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The Dy- and Ho–Ba–Cu–O Systems: Phase Relationships in Air at ~950°C and Crystal Chemistry Comparisons

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Phase equilibria in air at ~950°C are presented for the systems Ln_2O_3–$BaCO_3$–CuO, Ln = Dy and Ho, as a function of cation molar ratios. Symmetry data and unit cell parameters derived from powder X-ray diffraction data and phase compatibilities are presented for the seven Ln : Ba : Cu phases preparable in air between 930–980°C: '011,' $BaCuO_2$; '202,' $Ln_2Cu_2O_5$; '220,' $Ln_2Ba_2O_5$; '240,' $Ln_2Ba_4O_7$; '211,' Ln_2BaCuO_5; '123,' $LnBa_2Cu_3O_x$; and '184,' $LnBa_8Cu_4O_y$. A solid solution region which can exist in two crystallographic modifications prevails around '184.' No other compound exhibits solid solution. In the BaO-rich region phase compatibilities change above 950°C when the '220' phase converts into the '240' phase. The phases observed in the CuO-rich region of the Ln–Ba–Cu–O systems that exhibit '123'-type superconductivity, Ln = La–Tm, are correlated with Ln^{3+} ionic radii.

Introduction

The discovery of $YBa_2Cu_3O_{7-\delta}$ superconductivity at 90 K (*1*) sparked intensive studies of this and related compounds, and comparable levels of superconductivity have been reported in most Ln–Ba–Cu–O (Ln = lanthanoid) systems (*2–6*). Numerous experiments have demonstrated that the characteristics of the Ln–Ba–Cu–O phases depend greatly on the preparatory procedure (*7*). Impurity phases can also affect the sintering rate and crystal morphology and may act as flux-pinning centers. Thus knowledge of the phase compatibilities can help both to improve the properties of the bulk ceramics and to achieve specimen reproducibility. In addition, through comparative studies of phase equilibria our understanding of the physical properties of the high-temperature superconducting phase may be enhanced. Numerous Ln–Ba–Cu–O systems have been examined over the *entire composition range* at temperatures of ~900–1000°C in air: Ln = Y (*8–14*), La (*15–17*), Pr and Nd (*18*), Sm (*19*), Eu (*20*), Gd (*21, 22*), Er (*23*), and Tm (*24*). These studies have demonstrated that even at the same temperature phase compatibilities vary as the lanthanoid ion is changed.

We report herein the phase compatibilities and some crystal chemistry aspects in the pseudo-ternary and -binary regions of the title systems in the 930–980°C range typically necessary for attainment of equilibrium. To our knowledge only a partial subsolidus phase diagram of the CuO-rich region of the Ln = Ho system has been reported (*25*).

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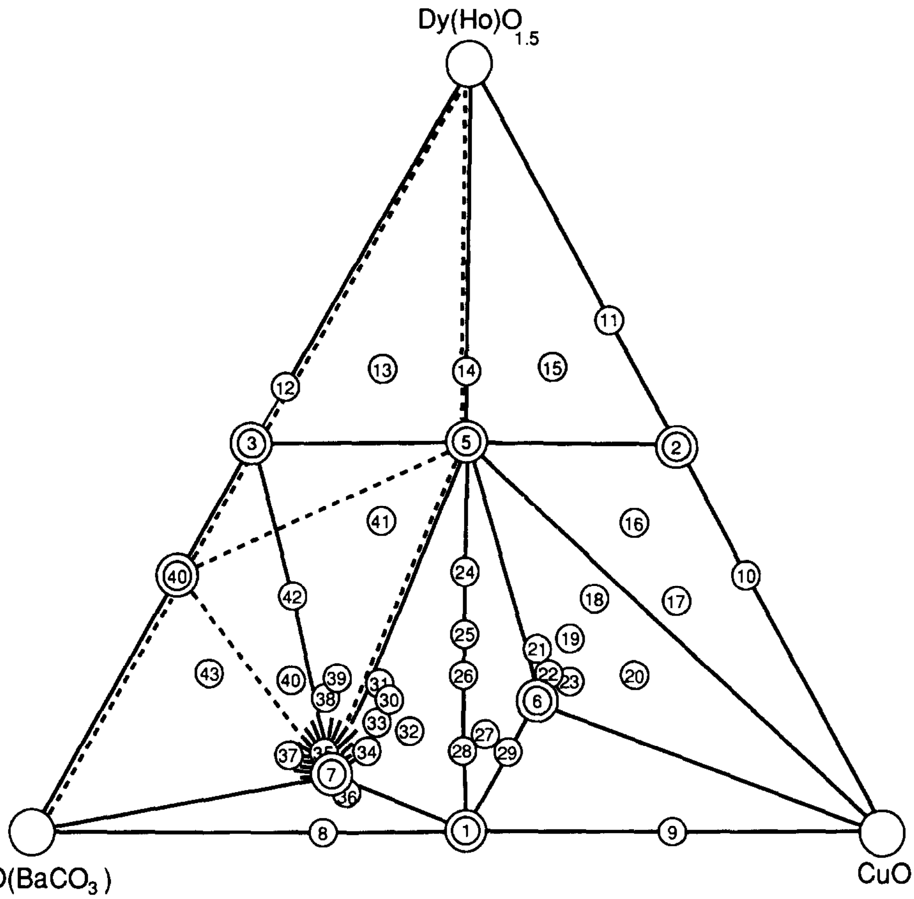

