JOURNAL OF SOLID STATE CHEMISTRY **121,** 498–501 (1996)
ARTICLE NO. 0070

LETTER TO THE EDITOR

Synthesis and Structure of A New Perovskite, $SrCuO_{2.5}$

Bai-Hao Chen[1] and Dave Walker
Lamont–Doherty Earth Observatory of Columbia University, Palisades, New York 10964

and

Bruce A. Scott and David B. Mitzi
IBM Thomas J. Watson Research Center, Yorktown Heights, New York 10598

Communicated by John B. Goodenough, November 27, 1995; accepted November 28, 1995

A new oxygen-deficient perovskite, $SrCuO_{2.5}$, was prepared at 950°C and 100 kbar pressure in a multianvil apparatus. Rietveld profile analysis, using X-ray powder diffraction data, was employed for the structural determination. $SrCuO_{2.5}$ is orthorhombic, *Pbam* (No. 55), $Z = 4$, $a = 5.424(2)$ Å, $b = 10.837(4)$ Å, and $c = 3.731(1)$ Å, which is related to the perovskite subcell by $\sqrt{2}a_p \times 2\sqrt{2}a_p \times a_p$, where a_p is the simple cubic perovskite lattice parameter. It consists of corner-shared CuO_5 square pyramids with oxygen vacancy ordering in the CuO_2 layers. The ordered oxygen vacancies create parallel pseudo-hexagonal tunnels where the Sr atoms reside, forming SrO_{10} polyhedra. Structural features with respect to oxygen vacancies, superstructures, and distortions are analogous to the type of ordering observed in $Sr_2CuO_{3+\delta}$. Superconductivity was not observed in $SrCuO_{2.5}$ down to 5 K. © 1996 Academic Press, Inc.

INTRODUCTION

Despite recent extensive studies of the $Sr_{n+1}Cu_nO_{2n+1+\partial}$ system (1–3), the origin of superconductivity in the high pressure phases of this system is still unclear. A number of studies have attempted to clarify this issue, but low superconducting volume fractions and complications due to the different oxygen vacancy orderings that are possible in these structures have left it unresolved. For example, efforts to confirm superconductivity in single phase $Sr_2CuO_{3+\partial}$ materials have not met with success (2–4). In order to reveal the origin of the superconductivity in this system, we have undertaken a careful investigation of the high pressure phase equilibria and the structure and superconductivity of phases in the Sr–Cu–O system.

It has previously been found that orthorhombic Sr_2CuO_3 (5), with corner-shared CuO_4 square planes, transforms to a K_2NiF_4-type $Sr_2CuO_{3+\partial}$ structure ($0.1 < \partial < 0.9$), containing oxygen vacancies in the CuO_2 planes under high oxygen pressure (1, 6). In addition, a supercell of $4\sqrt{2}a \times 4\sqrt{2}a \times c$ and $5\sqrt{2}a \times 5\sqrt{2}a \times c$, observed in the low ∂ phases (1, 4, 7), could arise from oxygen vacancy ordering in the CuO_2 planes, leading to the formation of CuO_2 chains, CuO_4 square planes, CuO_5 square pyramids, and/or CuO_6 octahedra. On the other hand, orthorhombic $SrCuO_2$ (8), with edge-shared CuO_4 square planes, transforms under high pressure to the tetragonal infinite layer structure, containing exclusively corner-shared CuO_4 square planes (9). If pO_2 is increased, however, we have found that a new oxygen-deficient perovskite $SrCuO_{2.5}$ with a unit cell of $\sqrt{2}a_p \times 2\sqrt{2}a_p \times a_p$ forms at high pressure. The structure of this new phase is the main subject of this communication.

EXPERIMENTAL

The precursor $SrCuO_2$ was obtained by firing $SrCO_3$ and CuO at 900°C several times with intermediate grinding and repelletizing steps. $SrCuO_{2.5}$ was prepared from a mixture of $SrCuO_2$ and $KClO_3$ (as the oxygen source) at a molar ratio 6:1, using an Al_2O_3 crucible at 950°C and 100 kbar for 20 h. A full description of the multianvil apparatus and the high-pressure experimental procedures has been published previously (10, 11).

