JOURNAL OF SOLID STATE CHEMISTRY 88, 368–383 (1990)

Oxidation and Reduction of $BaLa_4Cu_5O_{13+\delta}$

PETER K. DAVIES AND CYNTHIA M. KATZAN

Department of Materials Science and Engineering, University of Pennsylvania, Philadelphia, Pennsylvania 19104

Received March 5, 1990

The stability of the metallic, nonsuperconducting cuprate, $BaLa_4Cu_5O_{13+\delta}$, was investigated using thermogravimetric analysis and X-ray and electron diffraction. In air or oxygen this highly oxidized compound only loses small amounts of oxygen; and at 1000°C the formal copper valence is close to 2.3^+. To probe the chemical and structural factors that stabilize this high valence state, methods were developed to reduce the 145 structure. Under helium gas a new structure with $\delta \approx -0.5$ was obtained; however, the removal of additional oxygen could only be accomplished by reducing the samples at low temperatures under 15% H_2/85% Ar gases. Under these conditions two additional structures were isolated for phases with $\delta \approx -1.0$ and -2.0. The differences in the X-ray patterns of these new phases result from a change in the symmetry of the perovskite subcell from cubic to orthorhombic to tetragonal. Models for the reaction sequence involved a systematic reduction in the coordination of the octahedral Cu groups in the oxidized structure to square pyramidal, square planar, and finally linear coordination in the fully reduced samples. We propose that the stability of the fully oxidized structure is primarily a result of unfavorable Cu coordinations in the partially reduced samples.

1. Introduction

The recent discoveries of high temperature superconductivity in several copper oxides have created tremendous interest in the chemistry and physics of cuprate systems. Until recently the key chemical requirements for superconductivity included the occurrence of copper ions in two-dimensional $[CuO_2]$ sheets with a formal valence greater than two. With the discovery of *n*-type superconductivity in Ce-doped Nd_2CuO_4 (*1*), clearly these guidelines must be relaxed to include certain systems with a formal copper valence less than two. Prior to the recent intensive studies of copper oxide systems, relatively few compounds were known in which copper was stable in the 3^+ valence state. Among the examples were $NaCuO_2$, $KCuO_2$, $LaCuO_3$, $LaSrCuO_4$, and the compounds originally developed by Raveau *et al.*, including Sr-substituted La_2CuO_4 (*2*), and phases in the Ba–La–Cu–O system (*3, 4*), e.g., $BaLa_4Cu_5O_{13+x}$, $Ba_3La_3Cu_6O_{14+x}$. As a result of the recent superconductivity work, many new compounds can be added to this list.

In most of the highly oxidized perovskite-related cuprates, under ambient atmospheres the stable phase at high temperature contains oxygen vacancies and copper adopts a valence state less than or equal to 2. Subsequent oxidation of Cu to a higher valence is dependent upon the ability of the structure to intercalate oxygen and at least partially fill the oxygen vacancies. In some cases the oxidation of copper can also be achieved by "internal oxidation–reduction mechanisms," as perhaps demonstrated by the Tl compounds in which the mixing of

0022-4596/90 $3.00

the Tl $6s^2$ states at the Fermi level may facilitate an internal mechanism for oxidation of Cu without requiring large changes in the oxygen stoichiometry.

The design of new p-type and n-type cuprate superconductors will rely in part upon developing a fundamental understanding of the oxidation/reduction behavior of the copper oxides, and an evaluation of the stabilities of the perovskite-related structures with respect to the intercalation and deintercalation of oxygen. In an attempt to investigate some of the chemical factors that affect the structural stability of the cuprates, in this paper we report the results of a study of the structural stability of the metallic defect perovskite, $BaLa_4Cu_5O_{13+\delta}$. This compound is nonsuperconducting, presumably due to the lack of well-defined two-dimensional sheets, but is unusual in that the copper ions can exhibit an apparently stable formal valence in excess of 2.4^+ in the fully oxidized form (*5*).

Three ternary phases have been reported in the BaO–La_2O_3–CuO system at 950°C: $Ba_xLa_{2-x}CuO_4$ (*6*), $BaLa_2Cu_2O_6$ (*7*), $Ba_3La_3Cu_6O_{14}$ (*3*), and $BaLa_4Cu_5O_{13}$ (*4*). In the original work of Bednorz and Muller, (*8*), Ba-doped La_2CuO_4 was the first system found to show a high T_c fluctuation, with a 40 K transition occurring for a barium concentration of 0.15. $Ba_3La_3Cu_6O_{14}$ (or $Ba_{1.5}La_{1.5}Cu_3O_7$) shows a range of solid–solution up to compositions with $Ba_4La_2Cu_6O_{14}$. These solid–solutions are isostructural with $Ba_2YCu_3O_{7-x}$, and the barium-rich materials have been shown to superconduct up to approximately 80 K (*9*). Of the other compounds in this system, all are insulators with the exception of $BaLa_4Cu_5O_{13+\delta}$ which is metallic but does not superconduct (*5*).

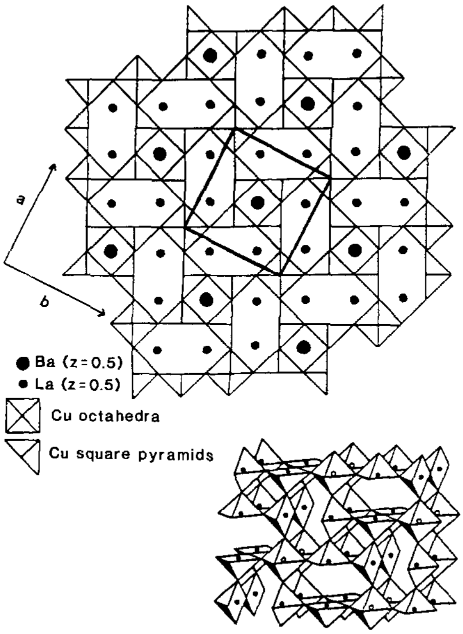

FIG. 1. Idealized structure of $BaLa_4Cu_5O_{13}$; projection along (001), and a perspective view of the Cu polyhedra. Ba and La omitted for clarity.

The structure of $BaLa_4Cu_5O_{13+x}$, first reported by Michel *et al* (*10*), is constructed from an oxygen-defficient perovskite framework, with barium and lanthanum adopting an ordered arrangement on the *A* sites in the lattice (see Fig. 1). The *A* site ordering occurs within the a–b planes of the host lattice leading to a tetragonal supercell, space group $P4/m$, which is related to the essentially cubic perovskite subcell by $a = a_p\sqrt{5} = 8.65$ Å, $c = a_p = 3.86$ Å. Neutron diffraction studies have established that the vacancies in the structure are ordered in tunnels along the c axis, and that the copper ions adopt octahedral and square pyramidal coordination (*10*). The copper polyhedra are corner-shared in a fashion that leads to 12-coordinate barium sites and distorted, 10-coordinate lanthanum sites.

