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The Gd–Ba–Cu–O System: Phase Relationships at ~950°C in Air

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A systematic X-ray powder diffraction study of the Gd_2O_3–$BaCO_3$–CuO system over the temperature range 920–980°C in ambient air is presented as a function of cation composition. In the pseudobinary regions the phases $BaGd_2O_4$, "$Gd_2Ba_4O_7$," Gd_2CuO_4, and $BaCuO_2$ were observed. Mass balance data suggest that "$Gd_2Ba_4O_7$" is actually $Gd_2Ba_4O_7 \cdot CO_2$. In the pseudoternary region the phases Gd_2BaCuO_5, $GdBa_3Cu_2O_y$, and $GdBa_2Cu_3O_{6.5+x}$ were identified. Although $GdBa_2Cu_3O_{6.5+x}$ exhibited minimal solid solution, $GdBa_3Cu_2O_y$ evidenced a significant solubility range. Lattice parameters are presented and from a phase analysis subsolidus relationships are constructed. The system is compared with related systems. © 1991 Academic Press, Inc.

Introduction

Discovery of high temperature superconductivity in the ternary region of the *Ln*–Ba–Cu–O (*Ln* = La–Lu, except Ce, Pr, and Tb) systems caused them to become an important as well as exciting area for study. Numerous experiments have demonstrated that the characteristics of the *Ln*–Ba–Cu–O phases depend greatly upon the preparatory procedure (*1*). Electron diffraction and phase studies of orthorhombic Y-"123" specimens prepared at relatively low temperatures under controlled O_2 partial pressures have demonstrated the presence of long range oxygen ordering and discrete superstructure phases which change with oxygen content (*2*). However, the global phase relationships of a number of *Ln* still remain unknown. Studies over the entire composition range have been established in the 900–1000°C temperature range in air only for the *Ln*–Ba–Cu–O systems: *Ln* = Y (*3–7*); La (*8, 9*); Pr and Nd (*10*); Sm (*11*); Eu (*12*); Er (*13*); and Tm (*14*). Similarities that might be expected when one trivalent lanthanoid ion is replaced by another have not been observed; lanthanoid ion size and basicity appear to be important factors in determining phase stability. Of the systems studied only those of the adjacent *Ln* pairs, Er and Tm, and Sm and Eu, appear to exhibit identical high temperature relationships.

The present study was undertaken to clarify phase relationships in the Gd–Ba–Cu–O system; to our knowledge only a partial subsolidus phase diagram in the CuO-rich region has been reported (*15*). We present a compilation of the compounds and phase compatibilities found in air in the 920–980°C temperature range which is high enough to

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allow equilibration in a resonable time frame, yet low enough to preclude melting.

Experimental

The reactants, Gd_2O_3 (99.9%, Research Chemicals, Phoenix, AZ), $BaCO_3$, and CuO (reagent grade, P. O. Ch, Gliwice, Poland), were monophasic by X-ray powder diffraction. Reagents 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 for 24 hr at 920–980°C, then air quenched by removal from the furnace. Some "123" products were annealed under a 1-bar dynamic O_2 atmosphere for 12 hr at 950°C and cooled subsequently to room temperature over a period of ~4 hr. Shorter cooling times did not appear to influence the structure of the products.

Phase analysis and characterization were effected by the Guinier X-ray powder diffraction technique as described previously (*11*). Lattice parameters calculated by a least-squares routine were refined with the program Appleman (*16*). X-Ray powder diffraction intensities were calculated with the program POWD12 (*17*).

In an effort to check for the presence of carbonate ions, the products of selected Gd–Ba–O mixtures were also subjected to mass balance and IR characterization. Mixtures of Gd_2O_3 and $BaCO_3$ in a 1 : 4 molar ratio, as well as a control sample of $BaCO_3$, were sintered 3 days at ~925°C, then subjected to X-ray powder diffraction analysis and, *via* the KBr procedure, to IR analysis. The mass loss of different ~1-g mixtures, heated at ~950°C, was monitored at 24 and 48 hr, after which X-ray diffraction data indicated onset of specimen decomposition as described below.

