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The Pr–Ba–Cu–O and Nd–Ba–Cu–O Systems: Phase Relationships at ~950°C

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Systematic X-ray powder diffraction studies of the Nd_2O_3–$BaCO_3$–CuO and PrO_x–$BaCO_3$–CuO systems at ~950°C in air are presented as a function of cation molar ratios. In the pseudo-binary regions $BaCuO_2$ was observed in both systems; Pr_2CuO_4 and $BaPrO_3$, and Nd_2CuO_4 and $BaNd_2O_4$, were observed in the Pr and Nd systems, respectively. $BaPr_2O_4$ could be prepared only in a reducing atmosphere. In the pseudo-ternary regions the '123' and '336' phases were observed in the Pr system; the '123,' '336,' and '311' phases were observed in the Nd system. In the Pr system extensive solid-solution prevails between the '110,' '123,' and '336' phases and between the latter two phases and CuO. In the Nd system solid-solution was observed between '311,' '123,' and '336' phases, and between the latter two phases and CuO.

Introduction

Discovery of high temperature superconductivity in the ternary region of *Ln*–Ba–Cu–O (*Ln* = La–Lu, except Ce, Pr, and Tb) systems caused them to become an important as well as interesting research area. Numerous studies have demonstrated that the characteristics of the *Ln*–Ba–Cu–O superconducting phases depend greatly upon preparatory procedure (*1*). An understanding of phase relationships is useful both for improving the properties of these materials and for achieving specimen reproducibility. Numerous reports detail structural and conductivity properties of the '123' (*Ln* : Ba : Cu) phases, but only a limited number of *Ln*–Ba–Cu–O systems have been studied as a function of lanthanoid ion. Phase relationships over the *entire composition region* in the 900–1000°C range have been published for the *Ln*–Ba–Cu–O systems: *Ln* = Y (*2–6*), La (*7–9*), Eu (*10*), Er (*11*), and Tm (*12*). Less detailed studies have been reported for the *Ln* = Ho (*13*) and Gd (*14*) systems. These studies have demonstrated that in this temperature range the stable compounds change as the lanthanoid ion is varied with the consequence that compound coexistence relationships differ. Lanthanoid ion size and basicity appear important in determining phase stability. From an examination of the phase relationships reported among the *Ln*–Ba–Cu–O systems only the adjacent heavier-lanthanoid Er and Tm systems appear identical; the lighter, more basic, lanthanoid systems exhibit markedly different behavior.

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We present the results of detailed studies of the Pr–Ba–Cu–O and Nd–Ba–Cu–O systems effected primarily in air at ~950°C. This temperature was chosen not only because it has been used extensively for '123' superconducting phase preparations, but also because at higher temperatures some phases melt and at lower temperatures the solid state diffusion process occurs too slowly to attain equilibrium within a reasonable time. In addition to presenting a phase diagram for both systems some properties of the intermediate phases that form are detailed.

Experimental

Reactants were Nd_2O_3 (99.9%, Research Chemicals, Phoenix, AZ), 'Pr_6O_{11}' (99.9%, Michigan Chemical Corp.), $BaCO_3$ (reagent grade, J. T. Baker Co., Phillipsburg, NJ), and CuO (reagent grade, Mallinckrodt, St. Louis, MO). Reagents were monophasic by X-ray powder diffraction. They were weighed to an accuracy of ±0.1 mg, hand-mixed under acetone with an agate mortar and pestle for 15 to 20 min, and then air-dried. The specimens were placed in alumina boats and fired in a tube furnace in air at ~950°C for 24 hr, then in most cases air-quenched to room temperature by removal from the furnace. Some sintered products were reground and annealed under a dynamic 1 bar oxygen atmosphere for 12 hr at ~930°C and cooled to room temperature over a period of ~4 hr.

Phase analysis and characterization were effected by the Guinier X-ray powder diffraction technique with monochromatized Cu$K\alpha_1$ radiation ($\lambda\alpha_1$ = 1.54050 Å) in a 114.6-mm-diameter camera evacuated to 10^{-3} Torr during exposure. NBS-certified Si powder [a = 5.43082(3) Å] served as internal standard. Reflection positions were determined with a Supper film reader; intensities were estimated visually. Lattice parameters calculated by a locally written least-squares routine were refined with the program APPLEMAN (*15*). X-ray powder diffraction intensities were calculated with the program POWD12 (*16*); calculations were effected on a VAX 11/750 computer.

