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Synthesis and Structure of $PrBa_2Cu_2Co_1O_{7+y}$: A New Nonsuperconducting Orthorhombic 123 System[1]

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$PrBa_2Cu_{3-x}Co_xO_{7+y}$ $(0 < x < 1)$ crystallizes in tetragonal structure for small values of x $(0.1 < x < 0.3)$ and in orthorhombic structure for $0.4 < x < 1$, as revealed by X-ray and electron diffraction studies. The end member $PrBa_2Cu_2CoO_{7.4}$ shows orthorhombic to tetragonal structural transition with decrease in oxygen content just as $YBa_2Cu_3O_{7-y}$(123) and $PrBa_2Cu_3O_{7-y}$(Pr123). From the structure and reactivity, the Co ion in $PrBa_2Cu_2CoO_{7+y}$ is suggested to occupy the Cu(2) (plane Cu) position and the oxygen excess over 7 to occupy the (0,0,1/2) position between the CuO_2–CuO_2 (CoO_2) sheets. The structure supports two types of labile oxygen, one associated with the chain Cu(1) and the other in the interlayer associated with the Co ion, as revealed by anaerobic oxidation of ammonia. © 1993 Academic Press, Inc.

1. Introduction

Extensive studies exist on the substitution of Cu by other transition metals in $YBa_2Cu_3O_{7-y}$(123) (*1–3*). While the trivalent ions such as Co^{3+} and Fe^{3+} are found to occupy the Cu(1) (chain Cu) position with the change of structure from orthorhombic to tetragonal 123, divalent Ni^{2+} and Zn^{2+} ions are found to occupy the plane Cu position and the structure remains orthorhombic. Superconducting transition temperature decreased in each of these substitutions. Except for Ce and Tb, all other rare earth ions could be substituted in place of the Y ion without change in the structure and all the $LnBa_2Cu_3O_{7-x}$ were superconducting except $PrBa_2Cu_3O_{7-x}$(Pr123) (*4–6*). Even though Pr123 crystallizes in the orthorhombic 123 structure, it is a semiconducting oxide (*7–10*). Since 123 and Pr123 have the same structure and Pr123 is semiconducting, 123/Pr123/123 lattice matched multilayers were grown in order to fabricate a superconductor/insulator/superconductor (SIS)-type Josephson junction (*11, 12*). The Josephson tunneling was observed in these structures, but the junction showed a superconductor/normal metal/superconductor (SNS)-type behavior without any gap, indicating that Pr123 has sufficient carriers (holes). In the hope of producing a semiconducting oxide in the orthorhombic 123 structure with a higher semiconducting gap, a Co ion was substituted in Pr123. Indeed, $PrBa_2Cu_2CoO_{7+y}$ has been synthesized for the first time having the orthorhombic 123 structure which is semiconducting. Here we report on the synthesis and structure of $PrBa_2Cu_{3-x}Co_xO_{7+y}$ $(0 < x < 1)$.

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2. Experimental

The $PrBa_2Cu_{3-x}Co_xO_{7+y}$ series of compounds were synthesized by heating stoichiometric amounts of Pr_6O_{11}, BaO_2, CuO, $CoC_2O_4 \cdot 2H_2O$ at 930°C for 48 h with two intermittent grindings. The pellets were cooled in oxygen from 930 to 30°C at a cooling rate of 1°C/min. The compounds were characterized by X-ray diffraction using Cu*Kα* radiation employing a JEOL JDX 8P powder diffractometer. Selected area electron diffraction of a few compositions were recorded in Phillips EM 301 electron microscope. Oxygen contents were estimated from iodometric titrations (*13*). Activation energy of desorption of the labile oxygen were studied by temperature-programmed desorption (TPD). In this study, 0.3 g of the oxide was heated at a rate of 15°C/min in a quartz tube after the sample was evacuated to 10^{-6} Torr. The desorbed gases in the temperature range 30–700°C were mass analyzed employing a quadrupole mass spectrometer. The evolved gas contained only oxygen in the present series of cobalt-substituted compounds. Reactivity of the labile oxygen was studied by following ammonia oxidation over these oxides under anaerobic condition. The reactivity of the cobalt-substituted oxide was compared with that of $La_{0.7}Sr_{0.3}CoO_3$.