Results and Discussion

Initial molar compositions, sample numbers, phases observed, and specimen colors are compiled in Table I. Phase relationships are presented in Fig. 1. The numbers designated in the figure are keyed to the sample numbers listed in Table I. Lattice parameters and structure types for the seven phases that were observed together with selected literature data are presented in Table II.

The Pseudobinary Regions

The $BaCO_3$–CuO region. Only the well-characterized cubic $Im\bar{3}m$ $BaCuO_2$ (*18, 19*) was observed. Other reported compounds (*5, 20*) are unstable under the reaction conditions employed in this investigation.

The Gd_2O_3–$BaCO_3$ region. Observed and calculated interplanar *d*-spacings and observed intensities for the previously unreported "$Gd_2Ba_4O_7$" are presented in Table III. The tetragonal lattice parameters (see Table II) agree well with those reported for the yttrium analogue (*21, 22*) and homologous "$Ln_2Ba_4O_7$" (*Ln* = Dy, Ho, Er, Tm, and Yb) species (*23*). However, on the basis of mass balance data the *Ln* = Y compound has been reported to be $Y_2Ba_4O_7 \cdot CO_2$ rather than $Y_2Ba_4O_7$ (*7*). Our mass balance data are consistent with this report, supportive of the oxidecarbonate formula.

Numerous IR analyses were performed in an effort to verify the presence of the carbonate ion. Carbonate bands were observed at 1460, 1065, 865, and 700 cm^{-1} in the heated $BaCO_3$ control specimen, but corresponding bands could not be found in the spectrum of an *Ln* = Gd compound which was very pure by X-ray diffraction. The absence of $BaCO_3$ reflections in the "$Gd_2Ba_4O_7$" X-ray diffraction pattern, unfortunately, does not ensure its absence from the specimen. The mass balance data could also reflect a small $BaCO_3$ impurity in $Gd_2Ba_4O_7$. A $BaCO_3$ level of less than 3% could explain the mass balance data, and would probably not be detected by X-ray powder diffraction. Attempts to prepare $Gd_2Ba_4O_7$ from Ba_2O_2 and CuO led to incomplete reaction as might be expected were CO_2 either present in the sample as an impu-

TABLE I

INITIAL MIXED CATION COMPOSITION AND PHASES OBSERVED IN THE $BaCO_3$–Gd_2O_3–CuO SYSTEM

Sample No.	Initial composition[a]	Phases observed	Color
1	0:1:1	$BaCuO_2$	Black
2	1:2:0	“$Gd_2Ba_4O_7$”[b]	White
3	1:1:0	$BaGd_2O_4$ + “$Gd_2Ba_4O_7$”	White
4	4:3:0	$BaGd_2O_4$ + “$Gd_2Ba_4O_7$”	White
5	2:1:0	$BaGd_2O_4$	White
6	2:0:1	Gd_2CuO_4	Black
7	1:0:1	Gd_2CuO_4 + CuO[c]	Black
8	2:0:3	Gd_2CuO_4 + CuO	Black
9	2:1:1	Gd_2BaCuO_5	Green
10	4:1:1	Gd_2BaCuO_5 + Gd_2O_3	Light green
11	7:1:2	Gd_2BaCuO_5 + Gd_2CuO_4 + Gd_2O_3	Dark green
12	7:2:1	Gd_2BaCuO_5 + $BaGd_2O_4$ + Gd_2O_3	Light green
13	1:3:2	$GdBa_3Cu_2O_y$	Black
14	1:4:3	$GdBa_3Cu_2O_y$ + $BaCuO_2$	Black
15	5:28:17	$Gd_{1-x}Ba_{3+x}Cu_2O_y$ + $BaCuO_2$	Black
16	5:61:34	$Gd_{1-x}Ba_{3+x}Cu_2O_y$ + $BaCuO_2$ + BaO	Black
17	1:4:2	$GdBa_3Cu_2O_y$ + BaO[c]	Black
18	1:3:1	Gd_2BaCuO_5 + $GdBa_3Cu_2O_y$ + BaO	Black and green
19	2:4:3	Gd_2BaCuO_5 + $GdBa_3Cu_2O_y$	Black and green
20	1:2:1	Gd_2BaCuO_5 + $GdBa_3Cu_2O_y$ + BaO[c]	Black and green
21	2:2:1	Gd_2BaCuO_5 + BaO[c]	Green
22	2:5:1	Gd_2BaCuO_5 + BaO	Green
23	2:7:1	Gd_2BaCuO_5 + BaO	Grey-green
24	4:5:1	Gd_2BaCuO_5 + “$Gd_2Ba_4O_7$”	Light green
25	5:4:1	Gd_2BaCuO_5+ $BaGd_2O_4$ + “$Gd_2Ba_4O_7$”[c]	Light green
26	1:2:3	$GdBa_2Cu_3O_{6.5+x}$	Black
27	3:3:4	$GdBa_2Cu_3O_{6.5+x}$ + Gd_2BaCuO_5	Black and green
28	1:4:5	$GdBa_2Cu_3O_{6.5+x}$ + $BaCuO_2$	Black
29	1:1:2	$GdBa_2Cu_3O_{6.5+x}$ + Gd_2BaCuO_5 + CuO[c]	Black and green
30	2:1:3	Gd_2BaCuO_5 + CuO	Brown and black
31	3:3:14	$GdBa_2Cu_3O_{6.5+x}$ + CuO + Gd_2BaCuO_5	Black and green
32	1:2:7	$GdBa_2Cu_3O_{6.5+x}$ + CuO	Black
33	2:9:9	$BaCuO_2$ + Gd_2BaCuO_5[c]	Black
34	2:5:5	$BaCuO_2$ + Gd_2BaCuO_5	Black and green
35	2:3:3	Gd_2BaCuO_5 + $BaCuO_2$[c]	Green and black