Magnetic susceptibilities of selected compounds were determined in a Quantum Design SQUID magnetometer at 500 Oe as a function of temperature in the range 5–300 K. The powdered specimen was loaded into a capped plastic vial which was inserted into the SQUID.

Results and Discussion

Initial molar compositions, phases observed, and specimen colors are tabulated for the Pr and Nd systems, respectively, in Tables I and II. Phases relationships in the respective systems are presented in Figs. 1 and 2. The numbers designated in the figures are keyed to the sample numbers listed in the tables. Lattice parameters and structure types for all phases observed in both systems and selected literature data are presented in Table III.

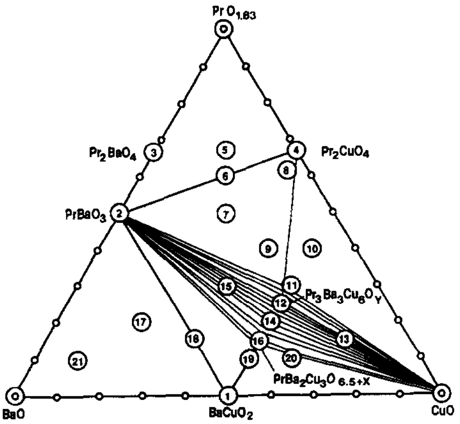

FIG. 1. Subsolidus phase relationships at 950°C in the Pr–Ba–Cu–O system. The numbers correspond to those listed in Table I. The lined area represents a solid–solution region. $BaPr_2O_4$ was prepared in a reducing atmosphere.

TABLE I

PHASES PRESENT IN THE PrO_x–$BaCO_3$–CuO SYSTEM

Sample No.	Initial composition[a]	Phases observed	Color
1	0:1:1	$BaCuO_2$	Black
2	1:1:0	$PrBaO_3$	Khaki
3	2:1:0	$PrBaO_3 + PrO_{1.833}$	Dark brown
4	2:0:1	Pr_2CuO_4	Black
5	4:1:1	$PrBaO_3 + PrO_{1.833} + Pr_2CuO_4$	Dark gray
6	3:1:1	$PrBaO_3 + Pr_2CuO_4$	Dark gray
7	2:1:1	$PrBaO_3 + Pr_2CuO_4 + Pr_{3+x}Ba_{3-x}Cu_6O_y$[b]	Black
8	13:1:7	$Pr_2CuO_4 + Pr_{3+x}Ba_{3-x}Cu_6O_y$[b]	Black
9	2:1:2	$Pr_2CuO_4 + Pr_{3+x}Ba_{3-x}Cu_6O_y + PrBaO_3$	Black
10	4:1:5	$Pr_2CuO_4 + CuO + Pr_{3+x}Ba_{3-x}Cu_6O_y$	Black
11	3:2:5	$Pr_2CuO_4 + Pr_{3+x}Ba_{3-x}Cu_6O_y + CuO$[b]	Black
12	3:3:6	$Pr_3Ba_3Cu_6O_y$	Black
13	3:3:14	$Pr_3Ba_3Cu_6O_y + CuO$	Black
14	2:3:5	$Pr_{1+x}Ba_{2-x}Cu_3O_y$	Black
15	6:6:7	$Pr_{3-x}Ba_{3+x}Cu_6O_y + PrBaO_3$	Black
16	1:2:3	$PrBa_2Cu_3O_y$	Black
17	1:3:1	$BaCuO_2 + BaO + PrBaO_3$	Dark brown
18	1:3:2	$BaCuO_2 + PrBaO_3$	Black–green
19	1:4:5	$BaCuO_2 + Pr_{1-x}Ba_{2+x}Cu_3O_y$	Black
20	1:3:6	$Pr_{1-x}Ba_{2+x}Cu_3O_y + BaCuO_2 + CuO$	Black
21	1:8:1	$BaCuO_2 + BaO + PrBaO_3$[b]	Gray

Note. Formulas are deduced from crystallographic and mixed composition data.

[a] Pr:Ba:Cu molar ratio.

[b] Trace amounts of compound detected.

Magnetic susceptibility–temperature plots of two praseodymium and one neodymium compound are presented in Fig. 3.

