Journal of the European Ceramic Society 16 (1996) 637–643
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0955-2219/96/$15.00

0955-2219(95)00182-4

Phase Equilibria and Crystal Chemistry in the System Sr–Ca–Cu–O Under High Oxygen Pressure

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(Received 31 May 1995; revised version received 27 September 1995; accepted 12 October 1995)

Abstract

Phase equilibria in the system SrO–CaO–CuO have been studied under high oxygen pressures. The recently discovered non-superconducting binary phase, $Sr_{0.74(3)}CuO_2$*, which is stable only under high oxygen pressure, forms a complete range of solid solutions with the structurally related phase,* $Ca_{0.81(1)}CuO_2$*. These materials have complicated superstructures and may form a family of Vernier phases, such as was found in* $Sr_{0.74(3)}CuO_2$*. Stabilities and oxygen stoichiometries of tetragonal* $Sr_{2-2x}Ca_{2x}CuO_{3+\delta}$ $(0.0 \leq x \leq 0.1)$ *and* $Sr_{14-14x}Ca_{14x}Cu_{24}O_{38+\delta}$ $(0.0 \leq x \leq 0.5)$ *solid solutions under high oxygen pressures are also discussed.*

1 Introduction

Discovery of high temperature superconductivity in Sr–Cu–O samples prepared under pressure has renewed interest in the study of Sr–Cu–O and related phase diagrams, under both high isostatic pressure and high oxygen pressures.[1-10] In air, at one bar, there are three phases in the SrO–CuO system with compositions Sr_2CuO_3, $SrCuO_2$ and $Sr_{14}Cu_{24}O_{38+\delta}$, all of which exhibit extensive Ca ⇔ Sr substitution.[6-11] Hiroi *et al.*[3] and others[4,12,13] reported superconductivity in $Sr_{n+1}Cu_nO_{2n+1+\delta}$ (n = 1, 2, 3...∞), prepared under high isostatic pressures (> 5 GPa), using $KClO_4$ as an oxidiser. Orthorhombic, non-superconducting Sr_2CuO_3, which forms in air at ambient pressure, transforms to tetragonal superconducting $Sr_2CuO_{3+\delta}$ (δ = 0·1), i.e. n = 1, when heated at 800–900°C under high pressure.[3,4,12,13] This phase has a highly oxygen-deficient K_2NiF_4 structure. A similar product prepared at 370°C in flowing oxygen using a copper hydroxometallate precursor, $Sr_2Cu(OH)_6$ had an oxygen excess of δ = 0·29 and was non-superconducting.[14] The orthorhombic to tetragonal phase transformation was also achieved by heating Sr_2CuO_3 at 400°C and 160 bar oxygen pressure.[1] TG analysis showed the oxygen content of these samples to be significantly higher, δ = 0·9, and the samples again non-superconducting.

Singh *et al.*[5] recently published results on the stability of (Ba, Sr, Ca)O–CuO binary phases as a function of oxygen pressure. The conditions used were 1, 15 and 200 bar in the temperature range 880–950°C. $Sr_2CuO_{3+\delta}$, $Sr_{14}Cu_{24}O_{38+\delta}$ and $Ca_{0.8}CuO_2$ were found to be stable under these conditions. We have recently synthesised a new high pressure phase, $Sr_{0.74(3)}CuO_2$, over the range 20–600 bar O_2 and at temperatures below 785°C;[15] this temperature range is significantly lower than that used by Singh *et. al.*[5]

A study of phase formation in the system Sr–Ca–Cu–O, at 950°C, under high isostatic pressures (10 kbar) has been reported by George *et al.*[6] and the results compared with those at 1 bar O_2. The main differences between these two sets of results are on the $SrCuO_2$–'$CaCuO_2$' join. The 'infinite-layer' phase,[16,17] $Sr_{0.15}Ca_{0.85}CuO_2$, and another ternary phase, $Sr_{0.3}Ca_{0.7}CuO_2$, are stable at 1 bar O_2 yet unstable at 10 kbar. In addition, the extent of $Sr_{1-x}Ca_xCuO_2$ solid solution is less at 10 kbar, $0 < x < 0.36$, than at 1 bar O_2, $0 < x < 0.62$.

The aim of our present studies was to better understand the phase equilibria in the Sr–Ca–Cu–O system under high oxygen pressures and to explore the possibility of tuning the oxygen content in different compositions to induce superconductivity. We report here the phase relationships in the system at 775°C and 350 bar oxygen pressure. These are lower temperatures and higher pressures than those used by Singh *et al.*[5] Results on oxygen stoichiometries and crystal chemistry of the various phases are also presented.

2 Experimental

Reagents used were $SrCO_3$ (Fisons, 99%), $CaCO_3$ (BDH, Analar) and CuO (Aldrich, A.C.S. 99+%).