Although $BaLa_4Cu_5O_{13+\delta}$ is not superconducting, this compound exhibits several unusual chemical and structural features. In contrast to many of the other highly oxidized cuprate perovskites, despite the high valence of copper, the oxygen stoichiometry in the 145 system has been reported to be quite inflexible (*4*). The structure resists further oxidation, which is not unexpected, but also reduction which is unusual. Most of the other cuprates can support a considerable degree of variation in the oxygen content, due to the capacity of the perovskite host to accomodate oxygen vacancies and the ability of copper to adopt multiple oxidation states. In the 145 material it is unlikely that the limited range of oxygen stoichiometry is due to kinetic limitations, such as a low mobility of the oxygen ions, as the structure contains well-defined pathways for oxygen diffusion. It seems more probable that this highly oxidized phase is inherently stable. It is intriguing that the apparently stable stoichiometry with $\delta \approx 0$ implies that in this structure copper maintains an oxidation state greater than two even at high temperature. For example, samples quenched in air from the synthesis temperature, ≈1000°C, show an effective copper valence of approximately 2.3^+, which is retained until bulk decomposition begins. From a thermodynamic viewpoint, a stable Cu valence $>2^+$ above 1000°C at $p(O_2) = 0.21$ atm is quite unusual.

In this work we investigate the stability of $BaLa_4Cu_5O_{13+\delta}$ with respect to oxidation and reduction. This involved treating samples under a variety of inert, reducing, and oxidizing gases. Previous studies have shown that it is possible to reduce the oxygen content to approximately 12.8 in air; transport measurements on that material indicated that, even though the copper valence was greater than two, the material becomes semiconducting when the oxygen content is less than 0 = 13 (*11*). The aim of this work was to examine the reasons behind the apparent stability of this highly oxidized compound, and to investigate if oxygen can be removed from the lattice without inducing bulk decomposition.

2. Experimental

Samples of $BaLa_4Cu_5O_{13+\delta}$ were synthesized following the guidelines of Michel *et al.* (*4, 10*). Appropriate amounts of dried La_2O_3, CuO, and $BaCO_3$ were ground together, prefired at 900°C for 16 hr, and refired in air at 1000°C for 48 hr with several intermediate grindings. Other batches were also synthesized using barium peroxide rather than barium carbonate and by performing all the firings under oxygen gas. In both cases the single-phase X-ray powder patterns agreed with those reported previously. The oxygen contents of the final products were determined by heating the samples in a DuPont 951 TGA under a flow of 15% H_2 in argon. By 900°C the samples were fully reduced to a mixture of barium and lanthanum oxides plus copper metal. Determination of the weight loss during the reduction allowed calculation of the initial oxygen contents.

Samples with oxygen stoichiometries ranging from $-2.6 \leq \delta < +0.2$ were prepared by heating the oxidized samples in the TGA under a variety of gases at temperatures ranging from ambient to 1050°C followed by a quench to room temperature. These samples were subsequently investigated by powder X-ray diffraction on a Rigaku DMAXB diffractometer using Cu$K\alpha$ radiation generated at 50 kV and 40 mA. The diffractometer was equipped with a curved graphite monochromator to reject fluorescence and to filter the lower energy wavelengths. Typical scans were continuous at 1°/min with sampling every 0.01° in the range 5–80° 2θ. The X-ray measurements were performed in air and no sample deterioration was observed during the scan period. All samples were carefully stored under appropriate dessicants throughout the duration of the work. Transmission electron microscopy was used as an aid to indexing the powder patterns of some of the reduced materials. These experiments were conducted using a Philips 400T microscope operated at 120 kV, and the samples were ground and dispersed on holey carbon grids in the usual manner.

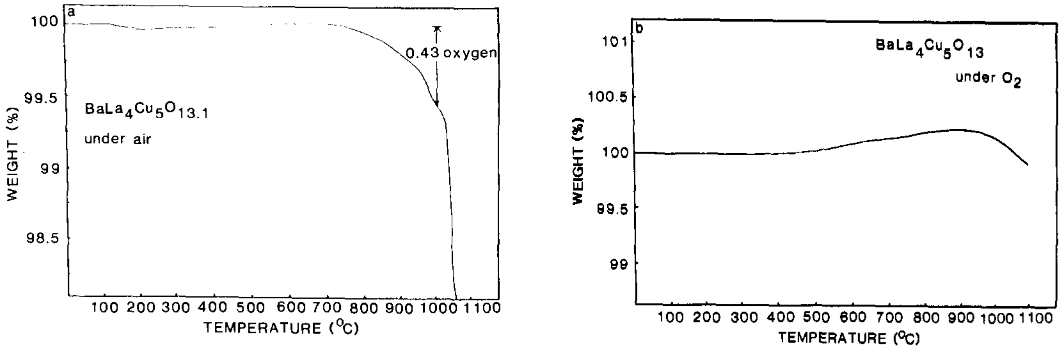

FIG. 2. Thermogravimetric curves for $BaLa_4Cu_5O_{13.1}$; (a) heated in air, (b) heated in pure oxygen.

3. Results

A preliminary series of experiments was designed to investigate the previous reports that the oxygen content of $BaLa_4Cu_5O_{13+\delta}$ is relatively inflexible in air and oxygen. The oxygen contents of samples slow-cooled and quenched from the final synthesis temperature of 1015°C were determined by thermogravimetry using forming gas (15% H_2/85% Ar). The oxygen stoichiometries of all the samples were quite insensitive to the cooling treatment and we found that δ was always ≈ 0. Because it is possible that a high ionic mobility of O^{2-} in the structure may permit partial intercalation of oxygen even during the short cooling times, the oxygen contents were monitored *in situ* in air in the TGA from 20 to 1100°C at scanning rates of 10°/min (see Fig. 2). Between 500 and 700°C a very small weight gain was observed; the maximum gain, 0.2 wt%, reflected the addition of approximately 0.15 oxide ions to the structure. At $\approx$750°C the samples began to lose weight and the loss at 1015°C corresponded to the deintercalation of $\approx$0.43 oxide ions. Above $\approx$1050°C a sharp loss in weight was due to the bulk decomposition of $BaLa_4Cu_5O_{13+\delta}$. Analyses of the evolved gases confirmed that none of the weight losses were due to the decomposition of any carbonate groups in the structure. To check that equilibrium was maintained at a scanning rate of 10°/min a sample was heated to 1000°C and held at this temperature for over 7 hr. No further weight changes were observed during the annealing, and other annealing experiments confirmed that this scan rate was appropriate to maintain constant equilibrium.

These experiments demonstrated that $BaLa_4Cu_5O_{13+\delta}$ is stable up to $\approx$1015°C in air with an oxygen content of $\approx O_{12.75}$, and that copper retains a formal average oxidation state in excess of two ($\approx 2.3^+$). Similar scans were also performed in pure flowing oxygen (see Fig. 2b). The small weight gain around 700°C was only slightly increased. The subsequent weight loss and decomposition were not affected to any significant degree by the higher pO_2, though may have shifted to higher temperatures by approximately 50°C compared to the scans in air. Annealing the original samples under pure oxygen at 500°C did not lead to any increase in the oxygen content beyond 13.15.