The Pseudo-Binary Regions

The $BaCO_3$–CuO region. Only the well-characterized cubic $I\,m\,\bar{3}\,m$ $BaCuO_2$ (*17*, *18*) was observed. The compounds Ba_2CuO_3 and Ba_3CuO_4 reported elsewhere (*5*) could not be prepared.

The Ln_2O_3–$BaCO_3$ region. The oxides $BaNd_2O_4$ and $BaPrO_3$ were obtained. Lattice parameters of orthorhombic, $CaFe_2O_4$-type $BaNd_2O_4$ agree well with reported values (*19*). Three additional phases have been observed in other *Ln*–Ba–O systems (*20*, *21*) in 900–1100°C temperature range. Systematic attempts to prepare similar compounds in the Nd–Ba–O system met with failure.

All X-ray powder diffraction reflections observed for $BaPrO_3$ were indexed with orthorhombic lattice parameters consistent with those obtained previously both by X-ray (*22*, *23*) and neutron (*24*) diffraction. The compound exhibits a distorted perovskite-type structure. According to Ref. (*19*) $BaPr_2O_4$ forms when a 1:2 molar mixture of $BaCO_3$ and $PrO_{1.5}$ is sintered in air. We prepared $PrO_{1.5}$ by reducing 'Pr_6O_{11}' with hydrogen at 950°C for 12 hr and attempted to repeat this synthesis, but every mixture with a composition greater than 50 mol% Pr yielded $BaPrO_3$ and $PrO_{1.833}$ (*25*). However, $BaPr_2O_4$

TABLE II

PHASES OBSERVED IN THE Nd_2O_3–$BaCO_3$–CuO SYSTEM

Sample No.	Initial composition[a]	Phases observed	Color
1	0:1:1	$BaCuO_2$	Black
2	1:4:0	$BaO + Nd_2BaO_4$	Light gray
3	1:2:0	$BaO + Nd_2BaO_4$	Light gray
4	1:1:0	$BaO + Nd_2BaO_4$	Light gray
5	4:3:0	$BaO + Nd_2BaO_4$	Light gray
6	2:1:0	Nd_2BaO_4	Light gray
7	3:0:1	$Nd_2O_3 + Nd_2CuO_4$	Black
8	2:0:1	Nd_2CuO_4	Black
9	1:0:1	$Nd_2CuO_4 + CuO$	Black
10	1:0:2	$Nd_2CuO_4 + CuO$	Black
11	1:0:3	$Nd_2CuO_4 + CuO$	Black
12	1:2:3	$NdBa_2Cu_3O_y$	Black
13	3:3:6	$Nd_3Ba_3Cu_6O_y$	Black
14	4:1:5	$Nd_2CuO_4 + Nd_{3+x}Ba_{3-x}Cu_6O_y + CuO$	Black
15	1:1:3	$Nd_3Ba_3Cu_6O_y + CuO$	Black
16	1:1:8	$CuO + Nd_3Ba_3Cu_6O_y + X$[b]	Black
17	1:2:4	$Nd_{1+x}Ba_{2-x}Cu_3O_y + CuO$[c]	Black
18	2:3:5	$Nd_{1+x}Ba_{2-x}Cu_3O_y$	Black
19	5:6:11	$Nd_{1+x}Ba_{2-x}Cu_3O_y$	Black
20	1:4:5	$Nd_{1-x}Ba_{2+x}Cu_3O_y + BaCuO_2$	Black
21	1:3:2	$Nd_3BaCuO_y + Nd_{1-x}Ba_{2+x}Cu_3O_y$	Black and brown
22	2:5:5	$Nd_{1-x}Ba_{2+x}Cu_3O_y + Nd_3BaCuO_y$	Black and brown
23	5:61:34	$BaCuO_2 + BaO + Nd_{1-x}Ba_{2+x}Cu_3O_y$[c]	Black
24	1:1:1	$Nd_3BaCuO_y + Nd_{1-x}Ba_{2+x}Cu_3O_y$	Black and brown
25	8:5:7	$Nd_3BaCuO_y + Nd_{1+x}Ba_{2-x}Cu_3O_y$	Brown and black
26	10:3:7	$Nd_3BaCuO_y + Nd_2CuO_4 + Nd_{3+x}Ba_{3-x}Cu_6O_y$	Brown and black
27	2:1:1	$Nd_3BaCuO_y + Nd_{1-x}Ba_{2+x}Cu_3O_y$	Dark brown
28	3:1:1	Nd_3BaCuO_y	Brown
29	7:1:2	$Nd_2CuO_4 + Nd_3BaCuO_y + Nd_2O_3$	Dark brown
30	8:1:1	$Nd_3BaCuO_y + Nd_2O_3$	Light brown
31	7:2:1	$Nd_3BaCuO_y + Nd_2BaO_4 + Nd_2O_3$	Light brown
32	3:5:2	$Nd_3BaCuO_y + Nd_{1-x}Ba_{2+x}Cu_3O_y$[c]	Dark brown
33	4:5:1	$Nd_2BaO_4 + Nd_3BaCuO_y + BaO$[c]	Gray
34	1:3:1	$Nd_3BaCuO_y + Nd_{1-x}Ba_{2+x}Cu_3O_y + BaO$[c]	Brown and black
35	1:8:1	$BaO + Nd_3BaCuO_y$[c]	Gray