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$CaCO_3$ and $SrCO_3$ were dried overnight at 300°C and CuO at 700°C, prior to weighing. Samples were weighed out, ground together in an agate mortar and pestle with acetone to form a paste, dried and fired in gold foil boats at 800–900°C for one night in air to decarbonate. Samples were then reground, pelleted (to promote reaction) and fired at 900°C for one day then 930°C for one day and finally 950°C for a further day, with intermediate regrinding and pelleting, to attain equilibrium and complete reaction in air.

These air-reacted samples were then subjected to further heating under high oxygen pressure. For this, samples were reground, repelleted and portions, 300–600 mg, wrapped in gold foil, placed in a ceramic boat and inserted into a Morris Research Inc. High Oxygen Pressure Furnace, model number HPS 5015E7. The starting pressure was adjusted so as to give the desired pressure, at the final annealing temperature,[15] which was varied from 50 to 600 bar. The temperature was raised at 10°C min^{-1} from 25°C to a maximum of 700–850°C then held for about 16-32 h, to ensure complete reaction, before cooling back to room temperature whilst maintaining pressure. For the $SrO–CaO–CuO_{1+\delta}$ phase diagram study, a uniform annealing temperature of 775°C and a maximum pressure of 350 bar was used.

A Philips PW1710 diffractometer, $CuK\alpha_1$ radiation, was used for routine crystalline phase identification. For accurate lattice parameter determination, a STOE STADI P diffractometer was used, in transmission mode, with a small linear position sensitive detector (PSD), Ge monochromator and $CuK\alpha_1$ radiation. Data were collected over the range $10° \leq 2\theta \leq 80°$ with Si as internal standard. Electron diffraction (ED) patterns for selected samples were recorded using a Jeol 2000EX TEMSCAN electron microscope operating at 200 kV.

Compositional analysis was carried out by electron probe microanalysis using a CAMECA SX51 EPMA instrument. Oxygen content was determined for selected samples using a Stanton Redcroft STA 1500 combined TG/ DTA. Samples were reduced using a heating rate of 10°C min^{-1} up to 950°C under an atmosphere of flowing $5\%H_2/95\%N_2$. The reduction reaction can be written as:

$$A_xCu_yO_{x+y+\delta}+(y+\delta)H_2 \rightarrow xAO + yCu + (y+\delta)H_2O$$

where A = Sr, Ca.

Magnetic susceptibility was measured using a Lakeshore AC 7000 Susceptometer.

3 Results and Discussion

The results on each of the binary joins are presented first, followed by results on the ternary system SrO–CaO–CuO, under high oxygen pressures.

3.1 The join $SrO–CuO_{1+\delta}$

Since there have been many studies reported on the phases that form in the system SrO–CuO at both ambient[7,8] and high pressure,[1–6] together with phase diagrams,[5–8] our studies have focused on (a) the stabilities and oxygen contents of the strontium cuprates and (b) the possible occurrence of any new phases. For each of the phases considered, results are as follows:

3.1.1 $SrCuO_2$ (1 : 1 phase)

Our results show that this phase is stable at all temperatures studied (ambient to 850°C) up to a maximum oxygen pressure of 50 bar. At higher pressures, $SrCuO_2$ decomposes to give a mixture of two other strontium cuprates, the nature of which is temperature dependent. At temperatures greater than 785°C, $SrCuO_2$ decomposes to a mixture of 2 : 1 and 14 : 24, in accordance with the results of Singh *et al.*[5] At temperatures lower than 785°C, $SrCuO_2$ decomposes to give a mixture of 2 : 1 and the new binary phase, $Sr_{0\cdot74(3)}CuO_2$.

3.1.2 Sr_2CuO_3 and $Sr_2CuO_{3+\delta}$(2 : 1 phase)

Orthorhombic Sr_2CuO_3 is stable in air[7–9] and at high isostatic pressures[6] but transforms to tetragonal $Sr_2CuO_{3+\delta}$ on annealing under high isostatic pressures with oxidiser[3] and high oxygen pressures.[1–5] Our studies on its stability at 775°C, showed that orthorhombic Sr_2CuO_3 was stable up to an oxygen pressure of about 200 bar but transforms to tetragonal $Sr_2CuO_{3+\delta}$, in agreement with the results of Singh *et al.*,[5] at higher pressures. An indexed X-ray powder pattern for tetragonal $Sr_2CuO_{3+\delta}$ is given in Table 1; reflections marked by an asterisk are due to the supercell $4\sqrt{2}a \times 4\sqrt{2}a \times c$ which is the same as that proposed by Hiroi *et al.*[3]

The oxygen excess of the tetragonal 2 : 1 phase, determined by thermogravimetric reduction in $5\%H_2/95\%N_2$, corresponded to $\delta = 0{\cdot}43(2)$. This value is slightly greater than for the sample prepared using a hydroxometallate precursor ($\delta = 0{\cdot}29$)[14] and much smaller than reported by Lobo *et al.*,[1] $\delta = 0{\cdot}9$. These values are all significantly higher than obtained using high isostatic pressures/oxidiser[3,4] where $\delta = 0{\cdot}1$.