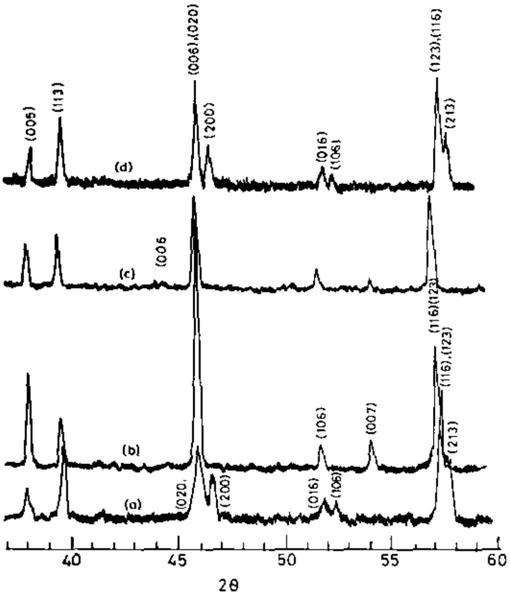

FIG. 1. Selected X-ray diffraction lines of $PrBa_2Cu_{3-x}Co_xO_{7+y}$; $x = 0$, curve (a); $x = 0.1$, curve (b); $x = 0.3$, curve (c); and $x = 1.0$, curve (d).

3. Results and Discussion

Selected X-ray diffraction lines for the series $PrBa_2Cu_{3-x}Co_xO_{7+y}$ ($x = 0$, 0.1, 0.3, and 1) are shown in Fig. 1. The splitting of (013) (103), (020) (200), (016) (106), and (213) (123) pairs of (*hkl*) values in Pr123 observed here (curve (a)) confirms the orthorhombic $YBa_2Cu_3O_{7-y}$-like structure (*9*). When Cu was substituted by Co (0.1 to 1.0), single-phase compounds were formed for all the compositions. For x in the range 0.1 to 0.3, splitting of the X-ray lines due to orthorhombic structure was absent (curves (b) and (c) of Fig. 1) and the diffraction pattern could be indexed having the tetragonal 123-like structure. For $x > 0.4$, the structure of the compounds was orthorhombic, as seen from the reappearance of the splitting of (020) (200), (016) (106), (123) (213), and other lines (curve (d)). Cell parameters, cell volume, and oxygen content for the series $PrBa_2Cu_{3-x}Co_xO_{7+y}$ are given in Table I. These data are for the fully oxygenated compounds. Variation in the cell parameters a, b, and c as a function of cobalt content in the $PrBa_2Cu_{3-x}Co_xO_{7+y}$ is shown in Fig. 2. Having determined the structure and the oxygen content, positions of the Co ion and excess oxygen over 7 have been examined.

Variation in the structure as a function of oxygen content in $PrBa_2Cu_2CoO_{7+y}$ was investigated. Selected X-ray lines of the compounds with different oxygen content are given in Fig. 3. The vacuum-annealed compound remained orthorhombic with $O_{6.98}$ (curve (b)). This was confirmed by re-

TABLE I

CRYSTALLOGRAPHIC LATTICE PARAMETERS[a] (Å), CELL VOLUME (Å^3), AND OXYGEN CONTENTS[a] FOR THE SERIES $PrBa_2Cu_{3-x}Co_xO_{7+y}$

Compound	Structure[b]	Lattice parameters a	b	c	Cell volume V	Oxygen content
$PrBa_2Cu_3O_{7-y}$	O	3.867	3.935	11.733	178.57	6.94
$PrBa_2Cu_{2.9}Co_{0.1}O_{7+y}$	T	3.910	3.910	11.695	178.79	7.02
$PrBa_2Cu_{2.8}Co_{0.2}O_{7+y}$	T	3.905	3.905	11.717	178.67	7.01
$PrBa_2Cu_{2.7}Co_{0.3}O_{7+y}$	T	3.901	3.901	11.723	178.39	7.12
$PrBa_2Cu_{2.6}Co_{0.4}O_{7+y}$	O	3.908	3.925	11.766	180.47	7.18
$PrBa_2Cu_{2.4}Co_{0.6}O_{7+y}$	O	3.901	3.929	11.766	180.33	7.19
$PrBa_2Cu_{2.2}Co_{0.8}O_{7+y}$	O	3.891	3.931	11.797	180.44	7.20
$PrBa_2Cu_2CoO_{7+y}$	O	3.881	3.932	11.761	179.47	7.42

[a] Lattice parameters are accurate within ±0.005 Å and the oxygen contents are within ±0.02.