Because the "nonreactive" gases did not produce any substantial changes in the oxygen stoichiometry of the structure, more reducing gases were employed in an attempt to remove oxygen from the lattice without inducing bulk structural decomposition. Forming gas was initially used to analyze the total oxygen content of the starting ma-

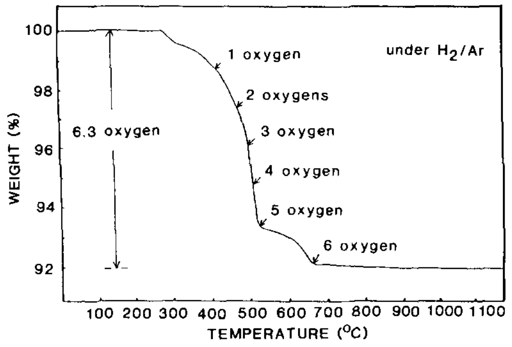

FIG. 3. Thermogravimetric analysis of $BaLa_4Cu_5O_{13.1}$ heated at 10°C/min under forming gas (15% H_2/85% Ar).

terials; during these experiments it was noted that the initial loss of oxygen occurred at relatively low temperatures (see Fig. 3). The first weight loss occurred at $\simeq$250°C, and by 650°C the material is completely reduced to copper metal, with no further weight change up to 1100°C. The first loss at 250°C corresponded to the removal of $\simeq$0.4 oxide ions from the structure and was identical to the high temperature, equilibrium losses observed under air and oxygen. The X-ray powder patterns of this partially reduced material were similar to those of the original "O_{13}" sample, and there was no evidence for bulk decomposition. These samples were dark brown and cell refinements indicated a small increase in the volume of the tetragonal supercell (see Table I).

To investigate materials with a broader range of stoichiometries, samples were heated at 10°/min to $\simeq$340°C and held isothermally for different times. After the desired weight loss was reached, the samples were quenched rapidly under forming gas and examined by X-ray diffraction. In this manner eight samples were prepared with oxygen contents between 12.7 and 10.6. When more than one oxide ion was removed, several new peaks appeared in the powder patterns (see Fig. 4). The most prominent of these were satellite peaks on either side of the four major reflections observed in the patterns of the fully oxidized samples, i.e., 210/001, 211/130, 420/002, and 341/501/132. These extra maxima increased in intensity as more oxygen was removed from the structure. An additional set of peaks appeared in samples with more than 1.2 oxide ions removed from the lattice (Fig. 4). Again several of these were satellites to the original reflections but at different d spacings to those noted above. The appearance of the second set of satellites was accompanied by a decrease, and eventual disappearance, of the first set as the compositions of the samples approached $BaLa_4Cu_5O_{11}$. When more than $\simeq$2.1 oxide ions were removed, the appearance of discrete reflections from copper metal and other diffuse peaks corresponding to unidentified Ba–La–Cu oxides indicated the onset of bulk decomposition.

For convenience, the phases giving rise to the two different sets of satellites are denoted phases II and III, and the original material phase I. Phase III was indexed using the powder pattern of a sample from which $\simeq$2.5 oxygens were removed. In this sample minor reflections from phase II and from Cu metal were also apparent. The peaks corresponding to phase III could be indexed using a tetragonal supercell based on a lattice in which the original cubic perovskite subcell was tetragonally distorted with $c_p < a_p = b_p$. The pair of satellite reflections observed about the 210/001 peak of phase I result from the removal of the degeneracy of the subcell parameters leading to two discrete reflections for 210/120 and 001 (see Fig. 5). Similarly this reduction in symmetry leads to the splitting of the major peak at $2\Theta \simeq 32°$ in phase I into the discrete 130/310 and 211 peaks. Using this distorted cell it was possible to index all the peaks in the

TABLE I

CELL PARAMETERS, COMPOSITIONS AND FORMAL COPPER VALENCES FOR PHASES IN THE $BaLa_4Cu_5O_{13+\delta}$ SYSTEM

Phase	δ	a(Å)	b(Å)	c(Å)	β(°)	Vol(Å^3)	Cu^{3+}	Cu^{2+}	Cu^{+}
I	+0.1	8.634	8.634	3.859	—	287.6	2.2	2.8	—
I	−0.2	8.645	8.645	3.862	—	288.6	1.6	3.4	—
I′	−0.5	8.756	3.839	8.676	90.62	291.6	1	4	—
II	−1.0	8.878	3.776	8.702	91.42	291.6	—	5	—
III	−2.0	8.884	8.884	3.714	—	293.2	—	3	2

phase III pattern, and least-squares refinement gave $a = b = 8.884 \pm 0.001$ Å, and $c = 3.714 \pm 0.001$ Å.

From the variation of the intensities of the phase III reflections with oxygen content, it appeared that the composition of this phase was close to O_{11} ($\delta = -2$). The removal of $\simeq 2$ oxygen ions from the original structure results in a decrease of 0.145 Å in the c axis and an expansion of 0.25 Å in the a and b axes. As compared to phase I with $\delta = +0.1$, i.e., $O_{13.1}$, the unit cell volume increases from 287.6 to 293.2 Å^3 (see Table I). The relative intensities and positions of lines calculated using the space group $P4/m$ gave a good agreement with the experimental pattern. The observed and calculated d spacings for the major reflections of $BaLa_4Cu_5O_{11}$ are given in Table II.

The indexing of phase II, with an oxygen concentration close to O_{12}, was more complicated. The splitting of several of the fun-

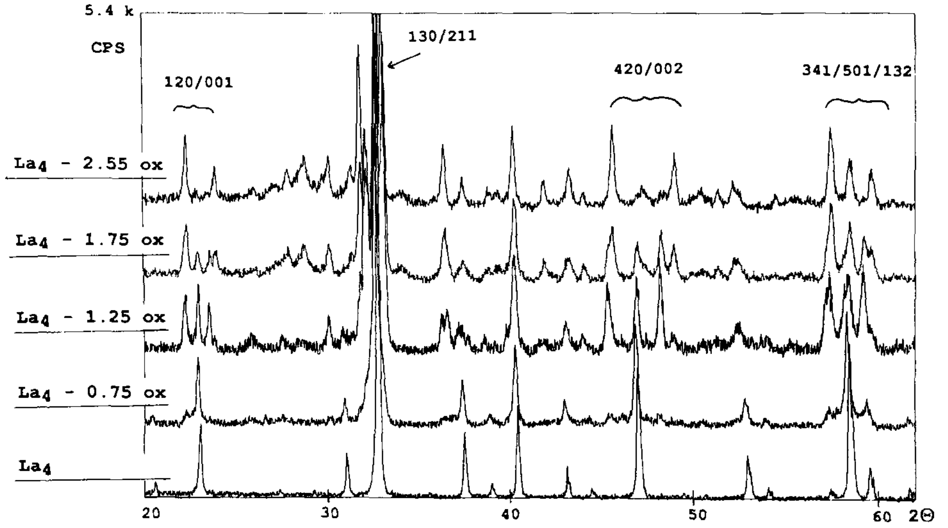

FIG. 4. Powder X-ray patterns from $BaLa_4Cu_5O_{13+\delta}$ for $\delta = +0.1$, $\delta = -0.75$, $\delta = -1.25$, $\delta = -1.75$, and $\delta = -2.55$.