Magnetic susceptibility measurements showed tetragonal 2 : 1 to be non-superconducting, consistent with the oxygen content analysis which suggested an average copper valence of 2·86(4)+.

The lattice parameters of $Sr_2CuO_{3+\delta}$ are also intermediate between those obtained by Hiroi *et al.*[3] and Lobo *et al.*,[1] Table 2. There appears to be

Table 1. Indexed XRD pattern for tetragonal $Sr_2CuO_{3+\delta}$

d_{obs}(Å)	d_{calc}(Å)	I/I_o	*hkl*
6·273	6·265	4	0 0 2
3·611	3·611	4	1 0 1
2·985*	2·984*	3	5 0 3*
	2·984*	—	4 3 3*
2·969*	2·969*	1	2 6 2*
2·902?		1	?
2·799	2·798	100	1 0 3
2·666	2·666	52	1 1 0
2·647*	2·645*	8	1 8 0*
	2·645*	5	4 7 0*
2·605*	2.604*	—	4 5 3*
2·088	2·088	30	0 0 6
	2·087	—	1 1 5
2·029	2·030	23	1 1 4
2·006*	2·004*	7	3 0 6*
1·990?		1	?
1·885	1·885	19	2 0 0
1·644	1·644	35	1 1 6
1·616	1·617	8	1 0 7
1·595*	1·594*	9	1 6 7*
1·564	1·563	20	2 1 3
1·528*	1·529*	4	1 11 5*
	1·527*	—	2 7 7*
1·447*	1·446*	2	1 12 5*
1·399	1·399	13	2 0 6
	1·399	—	2 1 5
1·350	1·350	6	1 1 8

a = 3·7695(6) Å.
c = 12·529(2) Å.
Space group = I 4/mmm (No. 139).
* = Lines indexed on the tetragonal supercell $4\sqrt{2}a \times c$.
? = Unidentified lines.

a trend in that a increases and c decreases with an increase in oxygen excess, δ. Although our lattice parameters for 2 : 1 are very similar to those of superconducting $Sr_2CuO_{3+\delta}$[3,4] our samples are non-superconducting. The crystallographic implications for such an observation are, at present, unclear.

To date, therefore, the only synthesis route to yield superconducting tetragonal $Sr_2CuO_{3+\delta}$ (Tc = 70 K) is that using high isostatic pressures/oxidisers.

3.1.3 $Sr_{14}Cu_{24}O_{38+\delta}$ (14 : 24 phase)

The 14 : 24 phase was stable under all temperatures and pressures used during this study. Thermogravimetric measurements showed the oxygen stoichiometry to vary with pressure: in air δ = 2·01(2) whereas after annealing at 350 bar O_2, δ = 3·03(2), suggesting that the 'ideal'[10,11] composition $Sr_{14}Cu_{24}O_{41}$ can be achieved only under high oxygen pressure.

Magnetic susceptibility measurements showed that this phase is non-superconducting, even after high oxygen pressure annealing. This is perhaps surprising because the average copper valence, 2·25, is close to the value observed in most other superconducting cuprates and suggests that the '14 : 24' structure type is not suitable for superconductivity.

3.1.4 $Sr_{0\cdot74(3)}CuO_2$ (3 : 4 phase)[15]

At temperatures lower than 785±10°C and oxygen pressures > 20 bar, the phase of approximate composition $Sr_3Cu_4O_{7+\delta}$ forms. Full details on its stability and crystal chemistry will be published elsewhere.[15] It is not stable at T>785°C even at the highest oxygen pressure used in the present investigations (600 bar) and instead, decomposes to give 14 : 24 and tetragonal $Sr_2CuO_{3+\delta}$. This explains why $Sr_{0\cdot74}CuO_2$ was not observed in previous high pressure (oxygen[5] or isostatic[6]) studies, which were confined to temperatures above 880°C.

Using both XRD and ED, it was found that *two* sub-cells were required to index all the reflections in the $Sr_{0\cdot74}CuO_2$ pattern. Both are orthorhombic, with two axes, a and c, in common.

Subcell I: a_I = 6·8182(12) Å,b_I = 3·7113(7) Å and c_I = 11·0203(17) Å;
Space group = I ba2 (No. 69) or Ibam (No. 72).
Subcell II: a_{II} = 6·8182(12) Å, b_{II} = 2·7290(3) Å and c_{II} = 11·0203(17) Å;
Space group = F mmm (No. 69).

