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The Synthesis and Structural Characterization of Sr_2CuO_{4-x}, $x \sim 0.1$

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Sr_2CuO_3 (orthorhombic, *Immm*) is converted at about 400°C under oxygen at 160 bar to $Sr_2CuO_{3.9}$ [tetragonal, *I4/mmm*; $a = 3.7907(7)$, $c = 12.417(2)$ Å], which is structurally related to La_2CuO_4. Although the formal Cu oxidation state in this material appears to be higher than any previously reported for Cu in an oxide environment (around +3.8), powder neutron diffraction data provide no evidence for O_2^{2-} or O_2^- ions, but are consistent with a highly defective structure containing Sr, Cu, and O vacancies. The cation vacancies are in a 2 : 1 ratio to maintain the stoichiometry, and the O vacancies are confined to the CuO_2 layers. Additional peaks in the neutron diffraction profile are indicative of an ordering process to give an extended, possibly incommensurate, structure. CuK-edge EXAFS suggests that the resulting local Cu coordination contains two very short Cu–O bonds (1.755 Å).

Introduction

Detailed studies of superconducting phases related to La_2CuO_4, e.g., $(La_{1-x}Sr_x)_2CuO_{4-y}$, are of fundamental importance for developing an understanding of high temperature superconductivity, since their structural chemistry (*1*) is very much simpler than that of other high-T_c oxide materials. The formal Cu oxidation state is clearly dependent on the extent of Sr substitution, x, but in practice the correlation of superconducting behavior and hole concentration is complicated since $y > 0$ when $x > 0.08$ due to the formation of vacancies at the equatorial oxygen sites in the CuO_2 layers (*2, 3*). In the absence of La, Sr_2CuO_3 is formed ($x = 1, y = 1$), which contains only divalent copper ions and vacancies on half the equatorial sites. The vacancies are ordered to give square CuO_4 units linked into chains (*4, 5*) as shown in Fig. 1, where the structural similarities between Sr_2CuO_3 and La_2CuO_4 are demonstrated. The use of high pressure techniques inhibits oxygen vacancy formation such that an integral anion sublattice is obtained for $x < 0.2$ at 100 bar (*6*), and for $x < 1$ at 3 kbar (*7*). The use of high oxygen pressures to stabilize copper as Cu(III) in materials such as $LaSrCuO_4$, and the presence of channels of empty anion sites in Sr_2CuO_3, suggested that a detailed examination of the influence of high oxygen pressures on the latter phase would be of value. In this paper, we report the synthesis, characterization, and structural properties of a new phase, Sr_2CuO_{4-x}, which nominally contains copper in an exceptionally high oxidation state (around +3.8). In view of this, attention has been focused on the nature of the anions present, and the possibility that the anomalous copper oxidation

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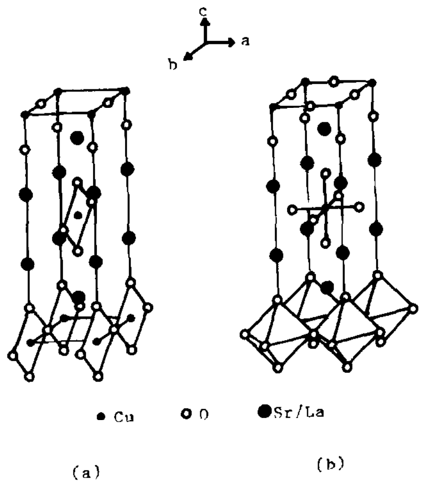

FIG. 1. Idealized structures of (a) Sr_2CuO_3 and (b) La_2CuO_4.

state could be rationalized by the presence of O_2^{2-} or O_2^- species has been explored.

Experimental

Pure Sr_2CuO_3 was synthesised by reacting high purity $SrCO_3$ and CuO in air at 950°C, and then subjected to a three stage heat treatment under 160 bar oxygen in a Baskerville autoclave: 425°C for 18 hr, 400°C for 18 hr, 350°C for 48 hr. Sr_2CuO_3 and the product from high pressure treatment were structurally characterized by powder X-ray diffraction (XRD) using a Philips PW 1050/70 diffractometer with CuKα radiation. Ambient temperature time-of-flight powder neutron diffraction data ($0.3 < d < 1.8$ Å) were collected from a sample treated at high pressure (ca. 5 g contained in an 8-mm-diameter vanadium can) using the diffractometer POLARIS at ISIS, Rutherford Appleton Laboratory. Structure refinement was based on the Rietveld method using a well-documented program (*8*). CuK-edge EXAFS data were recorded at 298 K at the Daresbury Synchrotron Radiation Source using station 7.1.