The sample was characterized with a Siemens D-500 X-ray powder diffractometer using Cu*Kα* radiation. The X-ray powder data were obtained in the range $4° < 2\theta < 80°$ with a step width of 0.02° and a counting period of 20 s. The structural parameters of the $SrCuO_{2.5}$ phase were refined by the FULLPROF program (12) in space group

---

[1] To whom correspondence should be addressed.

0022-4596/96 $18.00

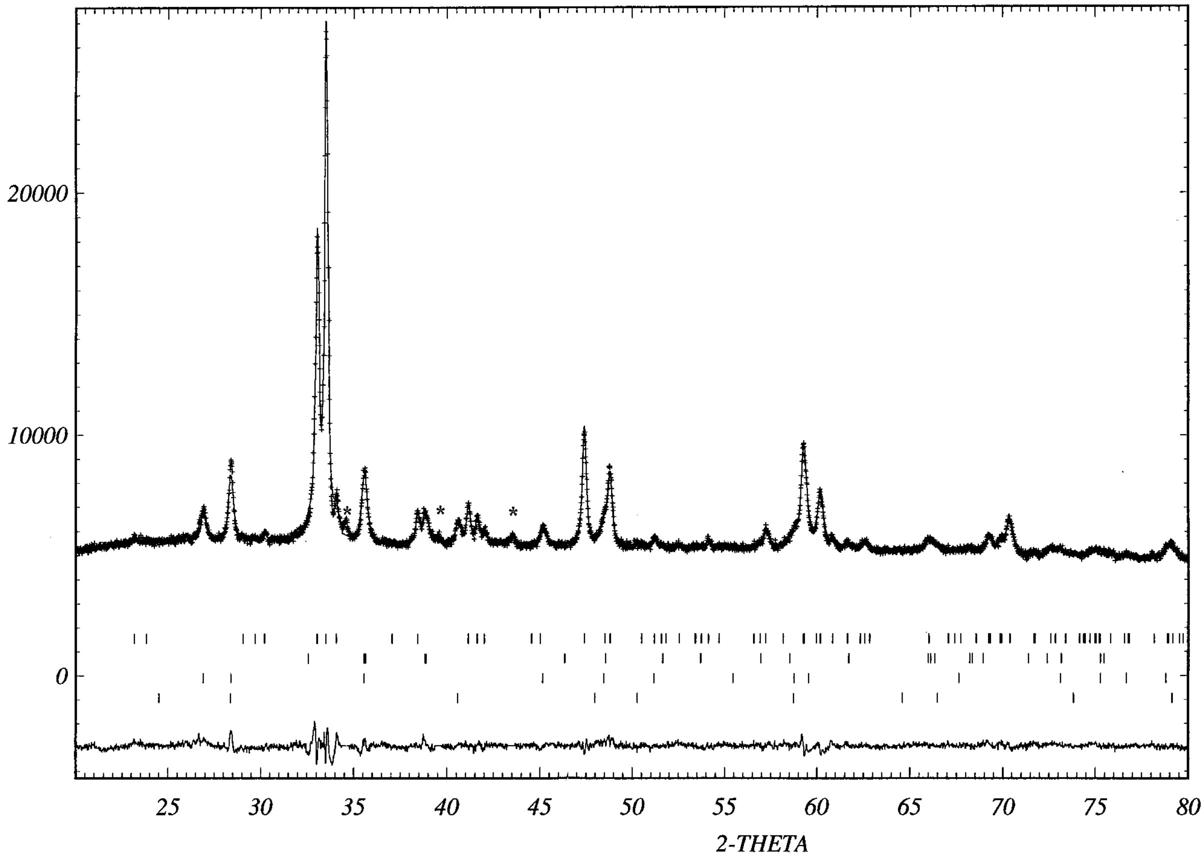

FIG. 1. Comparison of calculated (solid line) and observed (dots) X-ray patterns for $SrCuO_{2.5}$. Calculated reflections (vertical tick marks) from top to bottom refer, respectively, to $SrCuO_{2.5}$, CuO, SrO_2, and KCl. The bottom curve is the difference between calculated and observed patterns. Peaks presumably due to $Sr_3Cu_4O_x$ impurity are marked with asterisks.