FIG. 1. Subsolidus phase compatabilities in air at 930–980°C in the *Ln*–Ba–Cu–O (*Ln* = Dy, Ho) system. The dashed lines portray phase relationships above 950°C. The compounds are (1) '011,' $BaCuO_2$; (2) '202,' $Ln_2Cu_2O_5$; (3) '220,' $Ln_2Ba_2O_5$; (4) '240,' $Ln_2Ba_4O_7$; (5) '211,' Ln_2BaCuO_5; (6) '123,' $LnBa_2Cu_3O_x$; and (7) '184,' $LnBa_8Cu_4O_y$. Compounds '220,' '240,' and '184' may be oxidecarbonates.

Experimental

All specimens were prepared by a solid state reaction technique. High purity Ln_2O_3 (99.99%, Research Chemicals, Phoenix, AZ), $BaCO_3$ (reagent, J. T. Baker Co., Phillipsburg, NJ), and CuO (reagent, Mallinckrodt, St. Louis, MO) served as starting materials. Barium carbonate was dried by heating the powder at 200°C; Ln_2O_3 was heated at ~800°C; CuO was used as received. Stoichiometric quantities of the reagents weighed to an accuracy of ~0.1 mg were hand-mixed under acetone with an agate mortar and pestle, dried, and then mixed again. A similar heat treatment procedure was used for most preparations. Mixtures confined in alumina boats were heated at 930–980°C, ground, reheated at the same temperature, and then usually air-quenched by removal from the hot furnace so that they cooled to room temperature in about 5 min. In some instances mixtures were heated for 48 hr at 930°C with intermediate grindings and then cooled slowly in the furnace to ~300°C before removal.

All intermediate and final products were examined by X-ray powder diffraction with