The oxygen content of the material prepared at high pressure was compared with that of Sr_2CuO_3 by thermogravimetric reduction to SrO and Cu (Stanton Redcroft STA 780 analyzer, using a heating rate of 10°C min^{-1} to 930°C in a flowing gas mixture of 10% H_2/90% N_2). The Cu oxidation state was estimated iodometrically (*9*), using approximately 40 mg of sample, and the density was determined using a CCl_4 displacement technique and a 25-cm^3 density bottle. Electrical resistivity measurements were recorded between 4.2 and 298 K using a conventional four-probe dc technique in a helium-cooled cryostat.

Results and Discussion

Brown Sr_2CuO_3 (orthorhombic, space group *Immm*; a = 12.716, b = 3.916, c = 3.503 Å (*5*)) was transformed by the high pressure anneal to a black powder whose XRD pattern (Fig. 2) indicated a pure phase

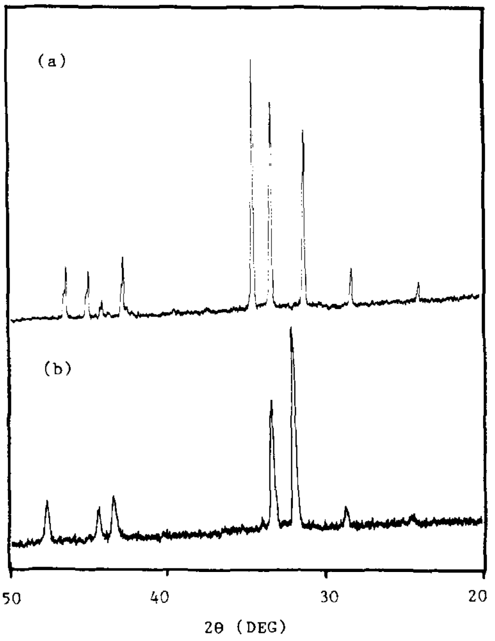

FIG. 2. Powder X-ray diffraction patterns for (a) Sr_2CuO_3 and (b) $Sr_2CuO_{3.9}$.

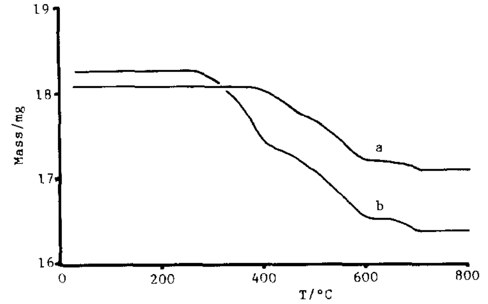

FIG. 3. TGA traces for (a) Sr_2CuO_3 (initial mass 18.10 mg, final 17.09 mg) and (b) $Sr_2CuO_{3.9}$ (initial mass 18.24 mg, final 16.38 mg).

with a structure (tetragonal, $I4/mmm$; a = 3.79, c = 12.42 Å) related to that of La_2CuO_4. Very weak peaks, which were apparent, could not be assigned to any likely impurity phase, and neutron diffraction data (discussed later) suggested that they were related to ordering effects in the primary phase. The prevention of impurities required careful temperature control, such that under some conditions SrO_2 and CuO impurities were formed, but no evidence of such contamination was apparent in the samples subjected to subsequent examination. Although Ca_2CuO_3 and Sr_2CuO_3 are isostructural, Ca_2CuO_3 was unaffected by high pressure oxygen treatments, and this presumably reflects the lower stability of the La_2CuO_4 structure type when small cations, such as Ca^{2+}, are substituted for La^{3+}. The fact that the La_2CuO_4 structure is not adopted by trivalent cations smaller than La^{3+} (e.g., Nd^{3+}, Y^{3+}) provides support for this inference.

