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X-ray Investigation of $Ba_2YCu_3O_6$

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Single-crystal X-ray diffraction and high-temperature X-ray powder diffraction have been used to characterize $Ba_2YCu_3O_6$. This compound, which is not a superconductor down to 4.2 K, is an oxygen-deficient form of the high-temperature superconductor $Ba_2YCu_3O_{7-x}$. The material is tetragonal and crystallizes in space group *P4/mmm*, $Z = 1$, with lattice constants $a = 3.8594$ (5) Å and $c = 11.814$ (4) Å. The structure is related to that of the orthorhombic superconductor, but the Cu layer, which contains partially occupied oxygen sites in the superconductor, contains no oxygen in this material.

Introduction

The structure of $Ba_2YCu_3O_{7-x}$ has been a matter of great interest and considerable discussion, since it was found that this material exhibited superconductivity at approximately 90 K. The general picture of a layered variant of perovskite has been established[1,2] with both X-ray and neutron diffraction techniques. It has been reported that this material undergoes a transition from the superconducting orthorhombic form to a tetragonal form at high temperatures, accompanied by a loss of oxygen. In an effort to understand how the oxygen loss is accommodated by the structure, an X-ray study of this transformation and the structure of the resulting material was undertaken.

Experimental Section

Reagent grade $BaCO_3$ (J. T. Baker), Y_2O_3 (Research Chemicals, 99.9% pure), and CuO, GR grade (EM Science, analyzed by H_2 reduction as 99.9% CuO), were weighed out in the 2:1:3 cation ratio. The mixture was wet-milled for 3 h in a polyethylene jar with dense ($^3/_8$ in. diameter) zirconia media in water containing a small amount of Triton X-100 wetting agent. The milled mixture was oven-dried at 120 °C overnight. The dried material was reacted by heating at 100 °C/h to 950 °C and holding for 24 h, followed by furnace cooling at <150 °C/h to room temperature. The reaction was carried out in an ambient air atmosphere with the powder bed less than a centimeter in depth. The black product was gently crushed in a porcelain mortar and pestle and was shown to be the orthorhombic perovskite $Ba_2YCu_3O_{7-x}$ by X-ray powder diffraction.

In order to examine the effects of treatment parameters, a tetragonal crystal suitable for structure determination was obtained from each of five different thermal/atmospheric treatments, starting with the same preparation of orthorhombic material. Three samples of the tetragonal phase were prepared by heating the orthorhombic material in flowing nitrogen to 500, 700, and 800 °C and then furnace cooling under flowing nitrogen to room temperature. In addition, a sample was prepared by heating and cooling the orthorhombic material under vacuum. A further sample was prepared by heating the material to 700 °C in air and then quenching to room temperature. Confirmation of the tetragonal phase in each of the samples was made by using X-ray powder diffraction. They were single phase, except for the quenched material, which was a mixture of the orthorhombic and tetragonal forms.

X-ray powder diffraction patterns were collected as a function of temperature by using a automated Rigaku horizontal goniometer equipped with a high-temperature accessory and filtered Cu Kα radiation ($\lambda = 1.541780$ Å). Specimens were packed into a platinum sample holder for the analysis. Atmospheres of flowing air or dry nitrogen could be introduced.

Single-crystal data were collected on a Nicolet P3F automated single crystal diffratometer using monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å) at room temperature. Small platelike single crystals (approx. 0.1 × 0.1 × 0.05 mm) were isolated from each of the five samples of the tetragonal material. An empirical absorption correction was applied to the data by using the fact that the laminar face of the crystals was the (001) face. The materials were assumed to be modified perovskites; therefore, atomic positions were assigned on the basis of this structure and refined by using the SHELXTL program package.[3] The function minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$. Additional experimental and crystallographic details are outlined in Table I.

Table I. Experimental and Crystallographic Details

formula	$Ba_2YCu_3O_6$
mol wt	650.2
space group	*P4/mmm*
cryst syst	tetragonal: $a = 3.8594$ (5), $c = 11.814$ (4) Å
vol, Å^3	176.0
Z	1
D_{exptl}, g/cm^3	6.14
μ, cm^{-1}	289.4
cryst dimens, mm	0.1 × 0.1 × 0.05
data collcd	$\pm h, \pm k, \pm l$
collcn technique	$\theta/2\theta$
scan range (2θ), deg	4–60
no.of reflcns collcd	1987
no. of unique reflcns	204
no. of unique obsd reflcns	204
criterion for observn	$F > 3\sigma(F)$
R_{merge}	0.0560
weighting scheme	unit weights
abs cor	empirical/laminar
laminar face	(001)
$R = \sum \|\|F_o\| - \|F_c\|\| / \sum \|F_o\|$	0.0382
no. of params, refined	18