[b] O—Orthorhombic; T—tetragonal.

ducing the oxygenated compound in ammonia only up to 400°C. However, anaerobic reaction with ammonia up to 600°C gave a single-phase tetragonal oxide with $O_{6.55}$ (curve (c)). The same is observed when the parent material is reduced with hydrogen at 10^{-3} Torr up to 600°C (curve (d)). When reduced further, the compound decomposed. The cell parameters and the oxygen content for different amounts of oxygen are given in Table II. The variation of the cell parameters as a function of oxygen content is shown in Fig. 4. For oxygen content higher than 6.70, the compound was orthorhombic. The variation of the cell parameters with oxygen content resembles that of 123.

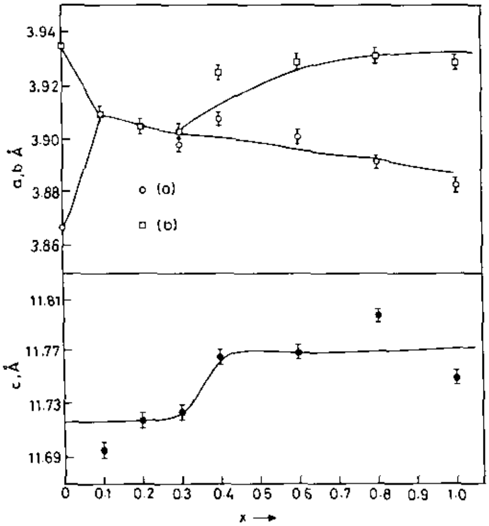

FIG. 2. Variation in the cell parameters, a, b, and c as a function of cobalt content, x, in $PrBa_2Cu_{3-x}Co_xO_{7+y}$.

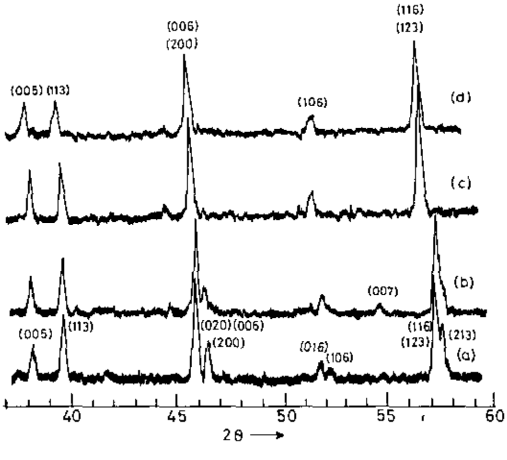

FIG. 3. Selected X-ray diffraction lines of $PrBa_2Cu_2Co_1O_{7+y}$ as a function of oxygen content; $O_{7.42}$, curve (a); $O_{7.02}$, curve (b); $O_{6.55}$, curve (c); and $O_{6.5}$, curve (d).

TABLE II

LATTICE PARAMETERS (Å) AS A FUNCTION OF OXYGEN CONTENT[a] IN $PrBa_2Cu_2CoO_{7\pm y}$

No.	Compound	Lattice parameters a	b	c	Cell volume V (Å^3)	Oxygen content
1.	$PrBa_2Cu_2CoO_{7+y}$ (Oxygen annealed)	3.881	3.932	11.761	179.47	7.42
2.	Sample 1 heated in NH_3 up to 400°C	3.880	3.923	11.736	179.00	7.02
3.	Sample 1 heated in NH_3 up to 450°C	3.890	3.924	11.757	179.46	6.93
5.	Sample 1 heated to 930°C and quenched at liquid N_2	3.906	3.930	11.788	180.95	6.88
6.	Sample 1 heated to 750°C in 10^{-6} Torr	3.910	3.931	11.760	180.75	6.75
7.	Sample 1 heated in NH_3 up to 550°C	3.926	3.926	11.771	181.43	6.72
8.	Sample 1 heated in NH_3 up to 600°C	3.927	3.927	11.753	181.26	6.55
9.	Sample 1 reduced in hydrogen up to 600°C	3.937	3.937	11.802	183.02	6.49

[a] The lattice parameters are accurate within ±0.005 Å and the oxygen contents are accurate within ± 0.02.