Thermogravimetric analysis (TGA, Fig. 3) revealed that the observed structural transformation was associated with oxygen incorporation into the empty channels of the Sr_2CuO_3 lattice to form a phase of composition $Sr_2CuO_{3.92(5)}$. Although such a formulation is compatible with the exceptionally high formal Cu oxidation state of +3.8, the presence of Cu^{4+} ions was considered to be unlikely, and no previous evidence has been found for Cu^{4+} in oxide systems. The existence of holes on the anion sublattice appeared to provide a more probable explanation of the results. The holes could be localized and associated with the formation of peroxide (O_2^{2-}) or superoxide (O_2^-) ions or, alternatively, be itinerant in an O 2p electron energy band. It should be noted, however, that the latter possibility would require a higher hole concentration than that proposed for high temperature superconductors. Iodometric titrations were consistent with a mean Cu oxidation state of +3.3, which corresponds to a composition $Sr_2CuO_{3.65}$ for a compound containing simple O^{2-} anions. This value represents a lower limit for the oxidizing power of the compound, since quantitive conversions are difficult to achieve titrimetrically. Since oxidizing anions such as O_2^{2-} could also interfere with the titration results, unequivocal interpretation of the chemical analysis was not possible. Consequently, the oxygen content determined by TGA, $Sr_2CuO_{3.92}$, was adopted as the most reliable representation of the phase composition.

Powder neutron diffraction data were collected to allow a detailed examination of the anion sublattice in $Sr_2CuO_{3.9}$. Interpretation was based on the K_2NiF_4 structure type implied by XRD, and the tetragonal space group $I4/mmm$ was found to provide better agreement with the observed profile than alternative orthorhombic groups. Refinement of the oxygen site occupancies resulted in full occupancy for O2, the axial oxygen, but only 70% occupancy for O1, the equatorial oxygen atoms in the CuO_2 layers. Since the implicit phase composition of such a model, $Sr_2CuO_{3.4}$, conflicts with the analytical results, the possible location of additional oxygen atoms in a variety of interstitial sites within the structure was explored. Particular attention was paid to plausible sites which would afford short O–O bonds compatible with O_2^{2-} or O_2^- ions, but

TABLE I

REFINED STRUCTURAL PARAMETERS FOR $Sr_2CuO_{3.9}$

					Thermal parameter (Å^2)			
Atom	Site	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	Cell occupancy
Sr	4*e*	0	0	0.3539(2)	2.2(1)	—	0.00(7)	3.62(10)
Cu	2*a*	0	0	0	1.7(1)	—	0.0(1)	1.81(5)
O1	4*c*	0	1/2	0	−0.3(1)	5.1(4)	0.7(1)	2.8(1)
O2	4*e*	0	0	0.1528(3)	3.1(2)	—	0.4(1)	4.0

$I4/mmm$; $a = 3.7907(7)$, $c = 12.417(2)$ Å

$R_p = 4.0\%$, $R_{wp} = 5.4\%$, $R_I = 13.5\%$, $R_{exp} = 1.2\%$

Average bond distances (Å)

Cu–O1 1.895(1) [×4]
Cu–O2 1.897(4) [×2]
Sr–O1 2.624(2) [×4]
Sr–O2 2.497(5)
2.682(2) [×4]

no satisfactory refinements were achieved for such models. However, when the possibility of cation vacancies was considered, the refinement converged to a significantly reduced weighted *R*-factor (from 7.2 to 5.4%), which accompanied a decrease in Cu and Sr site occupancies to around 0.9. Since no peaks in the XRD and neutron diffraction profiles were consistent with likely impurities, the Sr and Cu site occupancies were constrained to be equal in order to maintain the required 2 : 1 ratio. For this refinement (Table I) anisotropic motion for all atoms was allowed, and the implied stoichiometry was $Sr_2CuO_{3.8(1)}$, which is now in good agreement with the TGA result. Further support for this cation-deficient model was sought by determining the density. Being insensitive to the overall oxygen content of the phase, the density allowed the cation site occupancy to be estimated as 0.85(3), which agrees well with the neutron diffraction value of 0.91(2), given that the inherent errors associated with the density measurement would result in a reduced apparent occupancy.