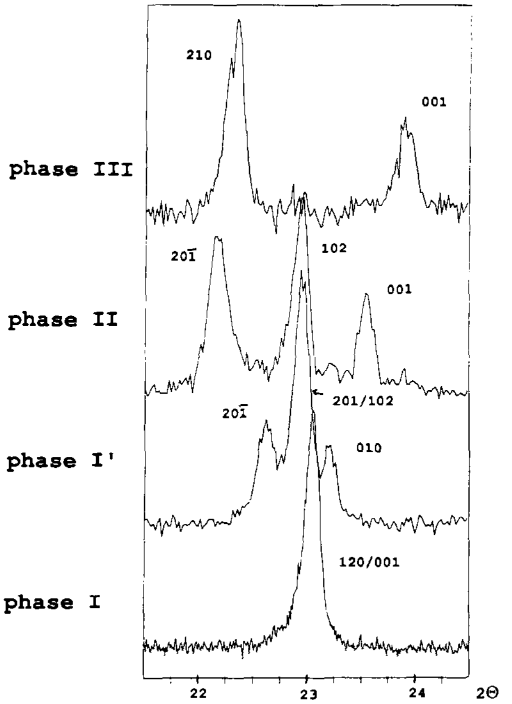

FIG. 5. Changes in the 210/001 powder X-ray peak of $BaLa_4Cu_5O_{13+\delta}$ during reduction; phase I, $\delta = 0.1$; phase I′, $\delta = -0.5$; phase II, $\delta = -1.0$; phase III, $\delta = -2.0$.

damental reflections of phase I into at least three satellites suggested that in this phase the perovskite subcell was orthorhombic. To fully index the X-ray patterns (see Fig. 6) it was necessary to obtain some information on the symmetry of the structure using electron diffraction. The TEM investigations were carried out on samples from which ≃1.25 oxygens had been removed from phase I. In the diffraction patterns along the [001] zone of the perovskite subcell, it was observed that the a^* and b^* vectors of the strong subcell reflections, and therefore a^* and b^* for the supercell ($100_p = 210_{supercell}$), were not equal and the fourfold symmetry had been removed. Because of the subcell distortion, the corresponding supercell was also distorted and the angle between the weaker ($h00$) and ($k00$) supercell reflections was greater than 90° (see Fig. 7). Figure 7 also shows that both the superlattice and sublattice spots are streaked or split, consistent with the formation of twins to relieve the strains caused by the distortion of the lattice. Using this information it was possible to completely index the powder patterns of phase II with a monoclinic supercell based on an orthorhombic subcell with $a_p \neq b_p \neq c_p$. The splitting of the originally degenerate 210/001 phase I reflections, {100} for the subcell, highlight these distortions (see Fig. 5). Least-squares refinement of the indexed pattern for phase II gave a cell with $a = 8.878 \pm 0.002$, $b = 3.776 \pm 0.002$, $c = 8.702 \pm 0.002$ Å, and $\beta = 91.41 \pm 0.03°$. Note that the b and c axes have been interchanged for convention. These lattice parameters and the corresponding

TABLE II

MAJOR X-RAY PEAKS OBSERVED FOR PHASE III, $BaLa_4Cu_5O_{11}$

h	k	l	d_{obsd} (Å)	d_{calcd} (Å)	I_{rel}
2	1	0	3.976	3.973	24
0	0	1	3.717	3.714	16
1	1	1	3.197	3.197	15
3	0	0	2.965	2.962	19
2	0	1	2.854	2.849	16
1	3	0	2.812	2.809	46
2	1	1	2.714	2.713	100
3	2	0	2.465	2.464	22
2	2	1	2.399	2.398	14
3	0	1	2.317	2.316	11
1	3	1	2.240	2.240	26
2	3	1	2.052	2.053	10
2	4	0	1.987	1.986	26
0	0	2	1.857	1.857	19
3	4	0	1.778	1.777	10
5	0	0	1.778	1.777	10
2	4	1	1.752	1.752	13
5	1	0	1.743	1.743	11
5	0	1	1.602	1.603	26
3	4	1	1.602	1.603	26
1	5	1	1.577	1.577	18
3	0	2	1.574	1.574	18
1	3	2	1.549	1.549	16

Note. $a = b = 8.884$ Å, $c = 3.714$ Å.

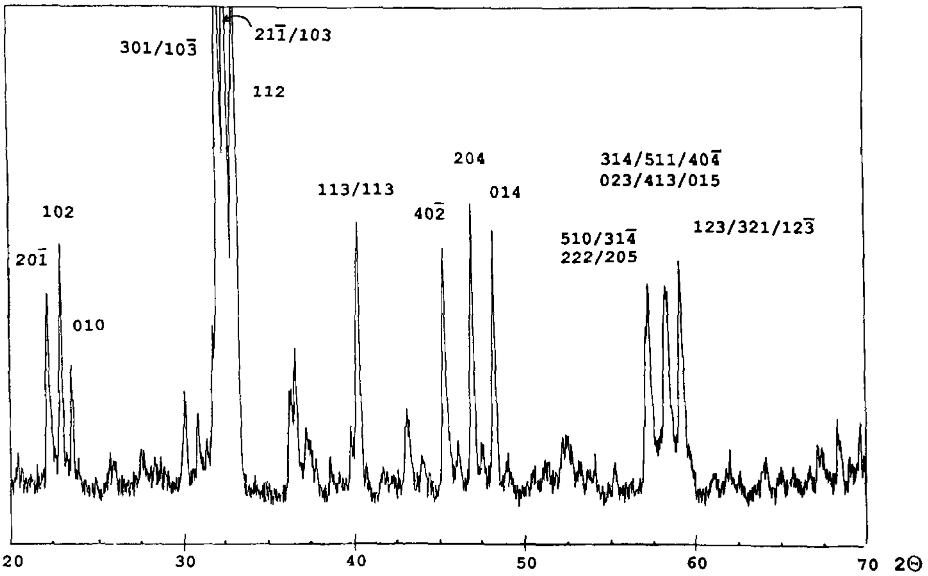

FIG. 6. Powder X-ray pattern for the monoclinically distorted phase II structure.