TABLE 1
Crystallographic Data for $SrCuO_{2.5}$[a]

		Positional and isotropic thermal parameters			
Atom	Site	x	y	z	B(Å^2)
Sr	4*h*	0.2964(5)	0.3775(5)	0.5	2.3(2)
Cu	4*g*	0.2731(9)	0.1298(9)	0.0	1.1(2)
O1	4*h*	0.262(2)	0.136(2)	0.5	3.3(2)
O2	4*g*	0.565(2)	0.230(2)	0.0	1.7(2)
O3	2*a*	0.0	0.0	0.0	0.6(5)

			Selected bond distances (Å) and angles (deg)				
Sr–O1	2.63(1)	[1×]	Cu–O1	1.87(1)	[2×]	O1–Cu–O1	174.5(8)
Sr–O1	2.82(1)	[1×]	Cu–O2	1.92(1)	[1×]	O1–Cu–O2	90.4(4)
Sr–O1	2.90(1)	[1×]	Cu–O2	1.90(1)	[1×]	O1–Cu–O2	87.3(4)
Sr–O1	2.53(1)	[1×]	Cu–O3	2.04(1)	[1×]	O1–Cu–O3	90.0(4)
Sr–O2	2.86(1)	[2×]				O2–Cu–O2	92.2(4)
Sr–O2	2.53(1)	[2×]				O2–Cu–O3	170.9(8)
Sr–O3	2.54(1)	[2×]				O2–Cu–O3	96.9(4)

[a] Space group *Pbam*. Cell parameters: a = 5.424(2) Å, b = 10.837(4) Å, c = 3.731(1) Å.

Pbam with a pseudo-Voigt peak-shape function. The refined parameters include lattice parameters, a zero-point error, atom positions at those for $NdCuO_{2.5}$ (11) as the starting model, isotropic parameters, occupancies, overall scale factor, peak-shape parameter, and full-width parameters. Attempts to refine the atom occupanies yield higher R values. Minor amounts of the impurity phases CuO, SrO_2, and KCl in the sample were also included for Rietveld refinement. However, the 2θ regions 34.4°–34.8°, 39.4°–39.7°, and 43.30°–43.70° with very weak reflections from an unidentified phase were excluded from the refinement. The final factors were $R_{wp} = 12.9\%$, $R_e = 7.98\%$, $R_b = 4.91\%$, and $\chi^2 = 2.62$.

The final product was also analyzed with a CAMEBAX electron microprobe to determine the stoichiometry of the title compounds. Magnetic susceptibility measurements were carried out on a Quantum Design model MPMS2 SQUID magnetometer by zero-field cooling $SrCuO_{2.5}$ to 5 K, applying a 10 Oe magnetic field, and collecting data from 5 to 160 K. Although the low room-temperature resistivity of the new phase was suggestive of metallic behavior, superconductivity was not observed in $SrCuO_{2.5}$.