This showed that either the sample was a phase mixture in which, remarkably, the values of two of the lattice parameters were identical, or the sample was a Vernier phase,[19] incommensurate along b. The latter interpretation was confirmed by further ED work. The coincidence (super) cell[19] is b = 92·79(1) Å (=$25b_I$ and $34b_{II}$).

$Sr_{0\cdot74(3)}CuO_2$ is non-superconducting. This is not very surprising because the average copper valence, 2·52(6), is too large for superconductivity in layered cuprates.

3.1.5 Phase equilibria of the system SrO–CuO at 775°C with varying oxygen pressure

At 775°C, our results show that the phase equilibria

Table 2. $Sr_{2-2x}Ca_{2x}CuO_{3+\delta}$ lattice parameters, oxygen excess (δ) and average copper valence after high oxygen pressure treatment

x	a	c	δ	*Average copper valence*
0.0	3·7695(6)	12·529(2)	0·43(2)	2·86(4)+
0·05	3·7568(5)	12·528(1)	—	—
0·1	3·7531(5)	12·507(2)	0·31(2)	2·62(4)+
0·0 (Hiroi *et al.*)	3·764	12·548	0·1	2·2+
0·0 (Lobo *et al.*)	3·7907(7)	12·417(2)	0·92	3·81+

are very dependent on pressure; three areas in particular show considerable variation, Fig. 1. Between 20 and 50 bar, compositions on the Sr- and Cu-rich side of 3 : 4 give phase mixtures of 1 : 1 + 3 : 4 and 3 : 4 + 14 : 24, respectively. Between 50 and 200 bar, the 1 : 1 phase is unstable and phase mixtures of orthorhombic 2 : 1 + 3 : 4 result. Above 200 bar, orthorhombic 2 : 1 transforms to its tetragonal modi-fication and so phase mixtures of tetragonal 2 : 1 and 3 : 4 exist for all compositions between 2 : 1 and 3 : 4.

3.2 The join CaO–$CuO_{1+\delta}$

Our results on this system (at temperatures less than 850°C and pressures up to 600 bar) are in good agreement with those reported by Singh *et al.*[5] (for temperatures greater than 880°C and pressures up to 200 bar).

3.2.1 Ca_2CuO_3

Ca_2CuO_3 decomposes in oxygen pressures greater than 10 bar, to give a mixture of $Ca_{0\cdot81(1)}CuO_2$ + CaO.

3.2.2 $Ca_{0\cdot81(1)}CuO_2$

There have been several reports on the phase $Ca_{1-y}CuO_2$.[5,7,20–22] It has an upper limit of thermal stability which increases with $P(O_2)$: 775±5°C in air,[7] 835±5°C in flowing oxygen[7,20,21] and above 950°C in high oxygen pressure.[5] The exact cation stoichiometry of the phase has been variously described as between $y = 0{\cdot}15$ and $0{\cdot}2$. Structural studies showed it to have a cation-deficient $NaCuO_2$-related structure.[20–24] Various superstructures, commensurate and non-commensurate, have been observed and are attributed to differences in the ordering of the Ca ions.[18,19] It was proposed[18] that ordering depends on cooling rate, Ca stoichiometry and oxygen partial pressure and is, therefore, a fairly complex phenomenon.

Our results show this phase to be stable at temperatures higher than 775°C when an oxygen pressure greater than 10 bar is used, in agreement with Singh *et al.*[5] Several compositions were prepared along the join CaO–CuO, in order to determine its exact stoichiometry. Only the compositions $Ca_{0\cdot80}CuO_2$ and $Ca_{0\cdot82}CuO_2$ were single phase by X-ray diffraction. The phase, therefore, appears to have an average composition, $Ca_{0\cdot81(1)}CuO_2$. Compositions on either side such as $Ca_{0\cdot85}CuO_2$ and $Ca_{0\cdot75}CuO_2$ were phase mixtures of CaO + $Ca_{0\cdot81(1)}CuO_2$ and $Ca_{0\cdot81(1)}CuO_2$ + CuO, respectively. Our formula is in general agreement with Siegrist *et al.*[20] and Singh *et al.*[5] but slightly different from that proposed by Babu and Greaves,[21] $Ca_{0\cdot85}CuO_2$.

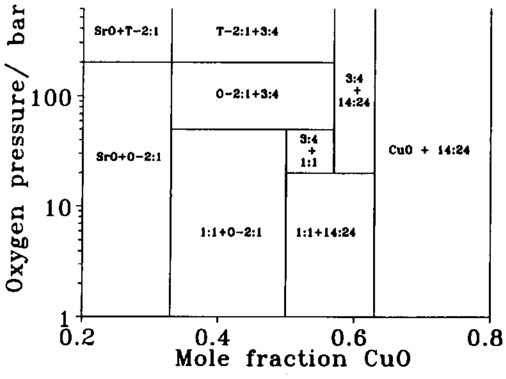

Fig. 1. Phase equilibria in the system SrO–$CuO_{1+\delta}$ at 775°C, as a function of oxygen pressure, after Ref. 15.