TABLE I

PHASES OBSERVED IN THE Ln_2O_3–BaO($BaCO_3$)–CuO (Ln = Dy AND Ho) SYSTEMS

Sample no.	Initial composition[a]	Heat treatment[b]	Phases observed	Color
1	0:1:1	950/24	$BaCuO_2$ = '011'	Black
2	1:0:1	950/48	$Ln_2Cu_2O_5$ + Ln_2O_3 + CuO	Blue-green
		1000/48	$Ln_2Cu_2O_5$ = '202'	Turquoise
3	1:1:0	930/14	$Ln_2Ba_2O_5$[c] = '220'	Cream
		980/20	$Ln_2Ba_4O_7$[c] + Ln_2O_3	Cream
4	1:2:0	930/14	$Ln_2Ba_2O_5$[c] + BaO	Cream
		980/20	$Ln_2Ba_4O_7$[c] = '240'	Cream
5	2:1:1	950/48	Ln_2BaCuO_5 = '211'	Green
6	1:2:3	950/48	$LnBa_2Cu_3O_x$ = '123'	Black
7	1:8:4	930/48[d]	$LnBa_8Cu_4O_y$ = '184'	Black-green
8	0:2:1	950/24	$BaCuO_2$ + BaO[e]	Gray
9	0:1:3	950/24	$BaCuO_2$ + CuO	Black
10	1:0:2	1000/48	$Ln_2Cu_2O_5$ + CuO	Dark turquoise
11	2:0:1	1000/48	$Ln_2Cu_2O_5$ + Ln_2O_3	Blue-green
12	4:3:0	930/14	$Ln_2Ba_2O_5$[c] + Ln_2O_3[f]	Cream
13	6:3:1	930/14	$Ln_2Ba_2O_5$[c] + Ln_2BaCuO_5 + Ln_2O_3[f]	White-green
		980/20	$Ln_2Ba_4O_7$[c] + Ln_2BaCuO_5 + Ln_2O_3	White-green
14	3:1:1	950/48	Ln_2BaCuO_5 + Ln_2O_3	Light green
15	6:1:3	1000/48	Ln_2BaCuO_5 + $Ln_2Cu_2O_5$ + Ln_2O_3	Light green
16	4:1:5	950/48	Ln_2BaCuO_5 + $Ln_2Cu_2O_5$ + CuO[f]	Green-blue
17	3:1:6	950/48	Ln_2BaCuO_5 + $Ln_2Cu_2O_5$ + CuO	Dark green
18	3:2:5	950/48	Ln_2BaCuO_5 + CuO[f] + $LnBa_2Cu_3O_x$[f]	Dark green
19	1:1:2	950/48	$LnBa_2Cu_3O_x$ + Ln_2BaCuO_5 + CuO[f]	Dark green
20	1:1:3	950/48	$LnBa_2Cu_3O_x$ + CuO + Ln_2BaCuO_5	Dark gray
21	12:16:25	930/48[d]	Ln_2BaCuO_5 + $LnBa_2Cu_3O_x$	Dark gray
22	2:3:5	930/48[d]	$LnBa_2Cu_3O_x$ + Ln_2BaCuO_5[f] + CuO[f]	Dark gray
23	8:11:21	930/48[d]	$LnBa_2Cu_3O_x$ + Ln_2BaCuO_5[f] + CuO[f]	Dark gray
24	1:1:1	950/48	Ln_2BaCuO_5 + $LnBa_2Cu_3O_x$[f]	Green and black
25	2:3:3	930/48[d]	Ln_2BaCuO_5 + $BaCuO_2$[f]	Green and black
		950/48	Ln_2BaCuO_5 + '011'[f] + $LnBa_8Cu_4O_y$[f,g] + '123'	Green and black
26	1:2:2	950/48	Ln_2BaCuO_5 + '011' + $LnBa_8Cu_4O_y$[f,g] + '123'	Green and black
		980/24	Ln_2BaCuO_5 + '011' + '123'[f]	Green and black
27	3:10:11	930/48[d]	$LnBa_2Cu_3O_x$ + '011' + Ln_2BaCuO_5[f]	Black
28	2:9:9	950/48	'011' + '211'[f] + $LnBa_2Cu_3O_x$[f] + $LnBa_8Cu_4O_y$[f]	Black
29	1:4:5	950/48	$LnBa_2Cu_3O_x$ + $BaCuO_2$	Black
30	1:3:2	950/48	Ln_2BaCuO_5[f] + $LnBa_8Cu_4O_y$[g] + '011'	Black-green
31	3:8:5	950/48	Ln_2BaCuO_5 + $LnBa_8Cu_4O_y$[g]	Dark green
32	1:4:3	950/48	$LnBa_8Cu_4O_y$[g] + $BaCuO_2$ + Ln_2BaCuO_5	Black-green
33	3:11:7	930/48[d]	$LnBa_8Cu_4O_y$[g] + Ln_2BaCuO_5 + $BaCuO_2$	Black-green
34	5:28:17	950/48	$LnBa_8Cu_4O_y$[g] + $BaCuO_2$	Black-green
35	1:6:3	930/48[d]	$LnBa_8Cu_4O_y$[h]	Black-green
36	5:61:34	950/48	$LnBa_8Cu_4O_y$ + '011'	Black
37	2:13:5	930/48[d]	$LnBa_8Cu_4O_y$[h] + 'X'[i]	Black-green
38	2:7:3	930/48[d]	$LnBa_8Cu_4O_y$[g] + Ln_2BaCuO_5[f]	Black-green
39	4:11:5	930/48[d]	$LnBa_8Cu_4O_y$[g] + Ln_2BaCuO_5	Black-green
40	1:3:1	930/48[d]	$LnBa_8Cu_4O_y$[g] + Ln_2BaCuO_5[f]	Black-green
41	2:2:1	930/14	Ln_2BaCuO_5 + $Ln_2Ba_2O_5$	Gray-green
		980/20	Ln_2BaCuO_5 + $Ln_2Ba_4O_7$[f]	Gray-green
42	6:11:3	930/14	$LnBa_8Cu_4O_y$[f,g] + $Ln_2Ba_2O_5$	Brown
		980/20	$LnBa_8Cu_4O_y$[g] + $Ln_2Ba_4O_7$ + $\mathrm{Ln_2BaCuO_5}$[f]	Gray-brown
43	2:7:1	930/14	BaO + $LnBa_8Cu_4O_y$[h] + '220'[f]	Black-brown
		980/20	BaO + '240'	Black-brown

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

[a] Ln : Ba : Cu molar ratio.