[a] *Ln* : Ba : Cu molar ratio.

[b] See text for discussion on “$Gd_2Ba_4O_7$.”

[c] Trace quantities of substance detected.

rity or absorbed from the atmosphere. Because of the reproducibility of the mass balance data and our inability to prepare the specimen when Ba_2O_2 was a reactant, we believe that this “240” phase is described best as a carbonate. We also attempted synthesis of the “$Ln_2Ba_4O_7$” species for Ln = Dy and Ho. Here again mass balance data are consistent with an oxidecarbonate, $Ln_2Ba_4O_7 \cdot CO_2$, suggesting that the data reported for this phase in (*23*) actually describe oxidecarbonates rather than pure oxides. The interaction of CO_2 with the yttrium-“123” compound was examined recently (*24*) and even specimens prepared in the absence of CO_2 were found to contain

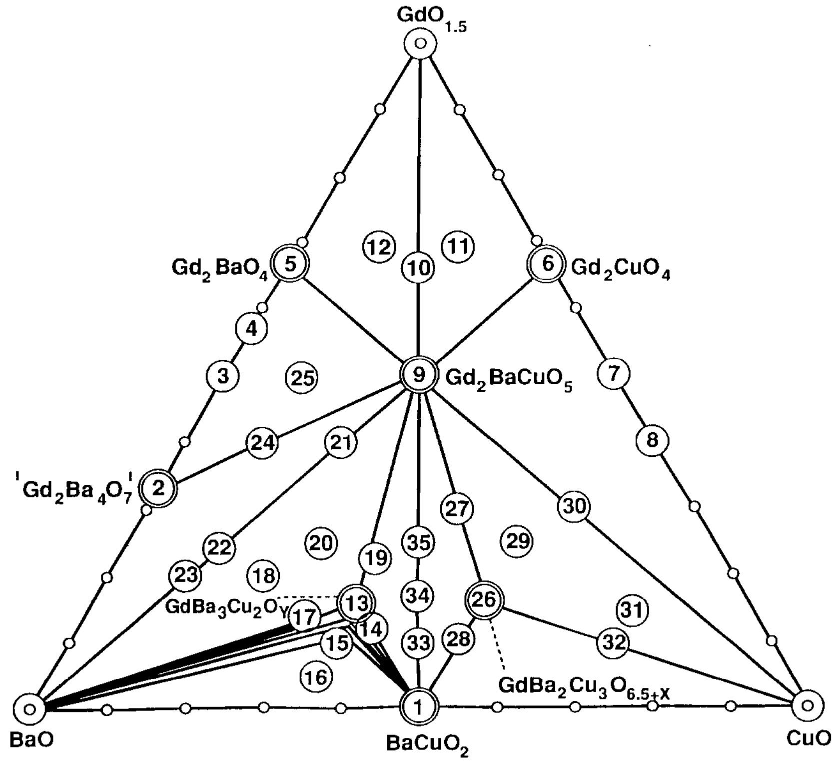

FIG. 1. Phase diagram projection on the Gibbs triangle of composition for the system Gd_2O_3–Ba CO_3–CuO at ~950°C (1223 K). Regions in which solid solution was observed are lined. See text for discussion on "$Gd_2Ba_4O_7$."