3.3 CaO–SrO binary join

The phase equilibria of this join at 350 bar oxygen are the same as in air at 1 bar.[25] At 775°C, there are two limited solid solutions: $Sr_{1-x}Ca_xO$ ($0 \le x < \approx 0{\cdot}15$) and $Ca_{1-y}Sr_yO$ ($0 \le y < \approx 0{\cdot}06$).

3.4 Phase diagram for the system SrO–CaO–$CuO_{1+\delta}$ at 775°C, 350 bar O_2

There have been several reports in the literature on phase equilibria in the system SrO–CaO–CuO in air,[7,24,25] 1 atmosphere of oxygen[6] and at 10 kbar isostatic pressure.[6] To date, however, there have been no studies under high oxygen pressures. We report here the phase relationships at 775°C and 350 bar oxygen pressure which correspond to the optimum conditions for formation of $Sr_{0\cdot74(3)}CuO_2$. Results are summarized in Fig. 2. Compositions studied are marked, with appropriate symbols referring to whether single-, two- or three-phase mixtures resulted once equilibrium conditions were obtained.

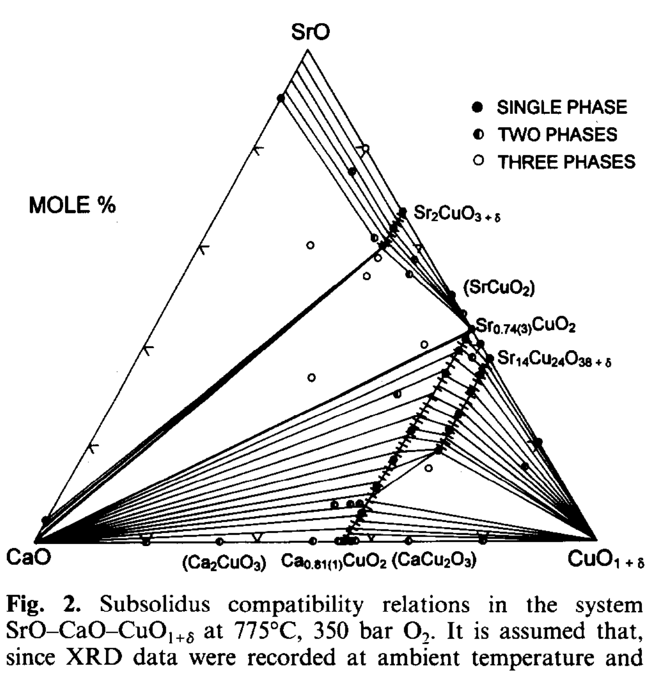

Fig. 2. Subsolidus compatibility relations in the system SrO–CaO–$CuO_{1+\delta}$ at 775°C, 350 bar O_2. It is assumed that, since XRD data were recorded at ambient temperature and pressure, no changes in the phase assemblages had occurred during cooling and release of pressure.

There are some noticeable differences in the phase equilibria between air[7,24,25] (or 1 bar O_2)[6] and 350 bar O_2 (at 775°C). The phases: $SrCuO_2$, Ca_2CuO_3, $CaCu_2O_3$, $Sr_{0·3}Ca_{0·7}CuO_2$ and $Sr_{0·15}Ca_{0·85}CuO_2$, which exist in air/1 bar O_2, do not exist at 350 bar O_2; conversely, $Sr_{0·74(3)}CuO_2$ exists at 350 bar O_2 but not at 1 bar.

The phase diagram shown in Fig. 2 is not a true ternary diagram as the oxygen content for copper oxide is not fixed. Instead, it is a ternary sub-section of the quaternary system: SrO–CaO–CuO–O. No attempt is made in Fig. 2 to show variations in oxygen excess, δ, of the phases present.

The diagram contains three single phase regions as follows:

3.4.1 $Sr_{2-2x}Ca_{2x}CuO_{3+\delta}$ ($0 \le x \le 0·1$) solid solutions

Tetragonal $Sr_2CuO_{3+\delta}$ can incorporate up to about 10% Ca by substitution for Sr, at 350 bar O_2. This is substantially less than in air[7] where an entire range of solid solutions forms between orthorhombic Sr_2CuO_3 and Ca_2CuO_3. The smaller range of solid solutions at high oxygen pressures appears to be associated with the instability of the K_2NiF_4/La_2CuO_4 structure when doped with smaller cations.[1] Table 2 shows the lattice parameters for x=0·0, 0·05, 0·1 at 775°C, 350 bar O_2. The unit cell contracts with x, as expected.

Thermogravimetric reduction of tetragonal $Sr_2CuO_{3+\delta}$ in 5%H_2/95%N_2 showed the oxygen excess to be δ = 0·43(2). For x=0·1, the excess was less, δ = 0·31(2), perhaps because the unit cell is smaller and can accommodate less extra oxygens. Predictably, the samples are not superconducting as the average copper valences, Table 2, are too high.