[b] °C/hr at temperature.

[c] Oxidecarbonate, according to (*13*).

[d] Cooled slowly.

[e] Cubic modification.

[f] Trace amount of phase present.

[g] '184' solid solution.

[h] Orthorhombic modification of '184' solid solution.

[i] Two unidentified reflections were observed.

TABLE II

LATTICE PARAMETER AND SYMMETRY DATA ON COMPOUNDS OBSERVED IN THE Ln_2O_3–BaO($BaCO_3$)–CuO (Ln = Dy AND Ho) SYSTEMS

Compound	Symmetry[a]	Unit-cell parameters			Ref.[b]	Notes
		a(Å)	b(Å)	c(Å)		
$BaCuO_2$	C	18.277(5)			(*30*)	
		18.2772(2)				
$Dy_2Cu_2O_5$	O	10.856(6)	3.5218(6)	12.474(4)		
		10.833(1)	3.5180(2)	12.477(1)	(*35*)	
		10.830	3.514	12.465	(*39*)	
$Ho_2Cu_2O_5$	O	10.798(3)	3.4926(8)	12.466(4)		
		10.798(1)	3.4921(3)	12.463(1)	(*35*)	
		10.818	3.503	12.477	(*39*)	
'$Dy_2Ba_2O_5$'[c]	T	4.3879(6)		11.393(2)		
'$Ho_2Ba_2O_5$'[c]	T	4.3711(7)		11.870(2)		
		4.376(2)		11.932(8)	(*42*)	For $Ho_3Ba_3O_{15}$
'$Dy_2Ba_4O_7$'[d]	T	4.3776(8)		28.755(8)		
		4.373(3)		28.79(5)	(*42*)	
'$Ho_2Ba_4O_7$'[d]	T	4.3607(5)		28.681(4)		
		4.357(2)		28.79(3)	(*42*)	
Dy_2BaCuO_5	O	12.207(5)	5.671(5)	7.141(4)		
		12.220(4)	5.680(2)	7.154(2)	(*45*)	
Ho_2BaCuO_5	O	12.195(5)	5.669(2)	7.143(1)		
		12.165(5)	5.655(3)	7.125(3)	(*42*)	
'$DyBa_8Cu_4O_y$'[e]	T	8.152(3)		8.076(5)		
		8.225(2)		7.995(1)	(*51*)	$a\sqrt{2}$, sample 30
		8.198(2)		8.017(3)		Sample 33
		8.194(4)		8.033(5)		Sample 38
	O	8.193(2)	8.130(3)	8.061(3)		Sample 35
		8.272(4)	8.126(2)	8.063(2)		Sample 37
'$HoBa_8Cu_4O_y$'[e]	T	8.146(3)		8.065(6)		
		8.216(1)		7.983(2)	(*51*)	$a\sqrt{2}$, sample 30
		8.192(3)		8.007(4)		Sample 33
		8.190(4)		8.024(6)		Sample 38
	O	8.189(4)	8.124(2)	8.045(4)		Sample 35
		8.269(3)	8.122(4)	8.049(5)		Sample 37
$DyBa_2Cu_3O_x$	O	3.8273(7)	3.8894(6)	11.711(1)		
		3.8257(9)	3.8841(8)	11.688(8)		Heated in O_2
		3.8284(8)	3.8888(8)	11.668(2)	(*2*)	
		3.830(3)	3.885(3)	11.709(3)	(*4*)	
$HoBa_2Cu_3O_x$	O	3.821(1)	3.888(1)	11.689(2)		
		3.8180(3)	3.8831(8)	11.675(7)		Heated in O_2
		3.8221(8)	3.8879(8)	11.670(2)	(*2*)	
		3.846(1)	3.881(1)	11.640(2)	(*4*)	

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

[b] This work, except as noted.

[c] Probably $Ln_2Ba_2O_5 \cdot CO_2$; see text.

[d] Probably $Ln_2Ba_4O_7 \cdot CO_2$; see text.

[e] Probably an oxidecarbonate; see text.

monochromatized Cu$K\alpha_1$ radiation in a 114.59 mm diameter Guinier camera as described previously (*18*). Theoretical X-ray powder diffraction intensities were calculated with the program POWD12 (*26*) on a VAX 11/750 computer. The Ln^{3+}, Ba^{2+}, and Cu^{2+} atomic scattering factors were from (*27*); that for O^{2-} was from (*28*).