High-Temperature Powder Diffraction Results

Starting with the orthorhombic material, the X-ray powder diffraction pattern was collected from room temperature to 800 °C in air. No attempt to go higher in temperature was made, since the transformation appeared complete and it was feared that higher temperatures could cause reaction with the platinum sample holder. The transformation to the tetragonal form is evidenced by dramatic changes in intensity of the major lines of the pattern. (See Figure 1.) This transformation under these conditions is totally reversible, with the orthorhombic form returning as the temperature is lowered to 500 °C. If the orthorhombic material is heated in nitrogen, the transformation to the tetragonal form takes place and, as long as the material is cooled under nitrogen, is irreversible. (See Figure 2.) If the tetragonal material is heated in air, the orthorhombic phase returns at 500 °C, before converting again to the tetragonal form at 700 °C. (See Figure 3.)

The transformations occurs rapidly, and diffraction scans taken as soon as the temperature stabilized (less than 5 min), were identical with those obtained 2 h later. The tetragonal perovskite structure also appears to be relatively stable. Only small amounts of Cu_2O could be identified in material that had been heated to 800 °C for 24 h in flowing nitrogen, while no decomposition could be observed in material that had been heated to 700 °C for 10 days.

Single-Crystal Structure Determination

The structures determined for the tetragonal crystals obtained from each of the samples are similar; thus, details are given in

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(1) Beno, M. A.; Soderholm, L.; Capone, D. W.; Hinks, D. G.; Jorgensen, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K.; Grace, J. D. *Appl. Phys. Lett.* **1987**, *51*, 57.

(2) Garbauskas, M. F.; Arendt, R. H.; Kasper, J. S. *Inorg. Chem.* **1987**, *26*, 3191.

(3) Sheldrick, G. M. "SHELXTL"; Nicolet Instrument Corp.: Madison, WI, 1983. Scattering factors from: *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. 4, pp 55–60, 99–101, 149–150.

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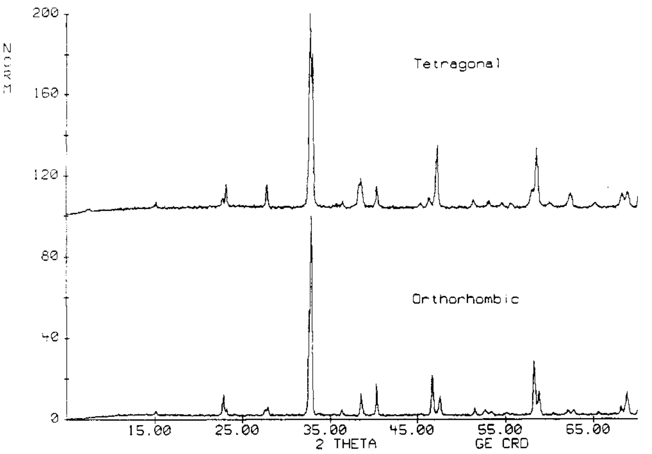

Figure 1. X-ray powder diffraction patterns of tetragonal and orthorhombic material.

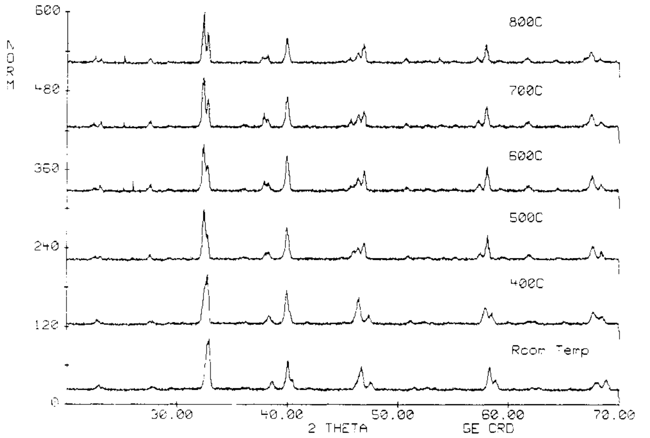

Figure 2. High-temperature X-ray powder diffraction patterns in dry nitrogen, starting with orthorhombic material.