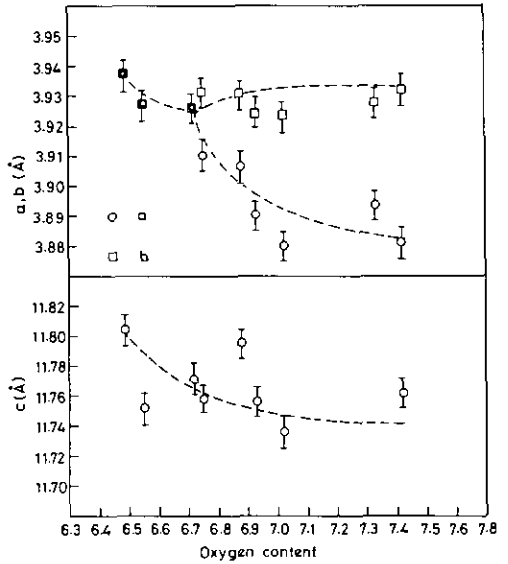

FIG. 4. Variation of cell parameters a, b, and c as a function of oxygen content in $PrBa_2Cu_2CoO_{7+y}$.

That the structures of $PrBa_2Cu_2CoO_{7.42}$ and $PrBa_2Cu_{2.9}Co_{0.1}O_{6.98}$ respectively are orthorhombic and tetragonal has been confirmed from the selected area electron diffraction studies (Fig. 5) (*14*). The cell parameters derived from the ED patterns compare well with the X-ray data.

The $PrBa_2Cu_2CoO_{7\pm 0.02}$ was still orthorhombic. By comparison of this structure with that of $YBa_2Cu_3O_{7-y}$, it can be assumed that one of the Cu ions is in the chain position, and the chain oxygen (0, 1/2, 0) is largely intact. The stoichiometry of the compound, when all the labile oxygen is removed, is $PrBa_2Cu_2CoO_{6.5}$. Charge balance of this compound can be done with one Cu in the +1 state and the other Cu in the +2, with Co in the +3 state. This is analogous to $YBa_2Cu_3O_6$, wherein the chain Cu is in the +1 oxidation state. Therefore, $PrBa_2Cu_2CoO_{7.42}$ is considered as the fully oxygenated parent orthorhombic oxide from