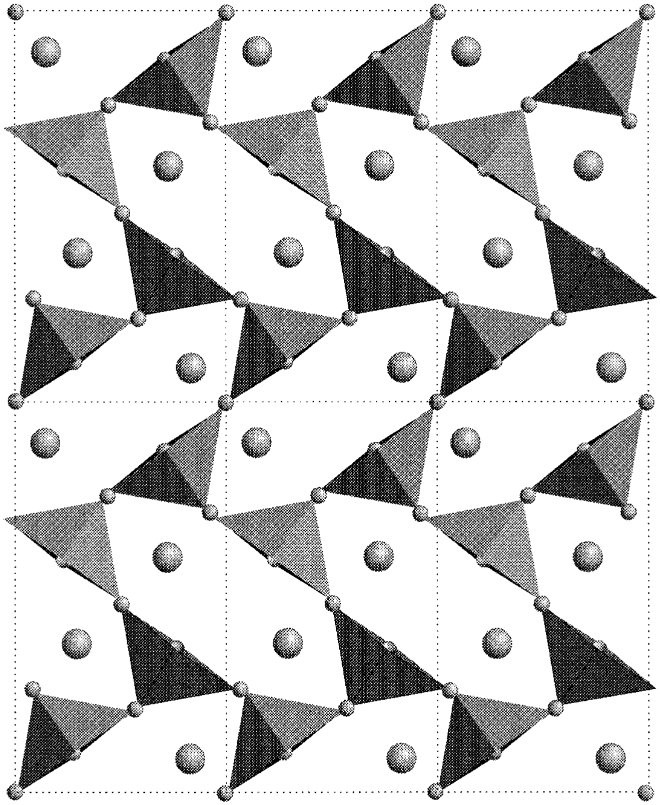

FIG. 2. Structure for $SrCuO_{2.5}$ projected on [001].

RESULTS AND DISCUSSION

The result of X-ray profile analysis shown in Fig. 1 indicates that the high-pressure synthesis yielded $SrCuO_{2.5}$, CuO, SrO_2, KCl, and a very small amount of an unidentified phase, presumably corresponding to the stoichiometry $Sr_{3\pm0.03}Cu_{4\pm0.04}O_x$ based upon electron microprobe analysis. The composition of the title compound was determined by electron microprobe to be $Sr_{1\pm0.01}Cu_{1\pm0.01}O_{2.5\pm0.05}$, and the Rietveld refinement is consistent with this stoichiometry. A summary of the refined crystallographic data for $SrCuO_{2.5}$ is given in Table 1, and its structure is presented in Fig. 2.

$SrCuO_{2.5}$ crystallizes in an orthorhombic symmetry with the $CaMnO_{2.5}$ structural type (13), having a perovskite subcell $a_p = a/\sqrt{2} = 3.835$ Å, $b_p = b/2\sqrt{2} = 3.831$ Å, and $c_p = c = 3.731$ Å. It consists entirely of corner-sharing CuO_5 square pyramids. The ordered oxygen vacancies create parallel pseudo-hexagonal tunnels where the Sr atoms reside, forming SrO_{10} polyhedra. In contrast, the low pressure form of $SrCuO_2$ (8) consists of edge-shared CuO_4 square planes and SrO_7 polyhedra, while the high pressure infinite layer form (9) consists of corner-shared CuO_4 square planes and SrO_8 polyhedra. The shorter a_p and b_p and longer c_p compared with those in the high pressure form of $SrCuO_2$ ($a = 3.926$ Å and $c = 3.432$ Å) result from oxygen vacancies in the (001) CuO_2 planes and the presence of the apical oxygens. The average Sr–O and Cu–O distances are 2.67 and 1.92 Å, respectively. These bond distances are similar to those observed in the other Sr–Cu–O compounds (5, 6, 8, 9). The O–Cu–O angle, which is 90° for the ideal cubic perovskite, varies from 87.30 to 96.9°.

The $CaMnO_{2.5}$-type structure was also found in La $CuO_{2.5}$ (14) and $NdCuO_{2.5}$ (11). Surprisingly, the unit cell volume of $SrCuO_{2.5}$ (219.3 Å^3) is almost the same as that of $NdCuO_{2.5}$ (219.1 Å^3), although the ionic radius of Sr (1.58 Å) is larger than that of Nd (1.41 Å) (15). This fact could be attributed to the presence of the smaller B-site cation Cu^{3+} in the former and to the smaller A-site atom in the latter, leading to the misfit between the NdO and CuO_2 layers.

The structural features of the title compound are analogous to those of $Sr_2CuO_{3+\partial}$ in that the oxygen vacancies in both are located in the CuO_2 layers (4, 6, 16). Both phases exhibit superstructures (1, 4, 7) related to those of the Ruddlesden–Popper (R–P) type (17). The supercells observed in $Sr_2CuO_{3+\partial}$ could be related to oxygen vacancy ordering, while $Sr_2CuO_{3.5}$ ($\partial = 0.5$) might be isostructural to $Ca_2MnO_{3.5}$ (18), with oxygen ordering in (001), as found in the title compound. In addition, an orthorhombic distortion in $Sr_2CuO_{3+\partial}$ was also observed by high-resolution synchrotron X-ray diffraction (4). The orthorhombicity, $(b - a)/a = 2.612 \times 10^{-3}$, where a and b are the subcell lattice parameters of the R–P phases, is greater than that of $SrCuO_{2.5}$ (9.128×10^{-4}). It is very difficult to observe such slight distortions and the determination of the symmetry requires the consideration of reflection conditions including those of the supercell.