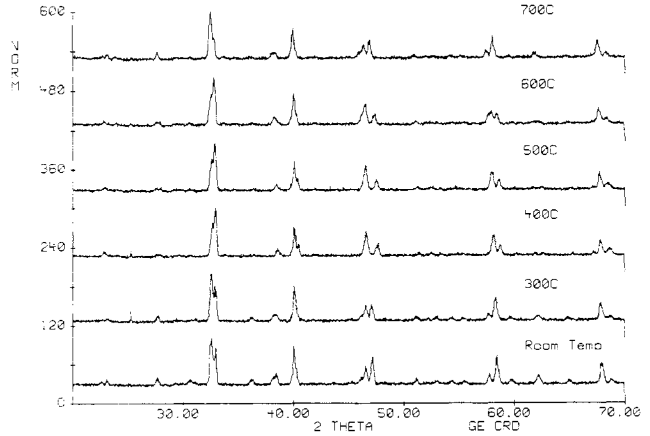

Figure 3. High-temperature X-ray powder diffraction patterns in air, starting with tetragonal material.

Table II. Atom Coordinates ($\times 10^4$) and Temperature Factors ($Å^2 \times 10^3$)

atom	x	y	z	$U_{\text{equiv}}{}^a$
Cu(1)	0	0	0	12 (1)
Cu(2)	0	0	3611 (2)	6 (1)
Y	5000	5000	5000	6 (1)
Ba	5000	5000	1946 (1)	8 (1)
O(2)	0	0	1524 (13)	16 (3)
O(3)	0	5000	3798 (8)	8 (3)

[a] Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

Table III. Bond Lengths (Å)

Cu(1)-Ba	3.568 (4)	Cu(1)-O(2)	1.801 (15)
Cu(2)-Y	3.184 (3)	Cu(2)-Ba	3.364 (4)
Cu(2)-O(3)	1.942 (2)	Cu(2)-O(2)	2.466 (13)
Y-Ba	3.608 (4e	Y-O(3)	2.396 (6)
Ba-O(2)	2.774 (4)	Ba-O(3)	2.918 (8)

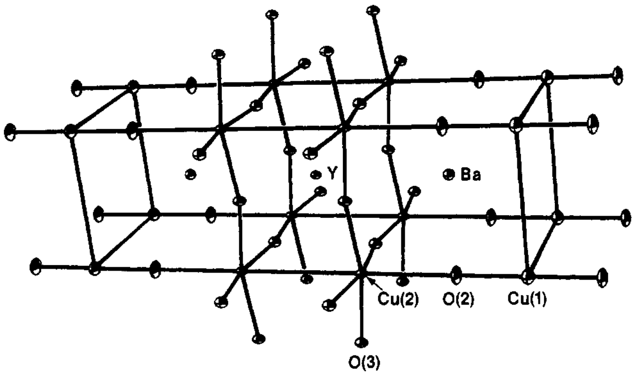

Figure 4. Thermal ellipsoid (50% probability) plot of $Ba_2YCu_3O_6$.

Table I for only the 700 °C, nitrogen preparation. There are no systematic absences in the data; therefore, the space group is not uniquely determined. *P*4/*mmm* was chosen because it had the highest symmetry of the possible space groups. The overall features are consistent with neutron diffraction results obtained for this phase prepared by heating in argon[4] and with X-ray results obtained for tetragonal phases close to this composition.[5,6] The positions of the heavy atoms as well as the positions of the fully occupied oxygen positions are similar to those found in the orthorhombic structure. The difference is in the Cu layers between the Ba layers. In the orthorhombic structure, these Cu layers contain partially occupied oxygen sites as well as unoccupied sites. In the tetragonal material, there is no oxygen at all in this layer. This reduces the coordination of Cu(1) from 4-coordinate square-planer in the orthorhombic crystal structure to a linear 2-coordinate arrangement in the tetragonal material, and destroys the Cu–O chains that are commonly accepted as responsible for the superconductivity of the material. A consideration of charge balance in the material suggests that while the orthorhombic material Cu exists in both the Cu^{2+} and Cu^{3+} oxidation states, in the tetragonal material it must exist as Cu^{2+} and Cu^{+}. A consideration of coordination and bond distances leads to the conclusion that the Cu(1) site contains a large amount, if not all, Cu^{+}. The Cu(1)–O(2) bond lengths of 1.801 (15) Å is similar to that found in Cu_2O[7] where the Cu–O distance is 1.85 Å. The Cu(1)–Cu(1) distance, which is the cell edge of 3.8594 (5) Å, is much longer than the Cu–Cu distance of 3.01 Å in Cu_2O. This may explain the readiness with which this structure assimilates oxygen in this layer.