Results and Discussion

Initial Ln_2O_3 : BaO($BaCO_3$) : CuO molar compositions, sample numbers, heating conditions, phases observed, and specimen colors are tabulated in Table I. In Table II lattice parameters and structure types for all phases observed are summarized together with selected literature data. The ternary phase compatibilities are illustrated in a Gibbs triangle in Fig. 1. The numbers in the figure are keyed to the sample numbers listed in Table I.

The Pseudo-binary Regions

The $BaCO_3$–CuO region. Three phases, BaO, CuO, and cubic $Im\bar{3}m$ $BaCuO_2$, (*29, 30*) were observed. Numerous Ba-Cu-O phases reported in other systems (*11, 31–33*) were not detected under the temperature/heating conditions used in this work. Repeated attempts to synthesize $BaCu_3O_4$ from an initial 1 : 3 $BaCO_3$: CuO mixture yielded only $BaCuO_2$ and CuO even after prolonged heating at different temperatures. This compound was reported to be a satellite phase (*34*) with $YBa_2Cu_3O_{7-\delta}$. Nor could Ba_2CuO_3 (*32*) be prepared under our experimental conditions; it was identified in related systems when Li_2CO_3 was used as a mineralizer (*9*). A third phase, $Ba_2CuO_{3+\delta}$, prepared by (*13*), is reported to decompose above 850°C (*32*) and should not be stable under our experimental conditions. It is indeed apparent that in this pseudo-binary region reaction conditions determine the product.

The Ln_2O_3–CuO region. Only turquoise-colored $Ln_2Cu_2O_5$ compounds were obtained. Extended heating at 1000°C with repeated grindings was required to prepare single-phase specimens. Both compounds are isostructural with related phases (*35*) and exhibit $Pna2_1$ symmetry (*36–38*). Unit-cell parameters (see Table II) agree well with literature values (*35, 39*). Neither phase appears to exhibit any substantial solubility.

The Ln_2O_3–$BaCO_3$ region. Two phases were observed: $Ln_2Ba_2O_5$ below 950°C and $Ln_2Ba_4O_7$ above that temperature. These (Ln = La–Lu) systems were investigated above 1000°C by Lopato (*40*), who found Ln_2BaO_4 and $Ln_4Ba_3O_9$. Subsequent investigations with Ln = Y as well as lanthanoid elements in the temperature range 900–1000°C revealed two additional compounds, $Ln_2Ba_2O_5$ and $Ln_2Ba_4O_7$ (*41*). The latter phase has also been formulated as $Ln_3Ba_3O_{7.5}$ (*42*). In the Y–Ba–O system these '220' and '240' compounds have been reported recently to be oxidecarbonates, $Y_2Ba_2O_5 \cdot CO_2$ and $Y_2Ba_4O_7 \cdot CO_2$, respectively (*13*). Our mass balance data obtained for initial mixtures of the molar ratio Ln : Ba = 1 : 2, where Ln = Gd, Dy, and Ho (*22*), are consistent with this report, and only a minimal yield of '240' could be prepared when BaO_2 was substituted for $BaCO_3$. It is possible, however, that in this temperature range some of the observed CO_2 content results from incomplete reaction or from absorption of $CO_2(g)$ from air. Klinkova, *et al.* (*43*) observed that during prolonged isothermal heating at 1130 K the mass of BaO_2 first decreased and then after 8 hr reached its initial value and exceeded it. Both $Ln_2Ba_2O_5$ and $Ln_2Ba_4O_7$, or their oxidecarbonates, crystallize in tetragonal symmetry (*44*); lattice parameters are presented in Table II. Above 950°C the '220' compound transforms into '240' according to the equations

$$2\,Ln_2O_3(s) + 4BaCO_3(s) \xrightarrow[940°C]{900°-} \begin{cases} 2\,Ln_2Ba_2O_5(s) + 4\,CO_2(g) \\ \text{or} \\ 2\,\{Ln_2Ba_2O_5 \cdot CO_2(s)\} + 2\,CO_2(g) \end{cases}$$

$$\xrightarrow[1000°C]{950°-} \begin{cases} Ln_2Ba_4O_7(s) + Ln_2O_3(s) \\ \text{or} \\ Ln_2Ba_4O_7 \cdot CO_2(s) + Ln_2O_3(s) + 3\,CO_2(g). \end{cases}$$

This decomposition dramatically changes the phase relationships observed as a function of temperature in the barium rich-region of the pseudo-ternary system.

The Pseudo-ternary Region

Three compounds were characterized: Ln_2BaCuO_5, '211'; $LnBa_8Cu_4O_y$, '184'; and $LnBa_2Cu_3O_x$, '123'.