a small concentration of CO_2. All of these complex basic oxides may contain some degree of CO_2 contamination.

At temperature above ~950°C $Gd_2Ba_4O_7 \cdot CO_2$ decomposes into $BaGd_2O_4$(s) and BaO(s). This transformation can be represented by

$$Gd_2O_3(s) + 4\,BaCO_3(s) \xrightarrow{<\sim 950^\circ C} Gd_2Ba_4O_7 \cdot CO_2(s) + 3\,CO_2(g) \xrightarrow{>950^\circ C} BaGd_2O_4(s) + 3BaO(s) + CO_2(g).$$

Previously characterized $BaGd_2O_4$ (*25, 26*), which is isostructural with orthorhombic $CaSc_2O_4$ (*27*), was also identified. Since only a portion of the $BaGd_2O_4$ X-ray powder diffraction pattern could be found in the literature (*26, 28*), the complete set of observed and calculated interplanar *d*-spacings and intensities is presented in Table IV.

It is noteworthy that $Ln_2Ba_2O_5$- and $Ln_4Ba_3O_9$-type phases characteristic of this region in the related heavy lanthanoid systems (*22, 23*) could not be prepared.

The Gd_2O_3–CuO region. The compound Gd_2CuO_4 has been reported and was the only phase observed. Its X-ray powder diffraction pattern was indexed with tetragonal lattice parameters that are in good agreement with reported values (*29*). X-ray powder diffraction intensities calculated with the atomic parameters reported for K_2NiF_4-type La_2CuO_4 (*30*) agreed well with observed values. Attempts to prepare the $Ln_2Cu_2O_5$-type compound reported for *Ln* = Y, Tb–Lu (*31*) met with failure.

TABLE II

LATTICE PARAMETER AND SYMMETRY DATA ON PHASES OBSERVED IN THE $BaCO_3$–Gd_2O_3–CuO SYSTEM

Compound	Symmetry[a]	Lattice parameters			Ref.[b]	Notes
		a(Å)	b(Å)	c(Å)		
$BaGd_2O_4$	O	10.488(3)	3.516(9)	12.261(3)		
		10.490	3.526	12.270	*(25)*	
"$Gd_2Ba_4O_7$"[c]	T	4.421(6)		28.603(5)		
Gd_2CuO_4	T	3.899(1)		11.898(4)		
		3.89		11.861	*(29)*	
$BaCuO_2$	C	18.277(5)				
		18.2772(2)			*(19)*	
Gd_2BaCuO_5	O	7.221(2)	12.313(4)	5.734(1)		
		7.226(2)	12.321(2)	5.724(1)	*(32)*	
		7.225	12.316	5.722	*(15)*	
$GdBa_3Cu_2O_y$	T	5.8089(9)		8.036(1)		
$Gd_{1-x}Ba_{3+x}Cu_2O_y$		5.818(1)		8.061(2)		*d*
$GdBa_2Cu_3O_{6.5+x}$	O	3.840(3)	3.901(2)	11.692(6)		
		3.834(2)	3.900(2)	11.674(3)		*e*
		3.859(1)	3.885(2)	11.759(3)	*(39)*	
$Gd_{1+x}Ba_{2-x}Cu_3O_y$		3.837(1)	3.886(2)	11.691(4)		

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

[b] This work, except as noted.

[c] Actual composition probably $Gd_2Ba_4O_7 \cdot CO_2$.

[d] Largest lattice parameters observed as x was varied.

[e] Annealed in a partial pressure of $O_2 \approx 740$ Torr.