Crystallographic coordinates for the 700 °C, nitrogen sample are provided in Table II while bond lengths are contained in Table III. The atom labelling used for the orthorhombic structure[2] has been preserved in these tables for consistency. There is, therefore, no O(1), the oxygen site that is partially occupied in the orthorhombic structure but totally vacant in the tetragonal material. The O(4) position in the orthorhombic material is now symmetry related to O(3) in the tetragonal structure. A plot of the structure can be found in Figure 4.

Discussion

These results illustrate the ease with which oxygen may be both extracted and then reintroduced in this material. The commonality

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(4) Santoro, A.; Miraglia, S.; Beech, F. *Mater. Res. Bull.* **1987**, *22*, 1007.

(5) Bordet, P.; Chaillout, C.; Capponi, J. J.; Chenavas, J.; Marezio, M. *Nature (London)* **1987**, *327*, 687.

(6) Nakai, I.; Sueno, S.; Okamura, F. P.; Ono, A. *Jpn. J. Appl. Phys.* **1987**, *26*, L788.

(7) Wyckoff, R. W. G. *Crystal Structures*; Wiley: New York, 1963; Vol. 1, p 331.

of the observed structure prepared under a number of conditions illustrates that the Cu layers between the Ba layers are those most easily affected. There has been a report, based upon the surface-sensitive technique of X-ray photoelectron spectroscopy (XPS),[8] that oxygen could be extracted from the Ba layers by preparing the material under vacuum, rather than under a reducing atmosphere, such as nitrogen or argon. We found no evidence for this in the material we prepared under vacuum. The crystal structure of this material contained oxygen vacancies only in the Cu layers between the Ba layers. Any Ba layer vacancy observed by XPS, is, therefore, a surface rather than a bulk phenomenon.

High-temperature neutron diffraction,[9] which is much more sensitive to oxygen than is X-ray diffraction, suggests that the high-temperature tetragonal form actually has oxygen in these Cu layers, but since the positions are now symmetry related, the population is uniformly distributed among the four positions. Our attempts at trying to prepare a quenched sample where the oxygen might be trapped in this layer were not successful. The powder pattern of this sample showed it to be a mixture of the tetragonal and orthorhombic forms. A tetragonal crystal was found (although the quality was not as good as the other preparations), and the structure was determined. Although there appeared to be some electron density in the oxygen positions of the Cu layers, the refinement of the occupancy of the site yielded standard deviations as large as the occupancy and large thermal parameters. We, thus, cannot conclusively identify any occupancy by oxygen in the tetragonal material we have examined. The existence of additional oxygen in the tetragonal material that first forms a high-temperature in air or oxygen, however, is supported by TGA analysis.[10] There is less weight loss at 700 °C in air or oxygen than there is in nitrogen, presumably due to more oxygen in the structure.

This exercise does illustrate, however, that it is very easy to obtain the orthorhombic material in a quenching experiment. Presumably, since the oxygen uptake is diffusion controlled, a thin layer of the oxygen-rich orthorhombic material may form in any sample that is quenched in air or oxygen. Reports of some superconductivity in tetragonal material[11] may be related to a small amount of the orthorhombic material on the surface of the tetragonal particles.

The facile transformation between the orthorhombic and tetragonal forms of this material illustrates both the rigidity of the perovskite framework and the mobility of oxygen in this system. Atmosphere and temperature are, therefore, important parameters to control in the fabrication of any devices containing this material. The oxygen-starved structure of the tegragonal form of the material could provide an interesting starting point for the introduction of other elements (e.g. F) into this framework.

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Supplementary Material Available: Table SI of anisotropic thermal parameters for the 700 °C nitrogen preparation structure (1 page); tables of observed and calculated structure factors for each of the five structures (3 pages). Ordering information is given on any current masthead page.

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(8) Schrott, A. G.; Park, S. I.; Tsuei, C. C., to be submitted for publication.

(9) Jorgensen, J. D.; Beno, M. A.; Hinks, D. G.; Soderholm, K. J.; Volin, K. J.; Hitterman, R. L.; Grace, J. D.; Schuller, I. K.; Segre, C. U.; Zhang, K.; Kleefisch, M. S., submitted for publication in *Phys. Rev.*

(10) Gallagher, P. K.; O'Bryan, H. M.; Sunshine, S. A.; Murphy, D. W. *Mater. Res. Bull.* **1987**, *22*, 995.