Note. Formulas are deduced from crystallographic and mixed composition data.

[a] Nd : Ba : Cu molar ratio.

[b] Some very weak reflections could not be identified.

[c] Trace amounts of substance observed.

could be prepared under more rigorous reducing conditions. A Pr : Ba = 2 : 1 stoichiometric mixture heated in argon at ~950°C for 12 hr yielded the pure compound. Its orthorhombic lattice parameters are in good agreement with those reported (*19*).

The Ln_2O_3–CuO region. The only air-stable compounds are Pr_2CuO_4 and Nd_2CuO_4. Both exhibit tetragonal symmetry; lattice parameters suggest structures related to that of a copper-based perovskite. Cox *et al.* recently determined the structure of Pr_2CuO_4

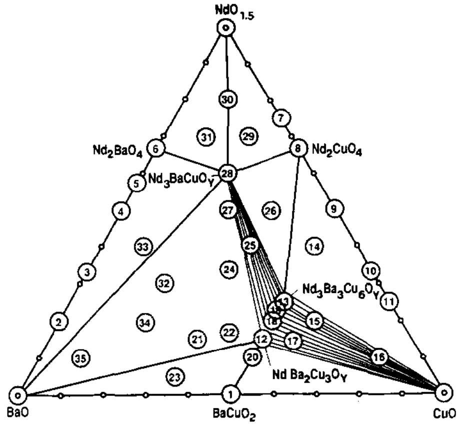

FIG. 2. Subsolidus phase relationships at 950°C in the Nd–Ba–Cu–O system. The numbers correspond to those listed in Table II. The lined area represents a solid–solution region.

by neutron diffraction (*26*); our Pr_2CuO_4 lattice parameters agree well with their 298 K values. The compounds $Y_2Cu_2O_5$ (*27*), $YCuO_2$ (*28*), and $YCuO_3$ (*27*) found in the Y–Cu–O system were not encountered in this work.

The Ternary Regions

PrO_x–$BaCO_3$–CuO system. Two compounds were observed: $PrBa_2Cu_3O_y$, '123,' and $Pr_3Ba_3Cu_6O_z$, '336.' The black '123' compound has a pseudo-tetragonal perovskite-type structure with $a = 3.9084(6)$ Å and $c = 11.843(4)$ Å. (The prefix 'psuedo' indicates that the difference between the a and b lattice parameters is less than two standard deviations of the measurement.) After it was heated in O_2 this compound showed the characteristic orthorhombic lattice parameters (see Table III). The orthorhombic cell volume is 3.29 Å^3 smaller than that of the tetragonal cell. A '123' cell volume decrease, per se, is not a good criterion of lanthanoid ion oxidation state since an increase in the copper ion oxidation state decreases the Cu–O(2) distances in the Cu–O sheets (a and b parameters) and increases the Cu–O(1) out-of-sheet distances (c parameter), potentially yielding a cell volume increase (*29*). However, the volume change observed here, approximately twice that found for the comparable neodymium and other closely related compounds, may indeed support a mixed-valence state for praseodymium.

The valence of Pr in the '123' compound is controversial. Magnetic susceptibility measurements suggest that the effective magnetic moment corresponds to an average formal valence of about 3.7 (*30, 31*). On the other hand, soft X-ray absorption spectroscopy (XANES) indicates the praseodymium to be trivalent (*30, 32*). However, it is possible that surface praseodymium ions are trivalent whereas in the bulk material the valence is higher. Numerous reports (*31–35*) establish the absence of superconductivity in the praseodymium '123' phase. The plot of χ versus T obtained from an O_2-heated (orthorhombic) $PrBa_2Cu_3O_y$ powder specimen (Fig. 3) shows paramagnetic properties between 5 and 300 K. One of the mechanisms postulated to explain the absence of superconductivity in the '123' compound is associated with Pr 4*f* electrons hybridizing with the hole carriers of the Cu(2) planes (*31*), thereby changing the effective number of these electrons and creating a Pr oxidation state intermediate between 3+ and 4+.