The Pseudoternary Region

Three phases are present: Gd_2BaCuO_5, "211"; $GdBa_2Cu_3O_{6.5+x}$, "123"; and $GdBa_3Cu_2O_y$, "132." The "green" "211" compound crystallizes in orthorhombic symmetry with lattice parameters (see Table II) in good agreement with literature values (*15, 32*).

The "123" phase when prepared in air yielded a well-defined monophasic X-ray powder diffraction pattern indexable on orthorhombic lattice parameters (see Table II) that agree well with literature values (*33*). This product did not show the Meissner effect at liquid nitrogen temperatures, but the high-T_c version could be prepared by reheating the orthorhombic specimen in a dynamic oxygen atmosphere ($pO_2 \sim 740$ Torr). Refined lattice parameters of the superconducting phase are slightly smaller than those of the nonsuperconducting analogue (see Table II); the unit cell volume decreases ~0.6 Å^3 from 175.1(2) Å^3 to 174.5(2) Å^3 upon oxidation. Similar volume changes have been reported for the Eu and Tm superconducting phases (*12, 14*). A unit cell volume decrease of 2.5 Å^3 was observed for $YBa_2Cu_3O_{7-\delta}$ (*34*) when δ was changed from 1 to 0 and presumably results from an increase in the copper ion oxidation state counterbalanced by the presence of additional oxide ions. Under the preparative procedure employed a "123" tetragonal modification could not be prepared.

Numerous Gd-rich "123" specimens yielded almost invariant lattice parameters that suggest only minimal solid solution. However, the "123" compound does exhibit a narrow solid solution region formed by gadolinium substitution on the Ba ion site. According to (*35*) the stability range of

TABLE III

MILLER INDICES, OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS, AND OBSERVED INTENSITIES FOR THE "$Gd_2Ba_4O_7$" ($Gd_2Ba_4O_7 \cdot CO_2$) PHASE

h	*k*	*l*	d_0(Å)	d_c(Å)	I_0[a]	*h*	*k*	*l*	d_0(Å)	d_c(Å)	I_0[a]
0	0	4	7.170	7.151	*m*	2	0	0	2.212	2.210	*vs*
1	0	1	4.366	4.369	*w*	2	0	4	2.110	2.112	*s*
1	0	3	4.020	4.011	*vw*	0	0	14	2.045	2.043	*m*
0	0	8	3.582	3.575	*vw*	2	1	3	1.9353	1.9358	*vw*
1	0	5	3.506	3.498	*m*	1	1	12	1.8952	1.8954	*vw*
1	1	0	3.125	3.126	*vs*	2	1	5	1.8692	1.8685	*w*
1	0	7	3.009	3.001	*vvs*	2	1	7	1.7802	1.7796	*vs*
1	1	4	2.868	2.864	*vw*	1	1	14	1.7106	1.7102	*m*
1	0	9	2.585	2.580	*s*	2	0	12	1.6208	1.6207	*w*
0	0	12	2.381	2.384	*vw*	2	1	11	1.5737	1.5738	*w*
1	1	8	2.356	2.353	*m*	2	2	0	1.5632	1.5629	*w*
1	0	11	2.244	2.241	*m*						

[a] Estimated from Guinier film.

the solid solution region $Gd_{1+x}Ba_{2-x}Cu_3O_y$ is limited to $0 \leq x \leq 0.2$, but our $Gd_{1.2}Ba_{1.8}Cu_3O_y$ preparation contained an impurity phase. Thus, the solubility limit must be less than $x = 0.2$. This discrepancy may result from different synthesis conditions, e.g., temperature of firing and annealing.

In the $BaCO_3$(BaO)-rich ternary region the tetragonal "132" phase was observed. Its lattice parameters are close to those reported for $YBa_3Cu_2O_y$ (*5*) and other analogous *Ln*-containing compounds (*36*). Interplanar *d*-spacings and intensities of the "132" phase are presented in (*36*). Samples produced from reactants in the mole ratio Gd : Ba : Cu = 1 : 3 : 2 always contained a small amount of the "211" green phase, an observation that correlates well with that of Roth *et al.* (*5*) on the yttrium analogue. Replacement of gadolinium in the "132" phase with Ba produces an extended phase region. Specimens of the nominal series $Gd_{1-x}Ba_{3+x}Cu_2O_y$ were prepared; lattice parameters of the preparation that yielded the largest cell volume are presented in Table II.