3.4.2 $Ca_{0·81(1-x)}Sr_{0·74x}CuO_2$ ($0·0 \le x \le 1·0$) solid solutions

There have been various reports on $Ca_{1-y}CuO_2$[5,7,20–22] but attempts to partially substitute Sr for Ca were unsuccessful.[17] Using modest temperatures (up to 800°C) and varying the starting pressure, a complete range of solid solutions forms between $Ca_{0·81(1)}CuO_2$ and $Sr_{0·74(3)}CuO_2$.

The synthesis conditions varied with composition: $Sr_{0·74(3)}CuO_2$ formed most readily at 775°C, 350 bar O_2 whereas for $Ca_{0·81(1)}CuO_2$, higher temperatures and lower pressures were required (850°C and 50 bar). Intermediate compositions required intermediate conditions although X-ray diffraction patterns showed that a small amount (≈5%) of 'Ca-doped 14:24' and CaO were present. This was attributed to partial decomposition on cooling in the high pressure furnace. Due to operational limitations of the furnace, it was not possible to quench samples from the annealing temperature/pressure.

This range of solid solutions, $Ca_{0·81(1-x)}Sr_{0·74x}CuO_2$ ($0·0 \le x \le 1·0$) is most unusual and clearly does not form by a simple Sr⇔Ca substitution mechanism: the alkaline earth content decreases with increasing Sr content. The XRD data of all compositions, $0·0 \le x \le 0·74$, showed the same $CaCu_{0·81(1)}O_2$-type orthorhombic sub-cell (equivalent to sub-cell II for $Sr_{0·74(3)}CuO_2$) lines and a number of additional reflections attributed to either another sub-cell or supercell(s). The intensity and nature of the additional reflections varied with composition as did the intensity of one or two $CaCu_{0·81(1)}O_2$-type subcell reflections, notably the 002 reflection which decreased with x.

The lattice parameters for one sub-cell of the $Ca_{0·81(1-x)}Sr_{0·74x}CuO_2$ solid solutions, are given in Fig 3. Overall there is a gradual increase in a, c and V with x, but a decrease in b. Superimposed on these changes, however, there may be at least three regions, $0·0 \le x \le 0·2$, $0·25 \le x \le 0·55$ and $0·65 \le x \le 1·0$ where the lattice parameters,

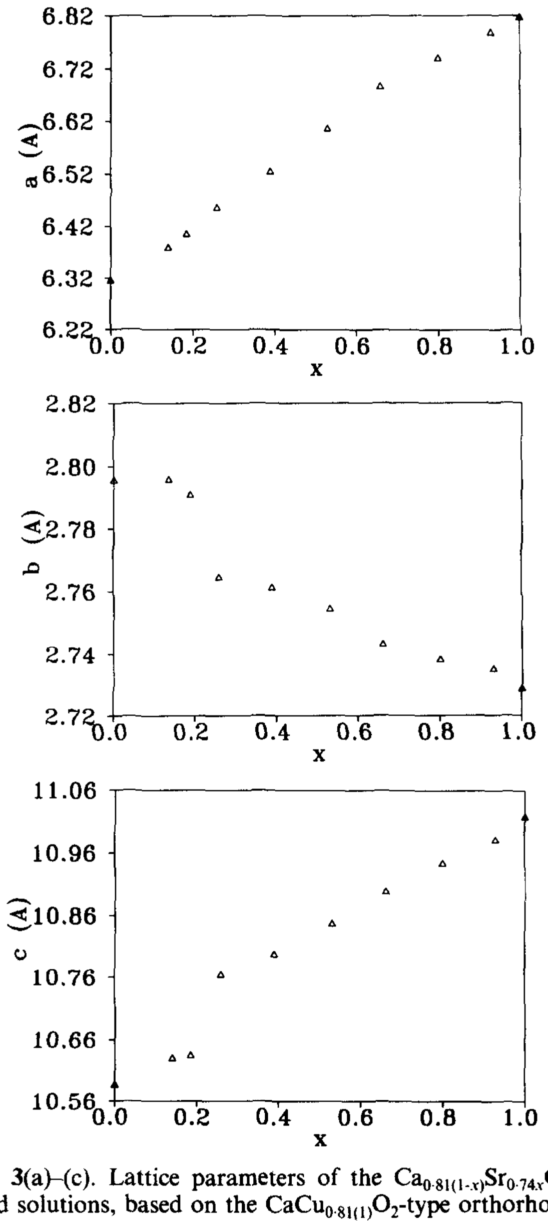

Fig. 3(a)–(c). Lattice parameters of the $Ca_{0·81(1-x)}Sr_{0·74x}CuO_2$ solid solutions, based on the $CaCu_{0·81(1)}O_2$-type orthorhombic subcell (equivalent to subcell II for $Sr_{0·74(3)}CuO_2$).