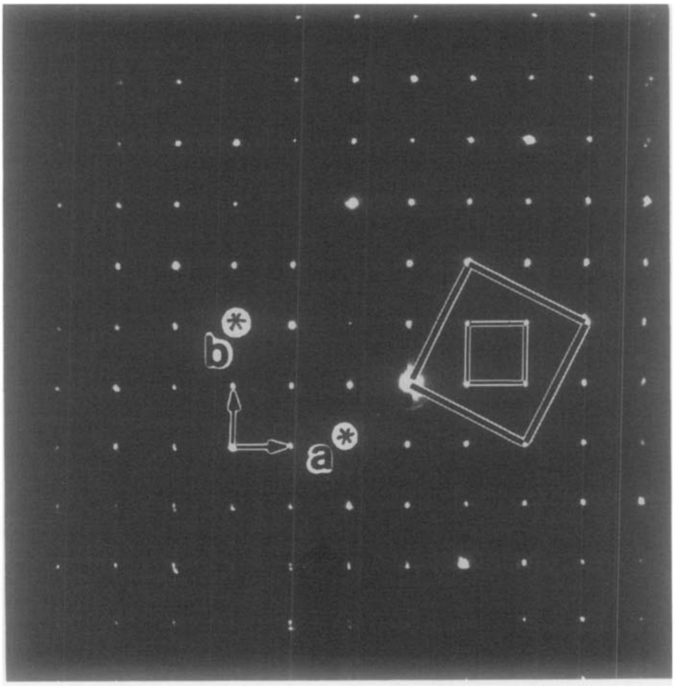

FIG. 7. Electron diffraction pattern of the *a–b* plane of phase II, the subcell (bold outline) and supercell are outlined.

TABLE III

MAJOR X-RAY PEAKS OBSERVED FOR PHASE II, $BaLa_4Cu_5O_{12}$

h	*k*	*l*	d_{obsd} (Å)	d_{calcd} (Å)	I_{rel}
2	0	−1	3.996	3.993	20
1	0	2	3.869	3.868	22
0	1	0	3.776	3.777	19
3	0	0	2.965	2.958	18
0	0	3	2.897	2.900	17
3	0	1	2.781	2.780	35
1	0	−3	2.778	2.776	35
2	1	−1	2.743	2.744	100
2	1	1	2.720	2.718	40
1	1	2	2.702	2.702	84
3	0	−2	2.474	2.475	11
2	0	−3	2.455	2.455	17
3	1	1	2.237	2.239	20
1	0	4	2.096	2.100	11
3	0	−3	2.096	2.097	11
4	0	−2	1.997	1.996	23
2	0	4	1.934	1.934	37
4	1	0	1.913	1.913	4
0	1	4	1.885	1.885	30
2	2	2	1.603	1.608	16
2	0	5	1.603	1.606	6
5	1	0	1.599	1.606	12
3	1	−4	1.599	1.605	12

Note. a = 8.878 Å, b = 3.776 Å, c = 8.702 Å, β = 91.41°

unit cell volume, 291.63 Å^3, fall between those of phases I and III. The powder pattern for phase II calculated using the space group *P*2/*m* (the highest monoclinic nonisomorphic subgroup of *P*4/*m*) gave an excellent fit to the observed profile. However, further studies will be necessary to confirm the exact symmetry of this phase. The observed and calculated *d* spacings and corresponding monoclinic indices of phase II are shown in Table III.

The reversibility of the reduction reactions was studied by thermogravimetry using flowing O_2 gas (see Fig. 8). All the samples containing the reduced phases II and III were reoxidized back to a single phase with $\delta \approx 0.1$ and the phase I structure. Because of the rapid mobility of oxygen in these structures, the reoxidation reactions occurred at temperatures as low as 240°C.

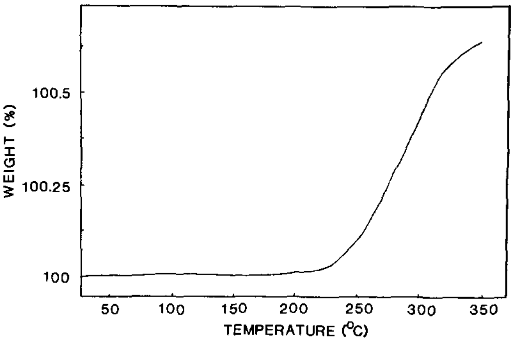

FIG. 8. Thermogravimetric curve for the reduced samples heated under pure oxygen gas.

As a final experiment, samples of $BaLa_4Cu_5O_{13.1}$ were heated to 1100°C under helium (see Fig. 9). Two discrete weight losses were observed. During the first loss, between 650 and 875°C, ≈0.57 oxide ions were evolved, and after the second loss at ≈950°C a total of ≈2.2 oxygens were removed. Samples quenched after the second weight loss were decomposed. However, samples quenched from the first plateau at ≈850°C showed a new set of satellites between the original

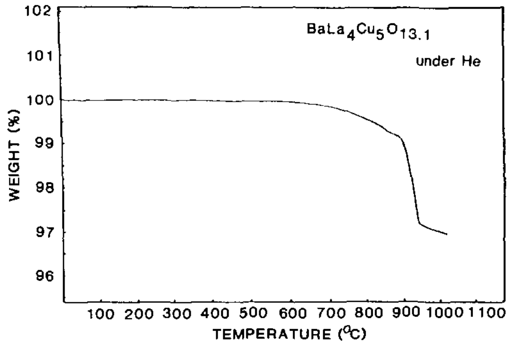

FIG. 9. Thermogravimetric analysis of $BaLa_4Cu_5O_{13.1}$ heated under helium at 10°C/min.

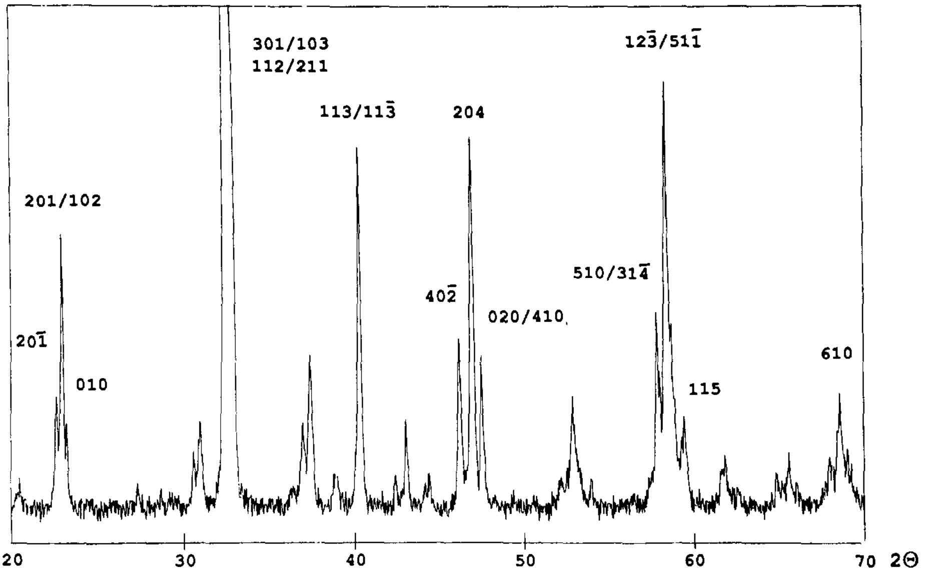

FIG. 10. X-ray pattern of phase I′, $BaLa_4Cu_5O_{12.5}$, prepared in helium.

peak positions of phase I and those of phase II (O_{12}) (see Figs. 5 and 10). This pattern could be indexed using an orthorhombic subcell and a monoclinic supercell similar to that observed for phase II. The refined cell parameters, $a = 8.756 \pm 0.005$, $b = 3.837 \pm 0.003$, $c = 8.676 \pm 0.005$ Å, $\beta = 90.62 \pm 0.05°$, were midway between those of phases I and II, and the monoclinic distortion was almost exactly half that observed for phase II. This phase was denoted phase I′ and had an oxygen content close to 12.5.