The praseodymium '336' phase was isolated as a black (see Table I) powder. A plot of its magnetic susceptibility, χ, versus T (Fig. 3) indicates paramagnetic behavior. The X-ray powder diffraction pattern showed strong reflections similar to those of $La_3Ba_3Cu_6O_{14.1}$ (*7*) and was indexed with tetragonal lattice parameters similar to those of the '123' phase. In contrast with the '123' lattice parameters, those of '336' remain essentially invariant upon heating in oxygen: $a = 3.8903(5)$ Å, $c = 11.640(2)$ Å for the air-quenched sample versus $a = 3.8907(5)$ Å, $c = 11.653(2)$ Å for the oxygen-

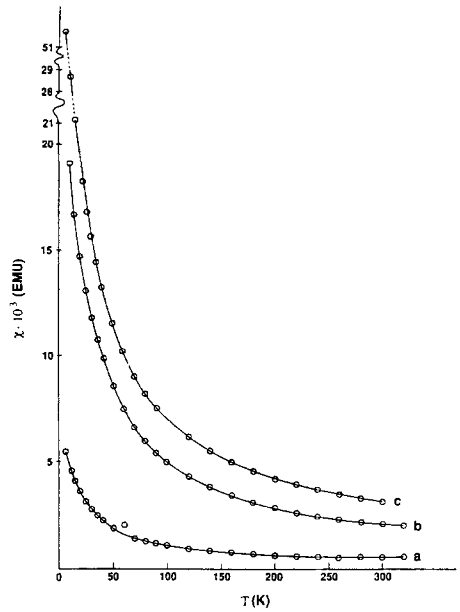

FIG. 3. The temperature dependence of the magnetization at 500 Oe for (a) orthorhombic $PrBa_2Cu_3O_y$, (b) $Pr_3Ba_3Cu_6O_y$, and (c) '123'-type $Nd_{1.44}Ba_{1.56}Cu_3O_y$.

annealed specimen. Since Pr can exhibit multivalency, it is of interest to compare these parameters with those of the comparable La and Nd compounds. The published ionic radius of Pr^{3+} is midway between those of La^{3+} and Nd^{3+} (*36*). However, a comparison of the unit cell volumes of the related $BaLn_2O_4$ compounds, *Ln* = La, Pr, Nd, suggests a smaller Pr^{3+} radius, ~2/3 from that of La^{3+} and ~1/3 from that of Nd^{3+} (*37*) rather than midway between them. A plot of the lattice parameters of the lanthanum '336' phase prepared under N_2, a = 3.904(1) Å and c = 11.714(5) Å (*38*), with those reported herein for the neodymium analogue suggests for Pr '336' parameters of a = 3.893 Å and c = 11.697 Å (V = 177.3 Å^3) with the larger Pr^{3+} radius, and a = 3.889, c = 11.691 Å (V = 176.8 Å^3) with the smaller one. The proximity of the observed unit cell volume (176.4 Å^3) to the estimated values suggests the presence of only Pr^{3+}.

The *Ln*–Ba–Cu–O systems, for *Ln* = Eu, Y, Er, and Tm, but not La, exhibit the "green" '211' phase. A praseodymium '211' phase could not be synthesized. Every mixture of this composition and those close to it when heated in air produced three phases: $BaPrO_3$, Pr_2CuO_4, and '336' $Pr_{3+x}Ba_{3-x}Cu_6O_y$.

Nd_2O_3–$BaCO_3$–CuO system. Three compounds, $NdBa_2Cu_3O_y$, $Nd_3Ba_3Cu_6O_y$, and Nd_3BaCuO_y, were characterized. Our diffraction pattern of the black '123' phase was indexable on orthorhombic symmetry with lattice parameters slightly larger than those reported previously (see Table III). While this phase did not show the Meissner effect at liquid nitrogen temperature, the 90 K superconducting phase was produced by reheating the orthorhombic specimen at ~950°C for 10 hr under a dynamic oxygen atmosphere. As expected, the refined lattice parameters of the superconducting phase are slightly smaller (see Table III) than those of the air-heated specimen.