Table 3. Variation of subcell b_I and b_{II} lattice parameters with composition for $Ca_{0\cdot81(1-x)}Sr_{0\cdot74x}CuO_2$ solid solutions

x	b_I *(Å)*	b_{II} *(Å)*	b *coincidence cell (Å)*
1·00	3·7113(7)	2·7290(3)	92·79(1) = $25b_I$ and 34 b_{II}
0·93	3·6588(6)	2·7353(6)	10·96(2) = $3b_I$ and $4b_{II}$
0·80	3·6105(8)	2·7384(11)	79·42(1) = $22b_I$ and $29b_{II}$
0·66	3·5981(18)	2·7404(19)	57·56(2) = $16b_I$ and $21b_{II}$

especially *b*, show discrete behaviour. Instead of a homogeneous solid solution across the entire range of *x* values, a family of phases may exist; they may all have Vernier character, similar to the $x = 1\cdot0$ end-member. For the high *x* values, $0\cdot65 \leq x \leq 1\cdot0$, the powder patterns may be indexed on a similar Vernier cell to $x = 1\cdot0$, Table 3. However, the period of the Vernier 'coincidence' (super) cell in the *b* direction, changes and the structural implications are, at present, unclear. Further studies on these phases are in progress.

Magnetic susceptibility measurements suggested that none of the compositions for the range $Ca_{0\cdot81(1-x)}Sr_{0\cdot74x}CuO_2$, were superconducting. This is presumably because the formal copper valences for these materials are too high, ranging from: 2·38(2)+ for $Ca_{0\cdot81(1)}CuO_2$ to 2·52(6)+ for $Sr_{0\cdot74(3)}CuO_2$.

3.4.3 $Sr_{14-14x}Ca_{14x}Cu_{24}O_{38+\delta}$ $(0\cdot0 \leq x \leq 0\cdot5)$ *solid solutions*

In air,[10,11,16,17] the 14 : 24 phase can substitute up to 50 mol% of Sr by Ca, to form $Sr_7Ca_7Cu_{24}O_{38+\delta}$. The solid solution limit, $x = 0\cdot5$, appears to be independent of temperature and O_2; however, for a given *x*, the lattice parameters and oxygen content, *δ*, vary, Figs 4 and 5. The *c* parameter varies most and is about 1% greater after high PO_2 treatment (775°C, 350 bar). The oxygen content, and thus formal copper valence (FCV), is higher for samples annealed at high PO_2; in both air and high oxygen pressure, *δ* drops initially with *x*, then stays approximately constant beyond $x \cong 0\cdot2$.

Magnetic susceptibility measurements show no evidence of superconductivity. With the exception of the $x = 0\cdot0$ sample annealed at 350 bar O_2, which had a FCV of 2·25, most of the compositions had a FCV too low for superconductivity. The non-superconductivity of $x = 0\cdot0$ suggests that the 14 : 24 structure type is not suitable for superconductivity.

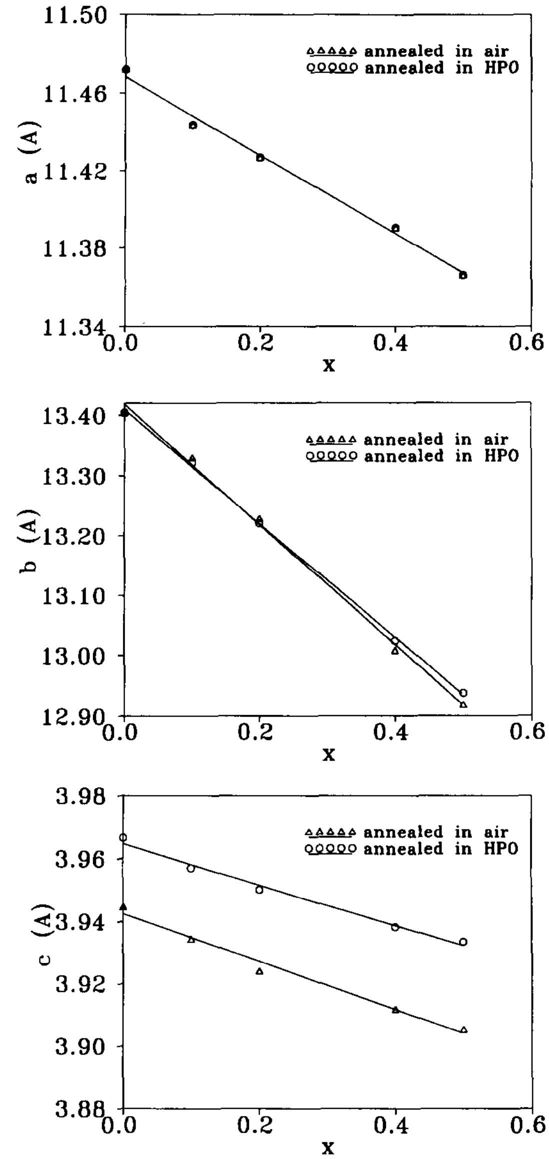

Fig. 4(a)–(c). Lattice parameters of $Sr_{14-14x}Ca_{14x}Cu_{24}O_{38+\delta}$ in air and high oxygen pressure (350 bar).