CONCLUSIONS

A new perovskite $SrCuO_{2.5}$ was prepared from $SrCuO_2$ and $KClO_3$ at 950°C and 100 kbar. Superconductivity was not observed down to 5 K presumably due to the absence of both two-dimensional CuO_2 layers and mixed valance Cu^{+2}/Cu^{3+}. However, the manner in which oxygen vacancies order in $SrCuO_{2.5}$ may provide insight into an important stabilizing mechanism in the plethora of phases observed in the Sr–Cu–O system at high pressure. Whether CuO_2 layers with ordered oxygen vacancies, or some other unusual arrangements, leads to superconductivity in these systems is an important question to resolve.

ACKNOWLEDGMENT

The authors thank Mr. Y. Wang for technical assistance. This work is contribution number 5440 from the Lamont–Doherty Earth Observatory of Columbia University and was supported by the National Science Foundation and the Department of Energy. Work at the IBM Watson Research Center was supported by the Electric Power Research Institute.

REFERENCES

1. Z. Hiroi, M. Takano, M. Azuma, and Y. Takeda, *Nature* **364,** 315 (1993).
2. H. Shaked, Y. Shimakawa, B. A. Hunter, R. L. Hitterman, J. D. Jorgensen, P. D. Han, and D. A. Payne, *Phys. Rev. B* **51,** 11784 (1995).
3. R. Feenstra, J. D. Budai, D. K. Christen, and T. Kawai, *Appl. Phys. Lett.* **66,** 2283 (1995).
4. T. Ami, M. K. Crawford, R. L. Harlow, Z. G. Li, T. Vogt, Q. Zhu, and D. E. Cox, *Physica C* **235,** 1003 (1994).
5. C. L. Teske and H. Muller-Buschbaum, *Z. Anorg. Allg. Chem.* **371,** 325 (1969).
6. R. C. Lobo, F. J. Berry, and Greaves, *J. Solid State Chem.* **88,** 513 (1990).
7. P. Laffez, X. J. Wu, S. Adachi, H. Yamauchi, and N. Mori, *Physica C* **222,** 303 (1994).
8. C. L. Teske and H. Muller-Buschbaum, *Z. Anorg. Allg. Chem.* **379,** 234 (1970).
9. M. Takano, Y. Takeda, H. Okada, M. Miyamoto, and T. Kusaka, *Physica C* **159,** 375 (1989).
10. D. Walker, *Am. Mineral.* **76,** 1092 (1991).
11. B.-H. Chen, D. Walker, E. Suard, B. Scott, B. Mercey, M. Hervieu, and B. Raveau, *Inorg. Chem.* **34,** 2077 (1995).
12. J. Rodriguez-Carvajal, "FULLPROF: A Program for Rietveld Refinement and Profile Matching Analysis of Complex Powder Diffraction Patterns." ILL, unpublished.
13. K. R. Poeppelmeier, M. E. Lenowicz, and J. M. Longo, *J. Solid State Chem.* **44,** 89 (1982).
14. J. F. Bringley, B. A. Scott, S. J. La Placa, R. F. Boehme, T. M. Shaw, M. W. McElfresh, S. S. Tail, and D. E. Cox, *Nature* **347,** 263 (1990).
15. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
16. Y. Shimakawa, J. D. Jorgensen, J. F. Mitchell, B. A. Hunter, H. Shaked, D. G. Hinks, R. L. Hitterman, Z. Hiroi, and M. Takano, *Physica C* **228,** 73 (1994).
17. S. N. Ruddlesden and P. Popper, *Acta Crystallogr.* **11,** 54 (1958).
18. M. E. Leonowicz, K. R. Poeppelmeier, and J. M. Longo, *J. Solid State Chem.* **59,** 71 (1985).