(11) Kini, A. M.; Geiser, U.; Kao, H.-C. I.; Carlson, K. D.; Wang, H. H.; Monaghan, M. R.; Williams, J. M. *Inorg. Chem.* **1987**, *26*, 1834.

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Variable-Temperature and Variable-Pressure NMR Kinetic Study of Solvent Exchange on $Ru(H_2O)_6^{3+}$, $Ru(H_2O)_6^{2+}$, and $Ru(CH_3CN)_6^{2+}$[1,2]

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Water exchange on ruthenium(II) and ruthenium(III) was studied by ^{17}O NMR and acetonitrile exchange on ruthenium(II) was studied by ^1H NMR spectroscopy as a function of temperature and pressure. For ruthenium(II), the kinetic parameters are as follows: (a) $Ru(H_2O)_6^{2+}$, $k^{298} = (1.8 \pm 0.2) \times 10^{-2}\ s^{-1}$, $\Delta H^* = 87.8 \pm 4$ kJ mol^{-1}, $\Delta S^* = +16.1 \pm 15$ J K^{-1} mol^{-1}, $\Delta V^* = -0.4 \pm 0.7$ cm^3 mol^{-1}; (b) $Ru(CH_3CN)_6^{2+}$, $k^{298} = (8.9 \pm 2) \times 10^{-11}\ s^{-1}$, $\Delta H^* = 140.3 \pm 2$ kJ mol^{-1}, $\Delta S^* = +33.3 \pm 6$ J K^{-1} mol^{-1}, $\Delta V^* = +0.4 \pm 0.6$ cm^3 mol^{-1}. This implies that the solvent exchange on Ru^{2+} occurs via an interchange I mechanism for both H_2O and CH_3CN. For ruthenium(III) in water the observed rate constant was of the form $k = k_1 + k_2/[H^+]$ where subscripts 1 and 2 refer to the exchange pathways on $Ru(H_2O)_6^{3+}$ and $Ru(H_2O)_5OH^{2+}$, respectively; the kinetic parameters are as follows: $k_1^{298} = (3.5 \pm 0.3) \times 10^{-6}\ s^{-1}$, $\Delta H_1^* = 89.8 \pm 4$ kJ mol^{-1}, $\Delta S_1^* = -48.3 \pm 14$ J K^{-1} mol^{-1}, $\Delta V_1^* = -8.3 \pm 2.1$ cm^3 mol^{-1}; $k_2^{298} = (1.1 \pm 0.2) \times 10^{-6}\ m\ s^{-1}$, $\Delta H_2^* = 136.9 \pm 6$ kJ mol^{-1}, $\Delta S_2^* = +100.5 \pm 18$ J K^{-1} mol^{-1}, $\Delta V_2^* = -2.1 \pm 1.4$ cm^3 mol^{-1}. Estimations of the first-order rate constant (using the relation $k_2 = k_{OH}K_{a1}$) and the corresponding activation volume for $Ru(H_2O)_5OH^{2+}$ are $k_{OH}^{298} = 5.9 \times 10^{-4}\ s^{-1}$ and $\Delta V_{OH}^* = +0.9$ cm^3 mol^{-1}. These data are conclusive for an associative interchange I_a mechanism for water exchange on $Ru(H_2O)_6^{3+}$ but for an I mechanism on the deprotonated species $Ru(H_2O)_5(OH)^{2+}$. These mechanistic results for low-spin ruthenium solvates are compared to those of other di- and trivalent transition-metal ions.

Introduction

A large number of substitution reactions on Ru(II) and Ru(III) have been investigated over the last 25 years. Most studies dealt with complexes in which only one ligand was replaced, the $(NH_3)_5RuX^{2+}$ ions playing a dominant role.[4] Information about the rates of such processes was often obtained from combined electron-transfer and substitution studies, and it was soon realized that substitution on Ru(III) could often be catalyzed by the

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(1) High Pressure NMR Kinetics. 34. Part 33: See ref 2.

(2) Cossy, C.; Helm, L.; Merbach, A. E. *Helv. Chim. Acta* **1987**, *70*, 1516.

(3) (a) University of Lausanne. (b) University of Bern.

(4) Endicott, J. F.; Taube, H. *J. Am. Chem. Soc.* **1962**, *84*, 4984. Stritar, J. A.; Taube, H. *Inorg. Chem.* **1969**, *8*, 2281. Taube, H. *Comments Inorg. Chem.* **1981**, *1*, 17 and references therein.

0020-1669/88/1327-0873$01.50/0