The experimental results permit construction of the phase diagram projection on the Gibbs triangle of composition as shown in Fig. 1. The phase subsolidus compatibilities in air near the investigation temperature of 950°C as determined by the seven phases described previously divide the diagram into eleven ternary regions. From one side this phase diagram is similar to those of the yttrium (*5*), erbium (*13*), and thulium (*14*) systems, and from the other side it is similar to that of europium (*12*). This behavior might indeed be expected given the ionic radii variation across the lanthanoids (*37*). Since the eruopium and yttrium systems differ appreciably, the Gd system might be expected to be transitory. The ternary gadolinium analogue of $Eu_3Ba_3Cu_6O_{13.5+x}$ "336," which is not present in the yttrium system, could indeed not be prepared. Other ternary phases, "123" and "211," present in both the Y and the Eu systems are also present here. The ternary "132" phase has been reported in the *Ln* = Sm–Tm (except Tb) and Y systems, but recent reports suggest that in the latter case it is actually a mixture of "152" and "253" phases (*4*). Since the "132" phase could never be prepared pure, our reaction conditions must be at the thermo-

TABLE IV

MILLER INDICES AND OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS AND INTENSITIES FOR $BaGd_2O_4$

h	k	l	d_o(Å)	d_c(Å)	I_o^a	I_c^b	h	k	l	d_o(Å)	d_c(Å)	I_o^a	I_c^b
1	0	2	5.274	5.293	*vw*	1	4	1	0	2.101	2.102	*s*	22
2	0	0		5.244		5	4	1	1	2.071	2.072	*m*	11
2	0	2	3.989	3.985	*m*	9	0	1	5	2.011	2.011	*w*	5
0	1	1	3.383	3.380	*m*	9	2	0	6	1.9046	1.9040	*s*	11
1	1	1	3.216	3.217	*m*	8	2	1	5	1.8781	1.8780	*m*	4
0	0	4	3.066	3.065	*vs*	44	4	1	3		1.8692		2
3	0	2	3.041	3.037	*vvs*	100	3	0	6	1.7571	1.7642	*s*	16
							0	2	0		1.7580		18
							6	0	0		1.7480		12
1	0	4	2.932	2.942	*vs*	7	1	1	6	1.7420	1.7422	*m*	17
1	1	2		2.929		71							
2	1	0	2.920	2.920	*s*	3	4	1	4	1.7332	1.7335	*s*	21
2	1	1	2.844	2.841	*w*	5	5	0	4		1.7311		4
1	1	3	2.584	2.583	*s*	21	5	1	2	—	1.7283		15
3	1	1	2.431	2.430	*m*	7	2	1	6	1.6745	1.6743	*w*	6
4	0	2	2.411	2.411	*w*	33	4	0	6	1.6117	1.6118	*vw*	3
2	1	3	2.376	2.376	*w*	1	4	1	5	1.5959	1.5959	*vw*	3
1	1	4	2.227	2.256	*w*	8							
2	0	5		2.221		0							
3	1	3	2.115	2.120	*vs*	9							
2	1	4		2.114		31							

[a] Estimated from Guinier film.

[b] Intensities calculated with $CaSc_2O_4$ atomic parameters (*27*) and the isotropic thermal parameters: Gd, 0.9; Ba, 1.0; O, 1.5 Å^2.

dynamic limit of phase stability. Composition–O_2 partial pressure phase studies on yttrium "123" phases suggest that this "132" phase could be prepared under lower partial pressures of oxygen (*38*).

In the pseudobinary *Ln*–Ba–O and *Ln*–Cu–O regions the "210" BaLn_2O_4 is common to the *Ln* = Eu, Gd and (above 1000°C) Y systems, but "240" $Ln_2Ba_4O_7$ occurs only for *Ln* = Gd and Y. The yttrium system also exhibits the "220" $Ln_2Ba_2O_5$ phase in common with the *Ln* = Er and Tm systems, and the latter evidence additionally a "430" phase, both of which are absent in the *Ln* = Gd and Eu systems. As a consequence of these differences the Gibbs triangular phase regions in the various systems differ considerably even though preparatory temperatures are essentially the same, ~950°C, and three pseudoternary phases are common across all systems studied. Thus, the gadolinium system along with that of yttrium appears transitory between those of europium and erbium/thulium.