Reactants in the mole ratio Nd : Ba : Cu = 1 : 1 : 2 produced a black compound isostructural with $La_3Ba_3Cu_6O_{14.1}$ (*7*). This phase was indexed on tetragonal lattice parameters (see Table III) by comparing its powder X-ray diffraction pattern to those of other '336' phases. These '336' parameters are similar to those of the praseodymium analogue and decreased only slightly when the specimen was heated in a dynamic oxygen atmosphere.

The neodymium green '211' phase could not be prepared. Instead, a new type phase obtained pure only from reactants in the molar ratio Nd : Ba : Cu = 3 : 1 : 1 was identified (*39*) in the more Nd-rich region. This phase is brown and shows reflections similar to those reported for tetragonal $La_{3.6}Ba_{2.4}Cu_{1.8}O_{9.6}$ (*40*); its lattice parameters are presented in Table III. It exhibits Curie–Weiss behavior between 5 and 300 K (*39*).

TABLE III

LATTICE PARAMETER AND SYMMETRY DATA ON $BaCO_3$–Nd_2O_3–CuO AND $BaCO_3$–PrO_x–CuO COMPOUNDS

Compound	Symmetry[a]	Lattice parameters			Refs.[b]	Notes
		a(Å)	*b*(Å)	*c*(Å)		
$BaCuO_2$	C	18.277(5)				
		18.2772(2)			(*18*)	
$BaPrO_3$	O	6.1843(4)	6.2130(5)	8.7289(7)		
		6.170(2)	6.214(3)	8.716(3)	(*22*)	
$BaPr_2O_4$	O	10.611(1)	3.6273(5)	12.492(1)		Prepared Ar
		10.611	3.621	12.476	(*19*)	
Pr_2CuO_4	T	3.9601(3)		12.230(1)		
		3.9615(1)		12.2140(5)	(*26*)	
$Pr_{0.9}Ba_{2.1}Cu_3O_y$	T	3.911(3)		11.854(5)		
$PrBa_2Cu_3O_y$	T^c	3.9084(6)		11.843(4)		
	O	3.8626(6)	3.9056(4)	11.774(1)		Heated O_2
	O	3.873(2)	3.915(1)	11.67(1)	(*31*)	
	T^c	3.905(2)		11.66(1)	(*44*)	Prepared O_2
	C^c	3.922(2)			(*46*)	
$Pr_{1.25}Ba_{1.75}Cu_3O_y$	T	3.904(1)		11.716(4)		
$Pr_{1.37}Ba_{1.63}Cu_3O_y$	T	3.898(1)		11.675(2)		
$Pr_{1.5}Ba_{1.5}Cu_3O_y$ ('336'-type)	T	3.8903(7)		11.640(2)		
		3.8907(7)		11.653(2)		Heated O_2
$Pr_{3.05}Ba_{2.95}Cu_6O_y$	T	3.883(1)		11.607(5)		
$BaNd_2O_4$	O	10.540(1)	3.5587(6)	12.396(1)		
		10.596	3.609	12.438	(*19*)	
Nd_2CuO_4	T	3.9421(2)		12.1659(3)		
		3.937		12.155	(*45*)	
$Nd_{0.95}Ba_{2.05}Cu_3O_y$	T	3.8989(5)		11.798(2)		
$NdBa_2Cu_3O_y$	O	3.8777(4)	3.9128(3)	11.781(1)		
		3.8670(7)	3.890(1)	11.788(2)		Heated O_2
		3.8546(8)	3.914(1)	11.736(2)	(*46*)	Prepared O_2
$Nd_{1.35}Ba_{1.65}Cu_3O_y$ ('123'-type)	O	3.8724(4)	3.8796(2)	11.781(1)		
$Nd_{1.44}Ba_{1.56}Cu_3O_y$ ('123'-type)	T	3.8884(6)		11.667(3)		
		3.8869(6)		11.668(1)		Heated O_2
$Nd_{1.5}Ba_{1.5}Cu_3O_y$ ('336'-type)	T	3.882(1)		11.680(3)		
		3.883(1)		11.691(2)		Heated O_2
$Nd_{3.53}Ba_{2.48}Cu_6O_y$ ('336'-type)	T	3.879(1)		11.584(3)		
Nd_3BaCuO_y	T	6.6993(5)		5.8199(7)		
$La_{3.6}Ba_{2.4}Cu_{1.8}O_{9.6}$	T	6.862(1)		5.871(1)	(*40*)	

Note. Formulas are deduced from crystallographic and mixed composition data.