Some weak peaks in the neutron diffraction profile (Fig. 4) were incompatible with the simple tetragonal unit cell, and the absence of equivalent peaks in XRD traces suggested that oxygen ordering effects were primarily responsible. However, satisfactory indexing on simple multiples of the tetragonal subcell proved impossible, and it is probable that an incommensurate superstructure exists. In this context, the refined structure from neutron diffraction data will correspond to an average over many simple subcells. Although the local environments around Cu and Sr are not accurately represented by such a description, the Cu–O and Sr–O bond distances implied by this model are given in Table I. Despite the uncertainties associated with these distances, bond valence sums for Cu and Sr were calculated using the method of Brown and Altermatt (*10*) for a random distribution of vacancies. Appropriate Cu^{3+} (*11*) and Sr^{2+} (*10*) parameters resulted in bond valence sums of 3.07 and 1.94 for Cu and Sr, and therefore provided no clear evidence for a large hole concentration, whether considered to be on Cu or O.

The local Cu coordination was examined using CuK-edge EXAFS data. The Fourier transform (Fig. 5) provided unequivocal evidence for a significantly different stereochemistry from that corresponding to the

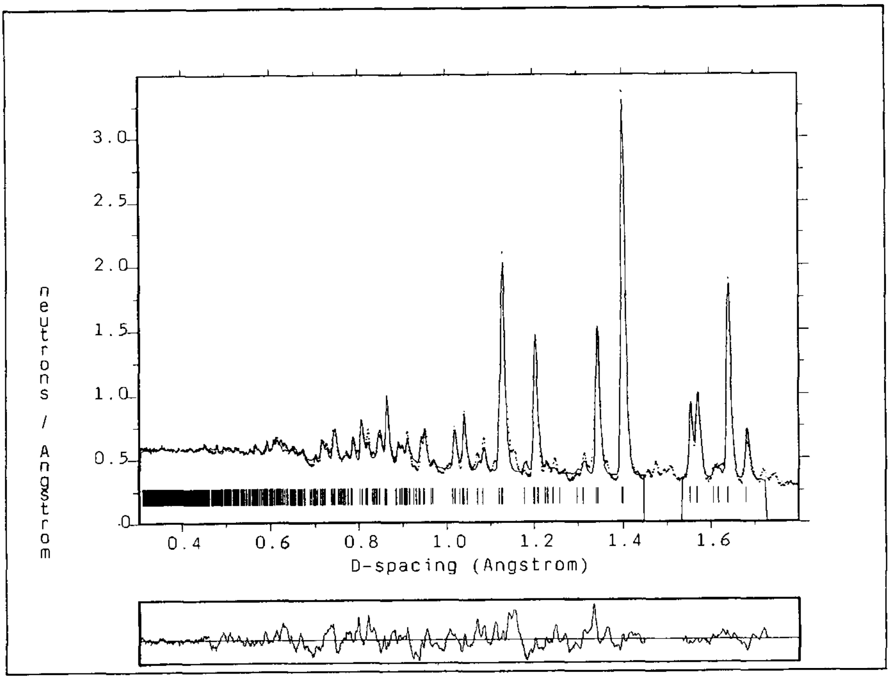

FIG. 4. Powder neutron diffraction profile (dots, observed; solid line, calculated) and subcell reflection positions for $Sr_2CuO_{3.9}$.

average structure deduced from neutron diffraction. In particular, the shoulder on the main peak was clearly indicative that some Cu–O bonds were substantially shorter than the value of 1.90 Å implied by the neutron diffraction refinement. Deconvolution of the composite peak implied two bonds at 1.755 Å and three at 1.89 Å, although the data were insensitive to the overall Cu coordination number. Bond valence summation for this environment gives an effective Cu valence of 3.77, which is very much higher than expected for a Cu(III) compound and, in fact, is quite close to the values deduced from TGA [3.84(10)] and neutron diffraction [3.6(2)].