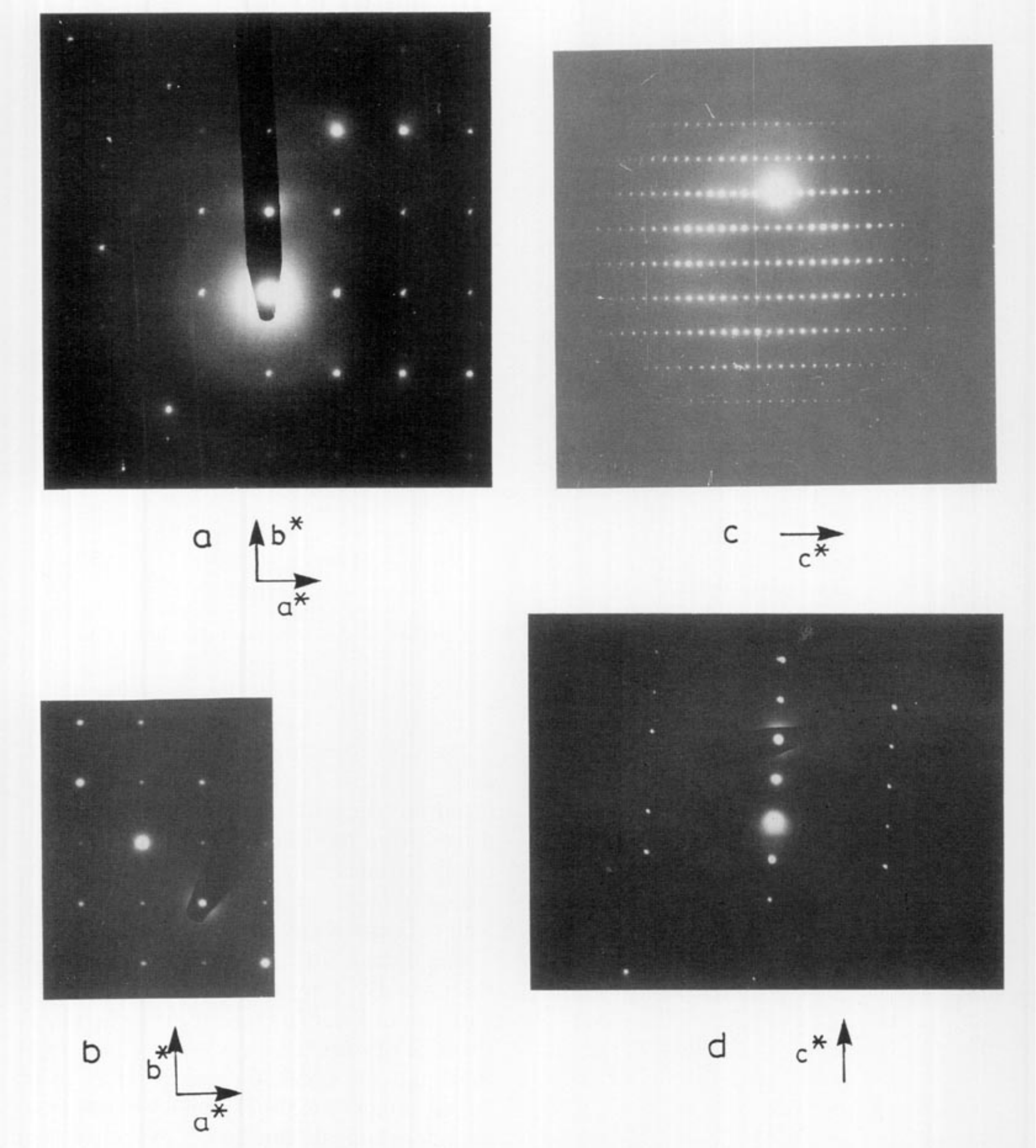

FIG. 5. (a) Selected area electron diffraction patterns of PrBa$_2$Cu$_2$Co$_1$O$_{7.42}$ and (b) PrBa$_2$Cu$_{2.9}$Co$_{0.1}$O$_{6.98}$ along the [001] zone axis; note that a^* and b^* are unequal in (a), indicating an orthorhombic cell, and $a^* = b^*$ in (b), indicating a tetragonal cell; (c) and (d) are the diffraction patterns in the [010] zone axis corresponding to oxides (a) and (b), indicating a triple perovskite cell.

TABLE III

POWDER X-RAY DATA FOR $PrBa_2Cu_2CoO_{7.42}$ AND $PrBa_2Cu_2CoO_{6.5}$

$PrBa_2Cu_2CoO_{7.42}$ $a = 3.881$ Å, $b = 3.932$ Å, $c = 11.761$ Å				$PrBa_2Cu_2CoO_{6.5}$ $a = b = 3.934$ Å, $c = 11.800$ Å			
d_{obs}	d_{cal}	I/I_0	hkl	hkl	d_{obs}	d_{cal}	I/I_0
11.746	11.761	4	001	001	11.809	11.800	6
3.905	3.920	16	003	003 100	3.958	3.933	13
3.855	3.881	6	100				
2.765	2.776	66	013	103 110	2.791	2.781	100
2.756	2.758	100	103				
2.333	2.352	9	005	005	2.357	2.360	8
2.254	2.258	16	113	113	2.271	2.271	8
1.961	1.960	28	006	006 200	1.969	1.967	23
1.961	1.966		020				
1.937	1.940	9	200				
1.755	1.754	4	016	106	1.759	1.759	7
1.740	1.749	3	106				
1.602	1.598	28	116	116 123	1.605	1.605	27
1.602	1.600		123				
1.590	1.590	14	213				
1.503	1.506	5	124	124	1.512	1.511	6
1.501	1.497	4	214				
1.391	1.388	8	026	206	1.389	1.390	12
1.380	1.379	11	206				
1.380	1.381	11	220				

which the labile oxygen is removed to give the tetragonal $PrBa_2Cu_2CoO_{6.5}$. The (*hkl*) parameters, relative intensities, and the *d* values of the orthorhombic and tetragonal phases are given in Table III.