[a] C, cubic; T, tetragonal; O, orthorhombic.

[b] This work, except as noted.

[c] Pseudo-tetragonal or pseudo-cubic phase.

TABLE IV

COMPARISON OF PHASES OBSERVED *in Air* AT ~950°C IN THE *Ln*–Ba–Cu–O (*Ln* = LANTHANOID) SYSTEMS

Ln	Phases reported															
	011	240[a]	220[a]	430	210	201	202	123	132	211	212	336	311	422	415	XP
La (*9*)	+				+	+		+			+	+		+	+	+[b]
Pr	+				+[d]	+		+				+				+[c]
Nd	+				+	+		+				+	+			
Eu (*10, 41*)	+				+	+		+	+	+		+				
Y (*4*)	+	+	+		+[e]		+	+	+[f]	+						
Er (*11*)	+	+[g]	+	+			+	+	+[g]	+						
Tm (*12*)	+	+	+	+			+	+	+	+						

Note. The first digit represents the lanthanoid content; the second, barium; and the last, copper. A '+' indicates the phase has been observed.

[a] 240 is actually $Ln_2Ba_4O_7 \cdot CO_2$ (*6, 47*); 220 is probably $Ln_2Ba_2O_5 \cdot CO_2$ (*6*).

[b] XP = $La_{2-x}Ba_xCuO_{4-(x/2)+\delta}$, according to Ref. (*9*).

[c] XP = $BaPrO_3$.

[d] $BaPr_2O_4$ preparable only in reducing atmosphere.

[e] According to Refs. (*20*) and (*48*) this phase exists above 1000°C.

[f] According to (*3*) '132' is absent; '253' and '152' are present instead.

[g] Our unpublished data.

Conclusions

Subsolidus ~950°C phase relationships established from the phase analysis results are presented in Figs. 1 and 2 for the Pr and Nd systems, respectively. The differences between the systems are striking and probably stem primarily from the greater praseodymium valence range. The phase diagram of the Pr–Ba–Cu–O system can be divided into 8 ternary compatible regions while that of Nd–Ba–Cu–O can be divided into 10. Only 3 ternary regions in the CuO-rich part of the diagrams are common between the systems.

The brown '311' phase appears unique to the Nd–Ba–Cu–O system. It is ubiquitous over much of the diagram. The stable '211'- and '132'-type phases found in closely related systems (*4, 41*) were not observed.

Between the compositions '123' and '336' both systems show solid–solution regions that were also found by Zhang *et al.* (*42*), although some of the details differ. These regions are lined in Figs. 1 and 2. Along the '123'–'336' tie line of the praseodymium system $Pr_{1+x}Ba_{2-x}Cu_3O_y$ solid solubility occurs over the limited composition range $-0.1 \le x \le 0.55$. All specimens showed tetragonal lattice parameters which decreased with increasing x values (see Table III). The crystal structure of the solid–solution $Nd_{1+x}Ba_{2-x}Cu_3O_y$ over the composition range $0.0 \le x \le 0.35$ is orthorhombic while that for $0.35 < x \le 0.76$ is tetragonal and exhibits paramagnetic properties (see Fig. 3). The upper limit of praseodymium substitution is less than would be expected from the Nd and La (*42, 43*) results, probably because the ion can exhibit mixed-valence. This mixed-valency definitely affects the Pr–Ba–Cu–O phase relationships and apparently also affects the superconducting properties of the '123' phase.

A summary of the phases reported stable in air near 950°C in selected *Ln*–Ba–Cu–O systems is presented in Table IV. A diversity of phase relationships results from changing the lanthanoid ion—from ionic radii size differences, the concomitant basicity variation, and the electronic structure change. The compounds observed in these Ln_2O_3–$BaCO_3$–CuO systems suggest that only the heavier Er and Tm systems are identical. Globally, the systems can be viewed in terms of the lighter and heavier lanthanoids with transitory variations within the two groups. Of the lanthanoids listed in Table IV only praseodymium has the ability to exhibit multiple valences and its system is unique.

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Note added in proof. Recent data indicate the Nd '311' and the La '422' structures are identical.

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