Refined lattice parameters for the well-characterized orthorhombic, *Pbnm*, green, '211' phase correlate well with literature values (*45*) (see Table II). However, the Ho-phase X-ray powder diffraction pattern contained several weak reflections that violate the *Pbnm* *b*-glide constraint. A similar observation has been reported for the yttrium analogue by Hazen *et al.* (*46*), who suggest that the weak reflections may be the result of deviations from the ideal '211' stoichiometry. However, that suggestion is inconsistent with the structure solution, which indicates an insensitivity to the exact content of the cation sites. Moreover, neither the '211' nor the '123' compound exhibits a detectable level of solid solubility.

In the barium oxide-rich portion of the *Ln*–Ba–Cu–O systems the '132' compound was identified first for *Ln* = Y (*9, 11, 12, 32*). Later, various researchers reported not only different formulas for this compound, but also different unit cell parameters. To our knowledge, in this composition region of the *Ln* = Y system additional compounds with the following Y : Ba : Cu ratios have been described: '143' (*13, 14*), '385' (*13*), '253' (*10*), '3 11 6' (*47*), '142' (*48*), '152' (*10, 13*), '163' (*14*), and '184' (*49, 50*). In view of the variations among these reports we focused special attention on this region. We reported lattice parameters for *Ln* = Dy and Ho '132' compounds previously (*51*), but pointed out that some samples contained traces of $BaCuO_2$. A more careful investigation shows that every specimen of this composition contains in addition traces of '211.' Moreover, all samples from closely related regions [samples 31–34, Table I] likewise have additional reflections, indicative that the true composition of the compound differs from '132.' A single phase was detected only for reactants in the mole ratio *Ln* : Ba : Cu = 184, a composition consistent with that reported by Osamura and Zhang (*49*) and Fjellvåg *et al.* (*50*) in the *Ln* = Y system. The X-ray powder diffraction patterns of both the Dy and Ho '184' compounds are indexable on tetragonal symmetry, in good agreement with published data (*49, 50*). Further investigation showed the influence of the *Ln* : Ba : Cu ratio on the structural evolution of the '184' phase. The X-ray diffraction reflections obtained for samples 35 and 37 (Fig. 1 and Table I) exhibit reflection splittings typical for a tetragonal-to-orthorhombic transition. The crystallographic data of the different compositions summarized in Table II both establish the presence of a solid solution region around the '184' composition and show that the *Ln* : Ba : Cu molar ratio influences its crystallographic modifications. These crystallographic relationships and the solubility limits need further study.

The lattice parameters of the '184' compound are closely related to those reported previously for '132' phases; the tetragonal *a*-axes show a 2 or $\sqrt{2}$ relationship to each other. A similar correlation exists between the '184' lattice parameters and those of '385,' '253,' '3 11 6,' and '163.' In addition, the orthorhombic modification of the '184' solid solution shows this same relationship to the orthorhombic '152' phase. These lattice parameter interrelationships and the two crystallographic modifications present in the '184' solid solution region (tetragonal and orthorhombic) help to explain the different results reported for the Y–Ba–Cu–O system. According to Abbattista *et al.* (*14*) and Karen and Kjekshus (*52*), '184' is an oxidecarbonate. We prepared the *Ln* = Dy(Ho)-'184' phases in oxygen when BaO_2 was substituted for $BaCO_3$ as a reactant; Pieczulewski *et al.* obtained comparable results for the *Ln* = Eu system (*53*).

The Dy(Ho)-'184' phases decompose at temperatures above 950°C. According to Osamura *et al.* (*54*), the following reaction occurs in the *Ln* = Y system in the temperature range 900–1000°C:

$$\text{'184'} + \text{'123'} \rightleftharpoons \text{'211'} + \text{'011.'}$$

This interconversion helps to explain the phase compatabilities we observed at various temperatures for samples that lie on the '211'–'011' tie line (Fig. 1 and Table I). However, it does not rule out the possibility that some of the different compositions reported for this compound may stem either from the narrow temperature range over which it is stable—the region between its formation from $BaCO_3$ and its decomposition—or from specimens that contain differing amounts of carbonate (*52*).