Having indexed the phases I′, II, and III, the X-ray patterns of all the samples with oxygen contents lying between those of the "stoichiometric" phases (O_{13}, $O_{12.5}$, O_{12}, and O_{11}) were all confirmed to be two-phase mixtures of the appropriate "end-members." The reproducibility of the formation of each of the new reduced structures was confirmed with other batches of $BaLa_4Cu_5O_{13\pm\delta}$. However, given the nonequilibrium nature of the technique used to prepare these phases, it was very difficult to isolate bulk, single-phase samples of phases I′, II, and III and most materials were invariably biphasic. For example, the contrast in images collected in the electron microscope for samples with ≃1.25 oxygens removed shows lamellae running through some of the grains. The grain in Fig. 11, imaged along [100], probably contains microphase intergrowths of phases II and III. It seems likely that the different cell distortions along the *b* and *c* axes of these two phases lead to the observed contrast. This was confirmed by spot splitting observed along b^* and c^* in the corresponding electron diffraction pattern. After a short exposure to the electron beam the lamellae in this particular grain disappeared, presumably due to reduction of the phase II regions to phase III. Correspondingly, the spot splitting in the electron diffraction patterns collected after the beam "damage" was absent. Some very weak extra reflections observed after the beam damaging may be consistent with the formation

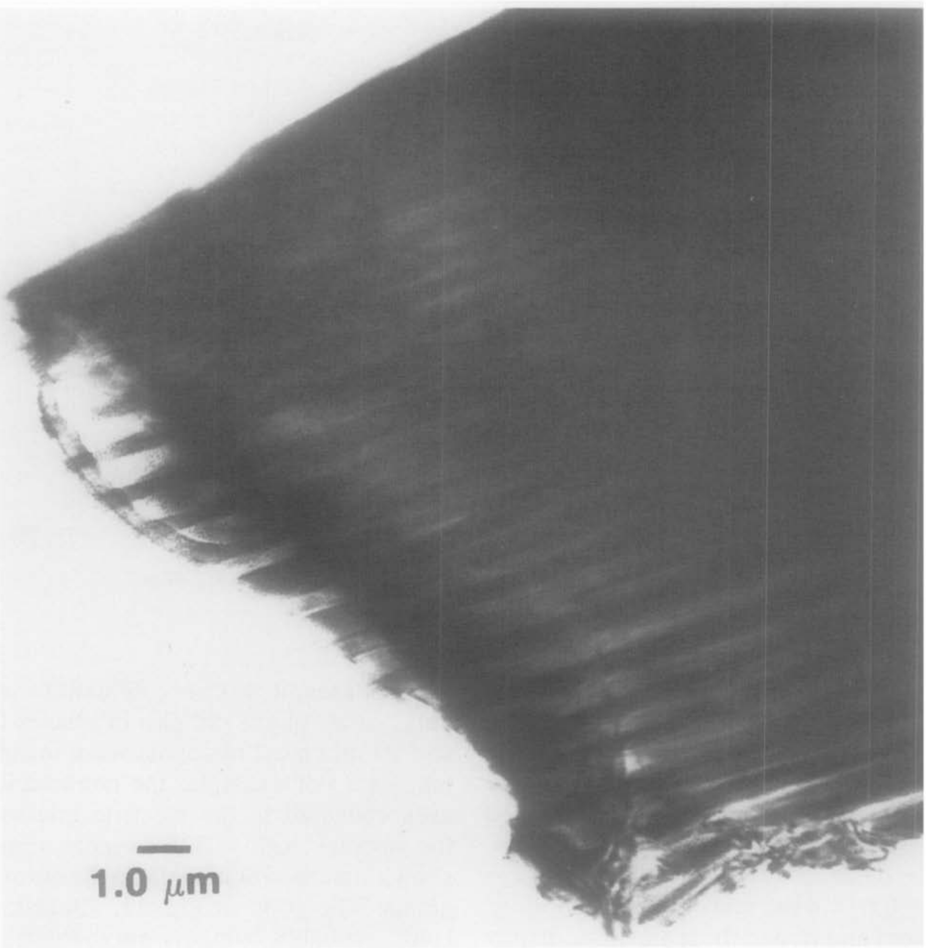

FIG. 11. Lattice image of the *b–c* plane of phase II.

of more complex superstructures during the damaging process. *In situ* studies using high resolution TEM are currently in progress.

In an effort to achieve complete homogeneity, several samples were annealed at 150°C after reduction under forming gas. Generally the annealing did not lead to any further changes in the X-ray patterns. However, two samples which were annealed overnight after the removal of 0.5 and 1.0 oxide ions, respectively, developed peaks characteristic of phase I′. These were previously seen only in He-treated samples.

4. Discussion

Our investigations of $BaLa_4Cu_5O_{13\pm\delta}$ have confirmed that the response of this ordered-perovskite system to oxidation and reduction is quite different to other perovskite-related cuprates. Thermogravimetric measurements under O_2 and air indicate that the highly oxidized structure only loses small amounts of oxygen as the temperature is increased up to ≃1040°C. Above this temperature significant oxygen losses are accompanied by bulk decomposition of the material into other barium–lanthanum cuprates. The weight losses at 1000°C show that at the synthesis temperature the stable compound has $\delta = -0.3$. Using formal copper valences to estimate the oxidation states in the compound, this corresponds to an average copper valence close to 2.3^+. Most other cuprates, most notably $Ba_2YCu_3O_{7-x}$ and $La_{2-x}Sr_xCuO_{4-y}$, deintercalate oxygen with increasing temperature and form high temperature structures in which the copper ions adopt an average valence state equal or less than two.

To probe the chemical and structural factors that stabilize this highly oxidized material, we focused on developing methods to reduce the 145 structure. By reacting samples at low temperatures with forming gas, up to 2.1 oxygen ions were removed from the lattice without inducing bulk structural decomposition; this led to the discovery of three new, metastable, oxygen-defficient phases in the $BaLa_4Cu_5O_{13+\delta}$ system.