A detailed neutron diffraction study of $YBa_2Cu_{2.2}Co_{0.8}O_{7+y}$ showed that the Co^{+3} ion occupies the Cu(1) position with the excess oxygen occupied in the (1/2,0,0) sites (*15*, *16*). Since the Co^{+3} ion favors octahedral coordination, occupation of oxygen in the (1/2,0,0) position leads to a tetragonal structure. This seems to be the case for small Co ion concentration, i.e., for x between 0.1 and 0.3 in $PrBa_2Cu_{3-x}Co_xO_{7+y}$ as well. For higher Co concentration, Co^{+3} ions are suggested to occupy the Cu(2) (plane Cu) positions. Had the cobalt occupied the Cu(1) position for $x > 0.4$ with the oxygen excess over 7 in the (1/2,0,0) position, the structure would have transformed to tetragonal symmetry. Alternatively, if cobalt occupied the plane Cu sites, oxygen in excess of 7 can take the (0,0,1/2) sites in the Pr plane between the CuO_2 sheets, converting the square pyramids into octahedra around the metal. This would retain the orthorhombic structure. Similar instances of excess oxygen occupying the (0,0,1/2) sites when the intersheet cation sites are occupied by large ions such as La^{3+} or Sr^{2+} have been reported in the literature (*17–19*). If all the vacant sites in the Pr plane are occupied by oxygen, the formula of the compound should be $PrBa_2Cu_2CoO_8$. But the maximum oxygen content observed is $O_{7.4}$. Therefore, only about 40% of the vacancies are occupied by oxygen.

Reactivity of Labile Oxygen

Oxygen content increased with increasing Co^{3+} content (see Table I). This is to be

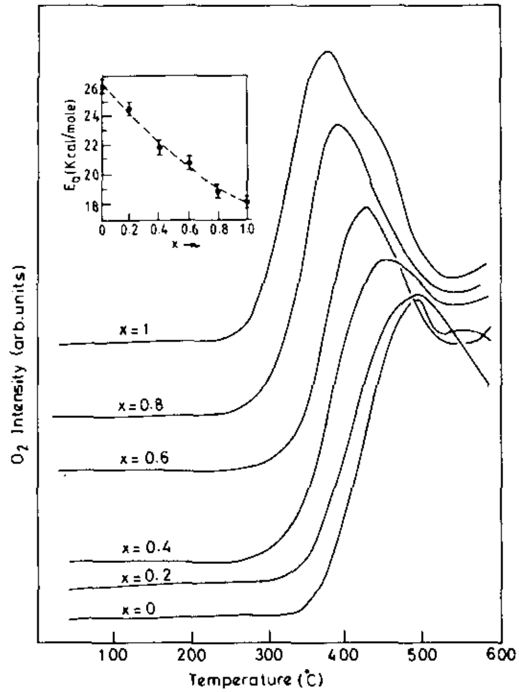

FIG. 6 Oxygen desorption thermograms from the fully oxygenated oxides, $PrBa_2Cu_{3-x}Co_xO_{7+y}$; $x = 0.0$, 0.2, 0.4, 0.6, 0.8, and 1.0. Inset shows E_a vs x.

expected since the Cu^{2+} ion is replaced by a Co^{3+} ion. How strongly the extra oxygen is bound has been determined by a temperature-programmed desorption study. The oxygen desorption thermograms for the series $PrBa_2Cu_{3-x}Co_xO_{7+y}$ for $x = 0, 0.2, 0.4, 0.6$, 0.8, and 1 are shown in Fig. 6. Activation energy determined from the Arrhenius plot (ln I vs $1/T$) decreased with increasing cobalt content, as shown in the inset of Fig. 6. The peak temperature of oxygen desorption of $PrBa_2Cu_2CoO_{7+y}$ is about 350°C and that of $PrBa_2Cu_3O_{7-y}$ is about 500°C. Activation energies of oxygen desorption of $YBa_2Cu_3O_{7-y}$ and $PrBa_2Cu_3O_{7-y}$ are 27 and 25 kcal/mole (*20*) and that of $PrBa_2Cu_2CoO_{7+y}$ is about 19 kcal/mole, which is substantially low. Therefore, desorbable oxygen in $PrBa_2Cu_2CoO_{7+y}$ is more labile than that of $YBa_2Cu_3O_{7-y}$.