The diffraction patterns of the black '123' phases were indexable on orthorhombic symmetry; our *a* and *b* parameters agree well with those reported previously, but our *c* parameter is slightly larger. Previously unreported powder X-ray diffraction data for these compounds are listed in Table III. Although extensive $Ln_{1\pm\varepsilon}Ba_{2\mp\varepsilon}Cu_3O_x$ solid solution regions have been reported for the lighter lanthanoid elements (*18, 19, 55–58*), no indication of solid solution could be found around either the holmium or the dysprosium '123' compounds. As a consequence, the crystallization region of these compounds occupies significantly less area in the compatability diagram than that observed in the *Ln* = La–Gd systems. It was noted that T_c of Ho-'123' phases decreased as specimen compositions differed from '123' (*25*). Our results show that as the composition deviates from '123' the product contains a progressively lower percentage of '123.' Heating Dy and Ho '123' phases at 950°C in an oxygen atmosphere yielded single-phase specimens with slightly shortened lattice parameters that evidenced a strong Meissner effect at liquid-nitrogen temperature.

Conclusions

Both Dy–Ba–Cu–O and Ho–Ba–Cu–O systems show identical crystal chemistry. The phase subsolidus compatibilities divide the Gibbs triangle $LnO_{1.5}$–BaO–CuO in Fig. 1 into 10 ternary regions. In the BaO-rich part of the triangle the composition of the equilibrium phases changes with temperature. This change is associated with the decomposition of $Ln_2Ba_2O_5 \cdot CO_2$ (or $Ln_2Ba_2O_5$) to $Ln_2Ba_4O_7 \cdot CO_2$ (or $Ln_2Ba_4O_7$) above 950°C. As expected, the behavior of these systems is related closely to that of thulium (*24*).

The phase compatibilities in the CuO-rich part of the diagrams are of most importance for understanding the material properties of the '123' compounds. A summary of the phases reported for this part of the *Ln*–Ba–Cu–O systems is presented in Table IV in correlation with the Ln^{3+} ionic radii,

TABLE III

MILLER INDICES, OBSERVED INTENSITIES, AND OBSERVED AND CALCULATED INTERPLANAR *d*-SPACING FOR $LnBa_2Cu_3O_x$, *Ln* = Dy AND Ho

$DyBa_2Cu_3O_x$				$HoBa_2Cu_3O_x$		
d_o(Å)	d_c(Å)	I_o^a	*h k l*	d_o(Å)	d_c(Å)	I_o^a
11.78	11.71	m	0 0 1	11.67	11.68	m
3.902	3.903	m	0 0 3	}3.890	3.896	s
3.891	3.889	m	0 1 0		3.888	
3.829	3.827	w	1 0 0	3.815	3.820	m
3.638	3.637	vw	1 0 1	3.628	3.631	w
3.241	3.239	vw	0 1 2	3.233	3.237	w
3.204	3.204	w	1 0 2	3.197	3.198	w
2.757	2.755	vs,b	0 1 3	2.751	2.752	vs,b
2.730	2.732	vs,b	1 0 3	2.725	2.728	vs,b
	2.728		1 1 0		2.725	
2.471	2.472	vw	1 1 2	2.468	2.469	w
2.343	2.342	m,b	0 0 5	2.335	2.337	s
	2.339		0 1 4		2.336	
2.326	2.325	m	1 0 4	2.321	2.321	m
2.237	2.236	s	1 1 3	2.231	2.233	s
1.9974	1.9978	vw	1 0 5	—	1.9942	—
1.9518	1.9518	m	0 0 6	1.9486	1.9483	m
1.9445	1.9447	s	0 2 0	1.9432	1.9438	s
1.9136	1.9136	s	2 0 0	1.9099	1.9103	s
1.7776	1.7771	w	1 1 5	1.7736	1.7743	m
1.7445	1.7445	vw	0 1 6	1.7420	1.7418	w
1.7408	1.7407	w	0 2 3	1.7388	1.7394	w
1.6738	1.6730	vw	0 0 7	1.6697	1.6699	w
—	1.6624		1 2 2	1.6611	1.6610	vw
—	1.6477		2 1 2	1.6447	1.6452	vw
1.5872	1.5874	s	1 1 6	1.5838	1.5848	vs,b
1.5840	1.5845	vs	1 2 3		1.5831	
1.5721	1.5717	s	2 1 3	1.5689	1.5693	vs
—	1.5369		0 1 7	1.5338	1.5344	vw
—	1.5329		1 0 7	1.5300	1.5301	vw
1.4962	1.4962	w	0 2 5	1.4942	1.4946	w
1.4915	1.4918	w	1 2 4	1.4903	1.4903	vw
1.4816	1.4819	w	2 0 5	1.4786	1.4793	m
	1.4811		2 1 4		1.4788	
1.4259	1.4262	w	1 1 7	1.4235	1.4238	m
1.3780	1.3776	s	0 2 6	1.3755	1.3760	s
1.3660	1.3664	w	2 0 6	1.3640	1.3640	w
1.3642	1.3640	s	2 2 0	1.3622	1.3625	vs,b