The first new phase, phase I′, with $\delta \approx -0.5$, can be indexed with a monoclinic cell. The monoclinic distortion results from a lowering of the symmetry of the perovskite subcell from cubic in phase I to orthorhombic in phase I′. The second phase, phase II, is formed for stoichiometries with $\delta \approx -1$. The X-ray patterns for this structure could again be indexed using a monoclinically distorted supercell and the distortion was approximately twice that observed for phase I′. A third new structure is stabilized when another oxide ion is removed from the lattice, i.e., for $\delta \approx -2$, in this phase the monoclinic distortion is removed and both the subcell and the supercell are tetragonal.

It was difficult to prepare these three metastable reduced structures in single-phase form. Analysis of the powder patterns revealed that in most samples at least two of the four phases were present, even after annealing under N_2 to achieve homogeneity; some lattice images also showed evidence for microphase separation. Aside from an apparently limited range of stoichiometry for the original oxidized phase between $O_{13.1}$ and $O_{12.7}$, no evidence was found for a continuous cell distortion as the concentration of oxygen in the lattice was decreased. The observation of biphasic powder patterns for samples between the "ideal" compositions of the three new phases indicates that the transitions in this system are first order and discontinuous, and that the reduced phases approximate line compounds with very small ranges of homogeneity. The behavior of this system is consistent with the nucleation and growth of oxygen-defficient domains of each new phase as the total oxygen content is reduced.

As expected, the weaker bonding in the reduced 145 structures is reflected by an increase in the unit cell volume. As phase I is reduced to its stability limit, $\delta \approx -0.3$, a small increase in the molar volume is observed, and the volumes of the new distorted structures increase in the III > II > I′ > I. The reduction of the copper valence readily explains the observed trends in the volumes of the 145 phases; however, the *a, b,* and *c* lattice vectors respond to the reduction process in quite different ways; *a* and *b* expand, though at different rates, whereas the *c* axis shows a systematic contraction.

First, let us consider the contraction of the cell along the *c* direction. From the arrangement of the polyhedra in the original structure, phase I, it is clear that the contraction of the *c* axis results from changes in the bond lengths within the copper octahedra. In $BaLa_4Cu_5O_{13}$ the neutron studies by Michel *et al.* (*10*) indicated that the octahedra are compressed along the *c* axis. This type of coordination is quite unusual for cuprate compounds in which the Jahn–Teller distortion usually leads to an elongated octahedral coordination. The compressed octahedron is probably an indication of the preferential occupation of this site by the Cu^{3+} ions. The c axis in the fully reduced phase III is 3.71 Å; this is almost identical to twice the Shannon bond length (*12*), 1.86 Å, for Cu^{+} in linear, twofold coordination with O^{2-}. Similarly, the c axis in phase II, 3.776 Å, is twice the bond length expected for Cu^{2+} in square planar coordination (cf., ≃3.78 Å in $Ba_2YCu_3O_7$). Therefore, a structural model for these transformations based on the systematic reduction of the coordination and valence of the copper octahedra to square planar Cu^{2+} and finally to twofold Cu^{+} would be consistent with the refined c parameters in the reduced phases. However, simply removing the equatorial oxide ions from the copper octahedra does not reproduce the observed stoichiometries of the reduced phases, would not explain the variations in a and b, and leaves the copper ions in the center of the cell in unlikely coordinations. Therefore, a model was developed in which only half of the oxide ions removed from the octahedra leave the structure, with the other half rearranging to occupy some of the vacancies present in the original lattice (see Fig. 12).

In phase I the supercell contains two vacancies located midway along the a and b axes. During the formation of phase II (O_{12}), we propose that two oxygen ions are removed from the copper octahedra, one is evolved from the lattice and the second occupies the vacant site along the a axis (see Fig. 12). This rearrangement leads to a "rotation" of the square pyramids in the center of the phase II supercell (Fig. 13). Filling only the vacancies along a necessarily removes the degeneracy of a and b, and is consistent with the experimental observation that a in phase II is 0.18 Å longer than b. Furthermore, this distortion also requires that the supercell undergoes a small monoclinic distortion (β = 91.42°). This model for phase II, which contains four corner-shared square pyramids and one corner-shared square plane, is consistent with the observed oxygen stoichiometry, [$4(CuO_{2.5}) + 1(CuO_2) = O_{12}$]. As described above, the coordination change from octahedral to square planar also readily explains the observed decrease in the c axis.

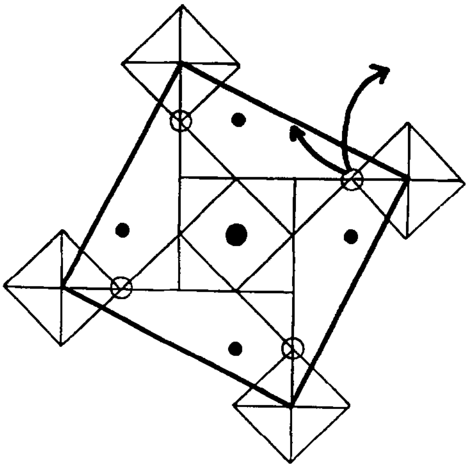

FIG. 12. Structural model for the extraction and relocation of the oxide ions during reduction.

Further reduction to phase III involves the loss of another oxygen and can be modeled by a similar mechanism. In this case we propose that the two remaining "equatorial" oxide ions are removed from the square plane, leaving copper in linear coordination. One of these ions leaves the structure, the other occupies the second original vacancy along the b axis, and the four square pyramids undergo another rotation (Fig. 13). As a result of these coordination changes, the a and b axes once again become equivalent and the monoclinic distortion is removed. As mentioned above, the c axis contraction is consistent with the formation of the linear O–Cu–O groups. This model also agrees with the observed stoichiometry, [$4(CuO_{2.5}) + (CuO) = O_{11}$].

In these idealized structural models for the transformations of $BaLa_4Cu_5O_{13-\delta}$, the barium ions remain, as expected, in 12-fold

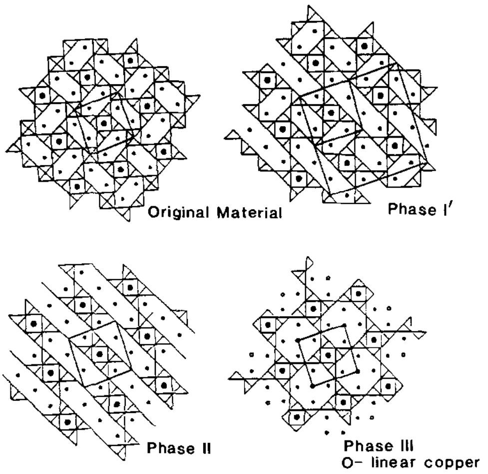

FIG. 13. Proposed model for the reduction of $BaLa_4Cu_5O_{13+\delta}$, showing the initial structure, phase I, $\delta = 0$; phase I′, $\delta = -0.5$; phase II, $\delta = -1.0$; and phase III, $\delta = -2.0$.

coordination. The lanthanum ions adopt somewhat irregular coordinations, as indeed they do in the original oxidized structure, changing from distorted 10-fold coordination to distorted 8-fold coordination. Although direct structural measurements using neutron diffraction will be necessary to confirm this scheme for the reduction reactions, these models do satisfy all the cell and stoichiometry changes observed in this work. They are also quite consistent with the copper valence in each phase. In phase II all the copper is divalent and adopts square planar or square pyramidal coordination, and in phase III the oxygen stoichiometry corresponds to the occurrence of 3 Cu^{2+} and 2 Cu^{+} ions; 1 Cu^{+} will occupy the 2-fold site, leaving the remaining square pyramidal ions with an effective valence of 1.75^{+}.