In $PrBa_2Cu_3O_{7-y}$, the Pr ion is found to be in the +3 state (*9*). Since the compounds studied here are prepared under similar conditions, the Pr ion is likely to be in the +3 state. Assuming the standard oxidation state for Pr^{3+}, Ba^{2+}, Cu^{2+}, and Co^{3+}, $PrBa_2Cu_2CoO_7$ forms the stoichiometric compound. Excess of 0.4 oxygen over 7 in the oxygenated compound thus creates 0.8 holes per formula unit; 0.8 holes can then be distributed between Cu and Co. Therefore, Cu^{3+} and Co^{4+} are likely to be present in this structure. This can be represented as follows:

$$Cu^{3+}\,O^{2-} \rightleftarrows Cu^{2+}\,O^{1-} \tag{1}$$

and

$$Co^{4+}\,O^{2-} \rightleftarrows Co^{3+}\,O^{1-}. \tag{2}$$

Iodometric titration cannot distinguish these two types of holes, since both Cu^{3+} and Co^{4+} ions liberate iodine. Oxidation of NH_3 over this compound giving NO seems to distinguish the two types of holes, as shown below.

Oxidation of ammonia over 123, Pr123, and $YBa_2Cu_2CoO_{7+x}$ has been studied earlier under anaerobic as well as aerobic conditions (*21*). In all these cases, NO was the important product evolved at a temperature at which oxygen desorption occurred. Figure 7a shows the typical thermograms for the anaerobic oxidation of ammonia over $PrBa_2Cu_2CoO_{7+y}$. The products were H_2O, N_2, and NO. Figure 7b shows the thermograms of NO obtained from anaerobic oxidation of ammonia over Pr123, $PrBa_2Cu_2CoO_{7+y}$, and $La_{0.7}Sr_{0.3}CoO_3$. Ammonia oxidation over Pr123 gave one NO peak at 500°C, indicating the presence of only one type of labile oxygen, namely, the chain-site (0,1/2,0) oxygen. Ammonia over $PrBa_2Cu_2CoO_{7+x}$ gave two NO peaks, one at 350°C and the second at 500°C. This experiment shows that there are two types of labile oxygen, one associated with the chain Cu at (0,1/2,0) and the other one at (0,0,1/2) asso-

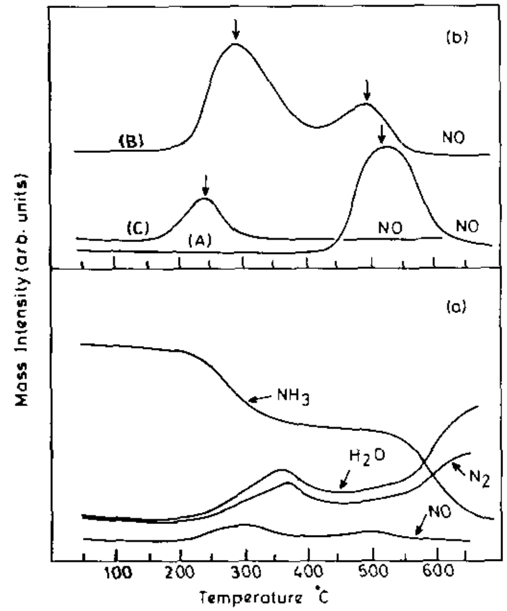

FIG. 7 (a) Thermograms of ammonia and the products N_2, H_2O, and NO when ammonia is passed over $PrBa_2Cu_2CoO_{7.42}$ under anaerobic condition: (b) Thermograms of NO when ammonia is anaerobically oxidized over $PrBa_2Cu_3O_{6.98}$ (curve A), $PrBa_2Cu_2CoO_{7.42}$ (curve B), and $La_{0.7}Sr_{0.3}CoO_3$ (curve C).

ciated with the Co ion in comparison with ammonia oxidation over $La_{0.7}Sr_{0.3}CoO_3$ (*22*). Thus, ammonia oxidation reaction can distinguish two types of holes given by equilibriums (1) and (2).

In conclusion, $PrBa_2Cu_2CoO_{7+y}$ is shown to crystallize in the orthorhombic 123-like structure with the Co ion most likely occupying the plane Cu(2) position. Doping level of holes is about the same as in 123, but the holes are shared between Cu and Co ions.

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Note added in proof. Recently we have shown that cobalt substitution occurs in La123 giving $LaBa_2Cu_2CoO_{7.4}$ and $LaBa_2CuCo_2O_8$ (*23*).

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