A summary of the phases reported over the temperature region 900–1000°C in *Ln*–Ba–Cu–O systems (where *Ln* = La, Pr, Nd, Sm, Eu, Gd, Y, Er, and Tm) is presented in (*11*). These data demonstrate the diversity of the phase relationships in the *Ln*–Ba–Cu–O systems. The diversity probably results from changes in the lanthanoid(III) ionic radii, the concomitant basicity variation, and possibly electronic structure differences. From this comparison it appears that these Ln_2O_3–$BaCO_3$–CuO systems must be divided into at least three subgroups: the first characteristic of La, the second specific for Eu, and the third common to the heavier lanthanoids, the Y-type elements, with a gradual variation within the latter group.

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References

1. See for example Y. Zhang, W. Wong-ng, B. Morosin, C. R. Hubbard, J. M. Steward, and S. W. Freiman, *Physica C* **152,** 130 (1988); R. J. Cava, J. J. Krajewski, W. F. Peck Jr., B. Batlogg, L. W. Rupp, Jr., R. M. Fleming, A. C. W. P. James, and P. Marsh, *Nature* **338,** 328 (1989); J. W. Severin, G. De With, and H. A. M. Van Hal, *Physica C* **152,** 159 (1988); R. S. Liu, C. T. Chang, and P. T. Wu, *Inorg. Chem.* **28,** 154 (1989); S. Jin, H. M. O'Bryan, P. K. Gallagher, T. H. Tiefel, R. J. Cava, R. A. Fastnacht, and G. W. Kammlott, *Physica C* **165,** 415 (1990).
2. See for example R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, *Nature (London)* **340,** 619 (1989); R. Beyers, B. T. Ahn, G. Gorman, V. Y. Lee, S. S. P. Parkin, M. L. Ramirez, K. P. Roche, J. E. Vazquez, T. M. Gür, and R. A. Huggins, *Physica C* **162–164,** 548 (1989).
3. L. Soderholm, D. W. Capone II, D. G. Hinks, J. D. Jorgensen, I. K. Schuller, J. Grace, K. Zhang, and C. U. Segre, *Inorg. Chim. Acta* **140,** 167 (1987); D. G. Hinks, L. Soderholm, D. W. Capone II, J. D. Jorgensen, I. K. Schuller, C. U. Segre, K. Zhang, and J. Grace, *Appl. Phys. Lett.* **50,** 1688 (1987); G. R. Wagner, A. J. Panson, and A. I. Braginski, *Phys. Rev. B* **36,** 7124 (1987); K. G. Frase and D. R. Clarke, *Adv. Ceram. Mater.* **2,** 295 (1987); G. Wang, S.-J. Hwu, S. N. Song, J. B. Ketterson, D. L. Marks, K. R. Poeppelmeier, and T. O. Mason, *Adv. Ceram. Mater.* **2,** 313 (1987); S.-J. Hwu, S. N. Song, J. B. Ketterson, T. O. Mason, and K. R. Poeppelmeier, *J. Am. Ceram. Soc.* **70,** C165 (1987); J. Hahn, T. O. Mason, S.-J. Hwu, and K. R. Poeppelmeier, *Chemtronics* **2,** 126 (1987).
4. W. Reichelt, H. Wilhelm, G. Försterling, and H. Oppermann, *Cryst. Res. Technol.* **24,** K26 (1989).
5. R. S. Roth, K. L. Davis, and J. R. Dennis, *Adv. Ceram. Mater.* **2,** 303 (1987).
6. K. G. Frase and D. R. Clarke, *Adv. Ceram. Mater.* **2,** 295 (1987).
7. D. M. DeLeeuw, C. A. H. A. Mutsaers, C. Langereis, H. C. A. Smoorenburg, and P. J. Rommers, *Physica C* **152,** 39 (1988).
8. L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, *J. Solid State Chem.* **37,** 151 (1981); S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, *Jpn. J. Appl. Phys.* **26,** L1 (1987); H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *Jpn. J. Appl. Phys.* **26,** L123 (1987).
9. D. Klibanow, K. Sujata, and T. O. Mason, *J. Amer. Ceram. Soc.* **71,** C267 (1988).
10. S. A. Hodorowicz, J. Czerwonka, and H. A. Eick, *J. Solid State Chem.* **88,** 391 (1990).
11. J. Czerwonka and H. A. Eick, *J. Solid State Chem.* **90,** 69 (1991).
12. S. A. Hodorowicz, A. Lasocha, W. Lasocha, and H. A. Eick, *J. Solid State Chem.* **75,** 270 (1988).
13. S. A. Hodorowicz, A. Lasocha, W. Lasocha, A. Chodorowicz, and H. A. Eick, *Acta Phys. Pol. A* **75,** 437 (1989).
14. E. Hodorowicz, S. A. Hodorowicz, and H. A. Eick, *Physica C* **158,** 127 (1989).
15. J. K. Liang, X. T. Xu, G. H. Rao, S. S. Xie, X. Y. Shao, and Z. G. Duan, *J. Phys. D.* **20,** 1324 (1987).
16. D. W. Appleman, D. S. Handwerker, and H. T. Evans, "Program X-Ray," Geological Survey, U.S. Department of the Interior, Washington, DC (1966).
17. D. K. Smith, M. C. Nichols, and M. E. Zolensky, "A FORTRAN IV Program for Calculating X-Ray Powder Diffraction Patterns, Version 10," Pennsylvania State University, University Park, PA (1983).
18. R. Kipka and H. Müller-Buschbaum, *Z. Naturforsch. B* **32,** 121 (1977).
19. M. T. Weller and D. R. Lines, *J. Solid State Chem.* **82,** 21 (1989).
20. C. L. Teske and H. Müller-Buschbaum, *Z. Naturforsch. B* **27,** 296 (1972).
21. W. Kwestroo, H. A. M. van Hal, and C. Langereis, *Mater. Res. Bull.* **9,** 1631 (1974).
22. L. M. Kovba, L. N. Lykova, and E. V. Antipov, *Russ, J. Inorg. Chem.* **28**(3), 409 (1983).
23. E. Hodorowicz, S. A. Hodorowicz, and H. A. Eick, *J. Solid State Chem.* **84,** 401 (1990).
24. T. B. Lindemer, C. R. Hubbard, and J. Brynestad, *Physica C* **167,** 312 (1990).
25. L. M. Lopato, *Ceramurgia Int.* **2,** 18 (1986).