The observation of phase I′ at a composition close to $O_{12.5}$ is also readily explained using the reduction mechanism described above. We propose that in this structure the removal of one oxide ion from each octahedron in phase I reduces the Cu coordination to square pyramidal. Half of the oxide ions are evolved from the lattice; the remainder populate half of the vacancies along the *a* axis in a manner that leads to a doubling of the supercell along *a* and *b* (see Fig. 12). Therefore, this structure is intermediate between those of phases I and II. This is consistent with the cell constants of I′, which lie almost exactly between those of phase I and phase II, and with the resultant monoclinic distortion, which is half that observed in phase II. Although no direct evidence for the doubling of the cell along *a* and *b* was found in the X-ray patterns, weak extra reflections observed in some electron diffraction patterns may support this model for phase I′.

The rapid reoxidation of the three new reduced phases can be readily understood from these structural models. In the reduced phases the location of the excess vacancies leads to the formation of large channels along *c*; it would be expected that the ionic mobility of oxygen within these tunnels will be high and that the kinetics of reoxidation will be fast. This is consistent with our experimental work on the oxidation of phases I′, II, and III, in which intercalation of oxygen was observed at temperatures as low as 200°C (see Fig. 8).

Using the above scheme for the reduction of $BaLa_4Cu_5O_{13}$, it is possible to speculate on the unusual stability of the highly oxidized phase I structure. In air or oxygen phase I does not undergo any of the phase changes observed in the reactive, reducing gas atmospheres. Even at the synthesis temperature the stable phase in this system has an oxygen stoichiometry close to $O_{12.7}$ and the average copper valence is greater than two. This oxygen content appears to represent the limit of the stability of the phase I structure. The experiments in this work demonstrate that further loss of oxygen leads to a substantial structural rearrangement and a significant cell distortion to form either the I′ or II structure. The apparent high stability of phase I may therefore be primarily due to the relative instability of the reduced structures. Although the cationic coordinations in our models for the I′ and II structures are not unusual, the rearrangements of the square pyramidal polyhedra in the center of the supercell result in the corner-sharing of an axial oxygen ion. Clearly this is an unstable feature; however, no alternative method, that gave satisfactory agreement with our X-ray data, was found to avoid this geometry in this part of the decomposition sequence. The most stable arrangement, where the corner-shared oxide ion is axial to one square pyramid and equatorial to the other, is found in the original phase I and in our proposed model for the final reduced structure, phase III. Given that our proposed decomposition scheme is correct, the instability of phase II may account for the apparent stability of the highly oxidized phase I structure.

It might be argued that at high temperature phase I should transform directly to phase III, with a structural arrangement which should be more stable than either I′ or II. However, the formation of the highly reduced phase III (average Cu valence = 1.6^+) under high temperature and low oxygen partial pressure conditions appears to be unstable with respect to melting and decomposition to other barium–lanthanum–copper oxides. A thermodynamic study of the relative stabilities of all these phases, by measurement of the partial molar enthalpies of oxygen in each reduced phase, is currently underway and should help to resolve some of these questions. In addition, we are examining the behavior of the closely related perovskite phase, $La_{8-x}Sr_xCu_8O_{20-\delta}$, in which the properties of the fully oxidized structure are quite similar to those of $BaLa_4Cu_5O_{13+\delta}$ (*13*).

Conclusions

We have confirmed that the oxygen content of the highly oxidized metallic cuprate, $BaLa_4Cu_5O_{13+\delta}$, is quite insensitive to oxidation or reduction under different oxygen partial pressures up to ≃1040°C. At the synthesis temperature copper apparently retains a formal valence greater than two. By using reducing gases such as 15% H_2/85% Ar, at low temperatures it is possible to stabilize three new reduced phases with oxygen contents corresponding to $\delta = -0.5$, -1.0, and -2.0, respectively. The fully oxidized structure has a limited range of stability with $-0.3 \leq \delta \leq +0.2$; to accomodate further reduction the compound undergoes a series of discrete structural rearrangements involving a monoclinic distortion of the cell to yield the new phases. Each of the reduced structures have a very limited range of stability and, in contrast to the behavior exhibited by $Ba_2YCu_3O_{7-x}$, in this system the transitions between the reduced phases are discontinuous. At present the best model for the observed structural changes involves the systematic removal of oxygen from the Cu octahedra in the fully oxidized material with the fully reduced structure containing linear Cu^+ groups. We propose that the apparent high temperature stability of the highly oxidized 145 structure is due to the instability of the first reduced intermediate phase which we suggest contains an energetically unfavorable corner-shared arrangement of the copper polyhedra.

Acknowledgments

This work was supported by the National Science Foundation under Grant DMR-88-19027. Central Facilities were funded by the NSF MRL program, Grant DMR88-19885. We also thank the University of Pennsylvania Research Foundation for equipment support.

References

1. T. Tokura, H. Takagi, and S. Uchida, *Nature (London)* **337**, 345 (1989).
2. N. Nyugen, F. Studer, and B. Raveau, *J. Phys. Chem. Solids* **44**, 389 (1983).
3. L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, *J. Solid State Chem.* **37**, 151 (1981).

4. C. Michel, L. Er-Rakho, and B. Raveau, *Mater. Res. Bull.* **20,** 667 (1985).
5. J. Torrance, Y. Tokura, A. Nazzal, and S. S. Parkin, *Phys. Rev. Lett.* **60,** 542 (1988).
6. C. Michel and B. Raveau, *Rev. Chim. Miner.* **21,** 407 (1984).
7. D. Klibanow, K. Sujata, and T. O. Mason, *J. Amer. Ceram. Soc.* **71,** C267 (1988).
8. J. G. Bednorz and K. A. Muller, *Z. Phys. B.* **64,** 189 (1986).
9. C. U. Segre, B. Dabowski, D. G. Hinks, K. Zhang, J. D. Forgenson, M. A. Beno, and I. K. Schuller, *Nature* (*London*) **329,** 227 (1987).
10. C. Michel, L. Er-Rakho, M. Hervieu, J. Pannetier, and B. Raveau, *J. Solid State Chem.* **68,** 143 (1987).
11. R. Vijayaraghavan, R. A. Mohan Ram, P. Ganguly, and C. N. R. Rao, *Mater. Res. Bull.* **23,** 719 (1988).
12. R. D. Shannon, *Acta Crystallogr., Sect. A* **32,** 751 (1976).
13. L. Er-Rakho, C. Michel, and B. Raveau, *J. Solid State Chem.* **73,** 514 (1988).