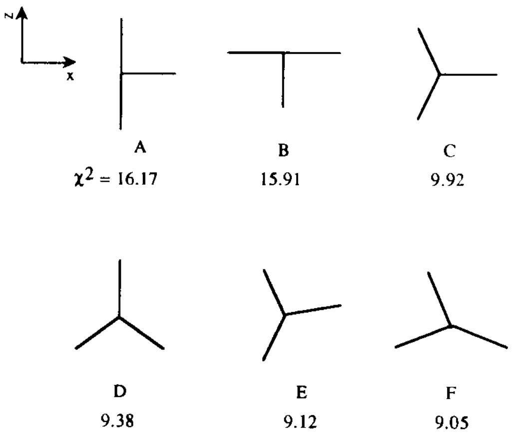

FIG. 2. Diagram showing different CO_3 group orientations tested in the initial structure refinement, together with the resulting χ^2 obtained for each model.

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[1] $\chi = R_{WP}/R_{EXP} \cdot R_{WP} = \{w_i[y_i(\text{obs}) - y_i(\text{calc})]^2/w_i y_i^2(\text{obs})\}^{1/2}. = \{[N - P + C]/w_i y_i^2(\text{obs})\}^{1/2}$, where N, P, and C are the number of observations. parameters, and constraints, respectively.

TABLE I

REFINED STRUCTURAL PARAMETERS FOR $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$

Atom	Position	x B_{11}	y B_{22}	z B_{33}	Site occupancy B_{13}
First disordered model at 4 K					
			$P4/mmm$		
		a = 3.91709(2) Å, c = 7.58149(6) Å			
Sr	$2h$	0.5	0.5	0.2264(2)	0.75
		0.18(1)	0.18(1)	0.75(4)	—
Ba	$2h$	0.5	0.5	0.2264(2)	0.25
		0.18(1)	0.18(1)	0.75(4)	—
Cu	$1a$	0.0	0.0	0.0	1
		0.01(2)	0.01(2)	0.79(5)	—
C	$1b$	0.0	0.0	0.0	1
		0.46(3)	0.46(3)	0.49(5)	—
O(1)	$2f$	0.5	0.0	0.0	1
		0.10(3)	0.03(3)	1.12(5)	—
O(2)	$8s$	0.313(1)	0.0	0.542(1)	0.125
		−0.4(4)	3.9(3)	4.8(8)	−2.1(2)
O(3)	$8s$	0.188(3)	0.0	0.377(2)	0.162(5)
		4.3(5)	0.7(1)	6.7(6)	5.6(4)
O(4)	$2g$	0.0	0.0	0.3341(7)	0.35(2)
		5.1(4)	5.1(4)	−0.9(9)	—

R-factors: R_P = 2.63%, R_{WP} = 2.03%, R_E = 0.70%, R_I = 8.60% (χ^2 = 8.34)

First disordered model at room temperature

a = 3.92814(5) Å, c = 7.6045(2) Å

Sr, Ba	z = 0.2270(3)	B_{11} = 0.64(3)	B_{33} = 1.42(8)	
Cu	B_{11} = 0.10(4)	B_{33} = 1.43(9)		
C	B_{11} = 0.90(6)	B_{33} = 0.92(11)		
O(1)	B_{11} = 0.23(5)	B_{22} = 0.39(5)	B_{33} = 1.52(9)	
O(2)	x = 0.315(2)	z = 0.539(1)	B_{11} = 0.0(2)	B_{22} = 5.6(6)
		B_{33} = 1.8(6)	B_{13} = −1.8(3)	
O(3)	x = 0.181(5)	z = 0.370(3)	B_{11} = 2.8(8)	B_{22} = 1.2(3)
		B_{33} = 6.2(7)	B_{13} = 3.7(5)	Site = 0.17(1)
O(4)	z = 0.3365(10)	B_{11} = 4.8(8)	B_{33} = −1.2(12)	Site = 0.33(4)

R-factors: R_P = 4.93%, R_{WP} = 3.69%, R_E = 2.47%, R_I = 6.05% (χ^2 = 2.23)

Second disordered model at 4 K

Sr, Ba	z = 0.2270(2)	B_{11} = 0.16(2)	B_{33} = 0.76(4)	
Cu	B_{11} = −0.04(4)	B_{33} = 0.84(5)		
C	B_{11} = 0.45(3)	B_{33} = 0.58(5)		
O(1)	B_{11} = −0.03(3)	B_{22} = 0.03(3)	B_{33} = 1.10(5)	
O(2)	x = 0.265(1)	z = 0.574(1)	B_{11} = 5.9(2)	B_{22} = 2.3(2)
		B_{33} = 15.8(8)	B_{13} = −10.3(4)	Site = 0.25
O(3)	x = 0.160(7)	z = 0.371(3)	B_{11} = 9.4(23)	B_{22} = −2.5(2)
		B_{33} = 2.1(12)	B_{13} = 8.5(17)	Site = 0.011(2)
O(4)	z = 0.3347(6)	B_{11} = 7.0(2)	B_{33} = −0.8(8)	Site = 0.454(9)

R-factors: R_P = 2.65%, R_{WP} = 2.08%, R_E = 0.70%, R_I = 8.21% (χ^2 = 8.76)

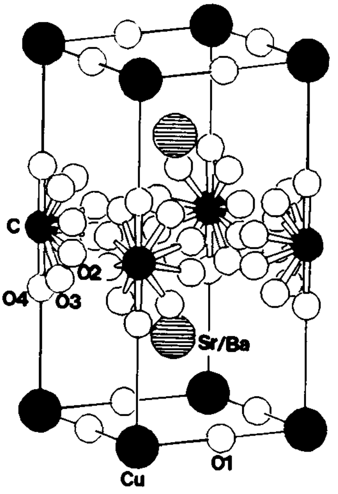

FIG. 3. A schematic representation of the structure of $Sr_{1.5}Ba_{0.5}CuO_2(CO_3)$, as derived from the neutron diffraction data.

the structure is illustrated in Fig. 3. It is particularly noteworthy that in these materials the carbonate group lies perpendicular to the plane of the alkaline-earth cations, compared with the parallel arrangement found in strontium and barium carbonates (*7*).

The carbon-oxygen bond lengths (first disordered model) at room temperature were found to be C–O(2) = 1.243 Å, C–O(3) = 1.218 Å, and C–O(4) = 1.272 Å. Given the disordered nature of the carbonate groups, the calculated bond angles have only limited meaning, but it can be assumed that within a given carbonate group the bond angles will be close to 120°. Babu *et al.* (*4*) have suggested that the distance from the copper to the oxygen atoms of the carbonate groups is such that the copper stereochemistry more closely resembles that of Nd_2CuO_4 rather than that of La_2CuO_4. However, the partial occupation of the O(4) site gives a Cu–O(4) bond length of 2.53 Å at 4 K, comparable with that found in La_2CuO_4. This structural feature imposes severe constraints on possible substitutionally induced metallicity (and potential superconductivity) in these materials. The presence of apical oxygen atoms may render the materials unsuitable for electron doping, and yet the incomplete occupancy of these sites may mean that hole doping also fails to produce metallic, and possibly superconducting, behavior. We have attempted several substitution experiments involving nominal substitution of electrons via rare-earth doping, or holes via alkali doping. To date, all have been unsuccessful. Further experiments are continuing into possible anionic substitutions (e.g. chloride) which may yield more promising results.

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