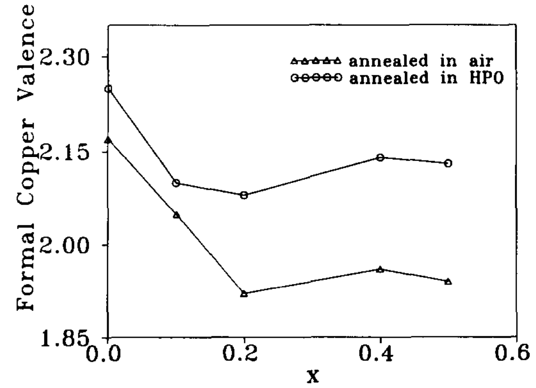

Fig. 5. Variation of Formal Copper Valence (FCV) with *x* for $Sr_{14-14x}Ca_{14x}Cu_{24}O_{38+\delta}$ in air and high oxygen pressure (350 bar).

3.4.4 *Compatibility triangles in the system* $SrO–CaO–CuO_{1+\delta}$ *at 775°C, 350 bar* O_2 *(Fig. 2)*

All compositions belonging to the $Sr_{2-2x}Ca_{2x}CuO_{3+\delta}$ $(0 \leq x \leq 0\cdot1)$ range of solid solutions are compatible with the $Sr_{1-x}Ca_xO$-based solid solution and the new binary phase, $Sr_{0\cdot74(3)}CuO_2$, to form two-phase regions. The Ca-rich end-member, $x = 0\cdot1$, is also compatible with $Ca_{1-y}Sr_yO$ to form two three-phase regions: $Sr_{1\cdot8}Ca_{0\cdot2}CuO_{3+\delta} + Sr_{0\cdot74(3)}CuO_2 + CaO$ and $Sr_{1\cdot8}Ca_{0\cdot2}CuO_{3+\delta} + Ca_{1-y}Sr_yO + Sr_{1-x}Ca_xO$.

The complete range of solid solutions, $Ca_{0\cdot81(1-x)}Sr_{0\cdot74x}CuO_2$ ($0\cdot0 \leq x \leq 1\cdot0$), is compatible with CaO forming a very extensive two-phase region. The compatibility of $Ca_{0\cdot81(1-x)}Sr_{0\cdot74x}CuO_2$ with Cu-rich phases depends on composition. Ca-rich compositions, $0 \leq x \leq 0\cdot15$, are compatible with CuO, whereas all others, $0\cdot15 \leq x \leq 1\cdot0$, are compatible with the 14:24 solid solutions. The 14:24 solid solutions are also compatible with CuO. There is also a small three-phase region between, $Ca_{0\cdot64}Sr_{0\cdot14}CuO_2$, $Sr_7Ca_7Cu_{24}O_{38+\delta}$ and CuO.

4 Conclusions

Phase equilibria in the system $SrO–CaO–CuO_{1+\delta}$ have been studied under high oxygen pressure and show significant differences from the phase equilibria in air.

The new binary phase, $Sr_{0\cdot74(3)}CuO_2$ which only forms under high oxygen pressures and has an upper limit of thermal stability of 785±10°C, forms a nominally complete range of solid solutions with $Ca_{0\cdot81(1)}CuO_2$. These materials have complicated superstructures and may instead form a family of Vernier phases.

Tetragonal $Sr_2CuO_{3+\delta}$ forms a limited solid solution $Sr_{2-2x}Ca_{2x}CuO_{3+\delta}$ ($0\cdot0 \leq x \leq 0\cdot1$) under high oxygen pressures whereas in air, orthorhombic Sr_2CuO_3 forms a complete range of solid solutions with Ca_2CuO_3.

The extent of Ca <=> Sr solubility in the 14:24 phase remains unchanged in high oxygen pressure, although there is an increase in the oxygen content for all compositions.

All of the Sr, Ca cuprate solid solutions have formal copper valences greater than 2+ under high oxygen pressures but none exhibit superconductivity.

The lattice parameters of our tetragonal $Sr_2CuO_{3+\delta}$ are quite similar to those for the superconducting analogue.[3] It is important to determine the detailed crystal structure of both forms in order to shed some light on the crucial structural features necessary for superconductivity.

Acknowledgement

We thank EPSRC for financial support.

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