The proposed structure is unusual, since vacancies exist on both cation sites and one oxygen site, but similar features are found in other phases related to K_2NiF_4. For example, La_2MnO_{4+x} contains no interstitial oxygen ions but has a 2 : 1 ratio of La and Mn vacancies (*12*), and La and O vacancies coexist in $La_{1.83}CoO_{3.87}$ (*13*). However, in contrast to these stoichiometries, a simple alternative structure would appear to be plausible for $Sr_2CuO_{3.9}$ involving complete occupancy of the cation sites and a virtually intact O1 sublattice. The observed highly defective structure must be stabilized by nonelectrostatic effects which may be related to the preference of Cu for coordination numbers less than six. Although the nature of the vacancy ordering in $Sr_2CuO_{3.9}$ is currently unknown, the concentration of vacancies on the O1 sites allows the presence of 5-coordinate or 4-coordinate Cu, in contrast to the octahedral coordination required for a model involving an integral O1 sublattice. In relation to plausible structural models, it is relevant to note that the phase $Sr_{14}Cu_{24}O_{41}$ has recently been found to have an incommensurate structure with planar 4-coordinate Cu ions (*14*).

The present study appears to be the first to indicate the possibility of copper oxidation states in excess of three (at least in a formal sense) in an oxide environment, although it is pertinent to note that Cu(IV) has been proposed in the mixed fluoride Cs_2CuF_6 (*14*). The implied oxidation state (around +3.8) is of relevance to the current interest in high temperature superconductivity in mixed copper oxides. An important chemical feature which has emerged from photoemission studies of such materials [see, for example, Ref. (*15*)] is that for degrees of oxidation above formal Cu(II), the holes appear to be in a band which is largely O 2*p* in character. Important questions therefore exist concerning the validity of cation oxidation state discussions in mixed copper oxides of this type. In the context of current discussions concerning the nature of holes in mixed copper oxides, the structural and electronic properties of $Sr_2CuO_{3.9}$ are of considerable interest, whether interpretation involves Cu in a very high oxidation state or an exceptionally high concentration of holes in an O 2*p* band. Preliminary measurements of electrical resistance using four-probe dc methods (Fig. 6) indicate that both Sr_2CuO_3 and $Sr_2CuO_{3.9}$ are semiconductors above 130 K, although $Sr_2CuO_{3.9}$ displays a much smaller temperature dependence. Since well-sintered $Sr_2CuO_{3.9}$ pellets are difficult to obtain—sintered Sr_2CuO_3 samples undergo morphology changes on subsequent high pressure oxygenation—the absolute values of resistance for Sr_2CuO_3 and $Sr_2CuO_{3.9}$ are probably not reliable. Nevertheless, the observed difference in temperature dependence appears to be significant. The reason for the change in slope of the resistance–temperature plot Sr_2CuO_3 at 130 K has not yet been investigated.

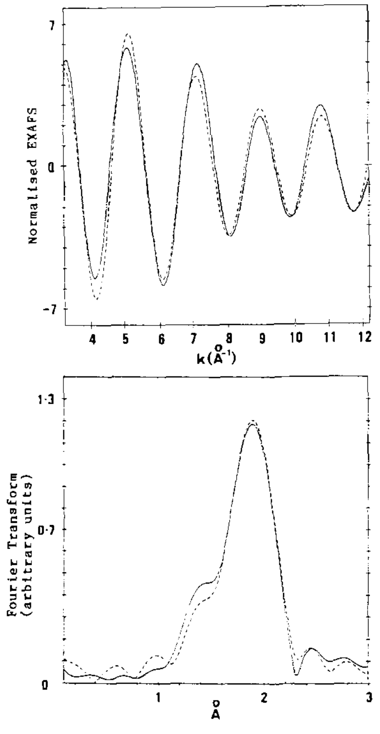

FIG. 5. EXAFS data for $Sr_2CuO_{3.9}$ (broken line, observed; solid line, calculated).

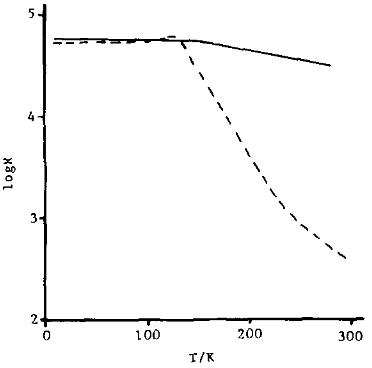

FIG. 6. Variation of resistance with temperature for Sr_2CuO_3 (broken line) and $Sr_2CuO_{3.9}$ (solid line).

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