26. T. L. Barry and R. Roy, *J. Inorg. Nucl. Chem.* **29,** 1243 (1967).
27. H. Müller-Buschbaum and H. G. Schnering, *Z. Anorg. Allg. Chem.* **336,** 295 (1965).
28. Powder Diffraction File, JCPDS: International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19801, Data 1983, File No. 19-105.
29. Powder Diffraction File, JCPDS: International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19801, Data 1983, File No. 24-422.
30. J. M. Longo and P. M. Raccah, *J. Solid State Chem.* **6,** 526 (1973).
31. N. Kimizuka, E. Takayama, S. Horiuchi, A. Yamamoto, and T. Fujita, *J. Solid State Chem.* **42,** 322 (1982).
32. C. Michel and B. Raveau, *J. Solid State Chem.* **43,** 73 (1982).
33. J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36,** 226 (1987).
34. C. N. Rao, *J. Solid State Chem.* **74,** 147 (1988).
35. K. Zhang, B. Dabrowski, C. U. Segre, D. G. Hinks, I.K. Schuller, J. D. Jorgensen, and M. Slaski, *J. Phys. C* **20,** L935 (1987).
36. S. A. Hodorowicz, E. Hodorowicz, A. Chodorowicz, and H. A. Eick, *Cryst. Res. Technol.* **24,** K71 (1989).
37. R. D. Shannon, *Acta Crystallogr. Sect. A* **32,** 751 (1976).
38. B. T. Ahl, V. Y. Lee, R. Beyers, T. M. Gür, and R. A. Huggins, *Physica C* **162–164,** 883 (1989).
39. J. A. Campa, J. M. Gomez de Salazar, E. Guiterrez-Puebla, M. A. Monge, I. Rasines, and C. Ruiz-Valero, *Phys. Rev. B* **37,** 529 (1988).