[a] s = strong; m = medium; w = weak; v = very; b = broad.

which appear to be the important factor in controlling the crystal chemistry of these compounds. The La–Ba–Cu–O system has the largest number of ternary compounds. This number decreases as the Ln^{3+} radii decrease. Each pseudo-binary Ln_2O_3–CuO system contains only one binary compound, either Ln_2CuO_4 or $Ln_2Ba_2O_5$. The largest lanthanoid cation, La^{3+}, crystallizes in a slightly distorted K_2NiF_4-type La_2CuO_4 structure in which La^{3+} is ninefold coordinated by oxide ions (*59, 60*). Intermediate-size lanthanoid cations (Pr^{3+}–Gd^{3+}) assume the Nd_2CuO_4 structure and are coordinated eightfold by oxide ions (*61*). Smaller lanthanoid cations (Dy^{3+}–Lu^{3+}) and yttrium form $Ln_2Cu_2O_5$ compounds with sixfold-coordinated *Ln* sites (*35–38*). Thus, a sharp structural transition is observed for a Ln^{3+} ion smaller than Gd^{3+}.

The transition in the pseudo-binary *Ln*–Cu–O systems can be related to other phase changes observed in the Gibbs triangle. A Ln^{3+} radius close to that of Gd^{3+} terminates the '336' phase and solid solution of the $Ln_{1\pm\delta}Ba_{2\mp\delta}Cu_3O_x$ type around the '123' phase (*18, 19, 55–58*). The first feature can be explained by similarities between the '336' (*15, 58*) and T′-Ln_2CuO_4 (*61*) structures, both of which show the same Ln^{3+} anion coordination numbers. The size compatibility between the Ba^{2+} and Ln^{3+} ions is probably the predominant factor governing the formation of the $Ln_{1\pm\delta}Ba_{2\mp\delta}Cu_3O_x$ solid solution. Although the La^{3+}–Gd^{3+} ionic radii are closer to that of Ba^{2+} than are those of Dy^{3+}–Lu^{3+}, it is nevertheless interesting that the limitations of the solid solution region correlate with the features described previously.

The composition at which the '211' phase is first observed also correlates with the Ln^{3+} radii and regions closely related to it. Reactants in the mole ratio *Ln* : Ba : Cu = 2 : 1 : 1 for *Ln* = Sm–Lu produce the commonly known "green" phase, Ln_2BaCuO_5. In this structure each Ln^{3+} ion is coordinated sevenfold by a capped trigonal prism of oxygen atoms. The '211' phase does not form with the lanthanoids that have ionic radii larger than that of Sm^{3+}, i.e., La^{3+} and

TABLE IV

COMPARISON OF THE LANTHANOID COORDINATION NUMBER FOR PHASES OBSERVED *in air* AT ~950°C IN THE CuO-RICH REGION OF SELECTED *Ln*-Ba-Cu-O SYSTEMS WITH Ln^{3+} IONIC RADII

		Coordination no. of Ln^{3+} in phase present						
Ln	Ionic radius[a] of Ln^{3+}	201	XP	202	336	123	211/422	415
La	1.216 Å	9	9[b]		8	8s[c]	8 and 10	?
Nd	1.163	8			8	8s	8 and 10	
Sm	1.132	8			8	8s	7	
Eu	1.120	8			8	8s	7	
Gd	1.107	8				8s	7	
Dy	1.083			6		8	7	
Y	1.075			6		8	7	
Ho	1.072			6		8	7	
Er	1.062			6		8	7	
Tm	1.052			6		8	7	

Note. The digits in the headings represent the *Ln* : Ba : Cu ratio.

[a] Ionic radii according to (*64*) for coordination number 9.

[b] XP = $La_{2-x}Ba_xCuO_{4-(x/2)+\delta}$ according to (*17*).

[c] s: solid solution $Ln_{1\pm\delta}Ba_{2\mp\delta}Cu_3O_x$.

Nd^{3+}. These ions form a "brown" compound (*18, 62*), which for lanthanum and neodymium is reported to be $Ln_4Ba_2Cu_2O_{10}$. The structure of the lanthanum phase is composed of LaO_8 and LaO_{10} polyhedra (*63*) which provide adequate space to accommodate the La^{3+} ions.

In summary, the Ln^{3+} ionic radii exert a controlling influence on both phase and solid solution formation in the CuO-rich region of the *Ln*-Ba-Cu-O systems.

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References

1. M. K. WU, J. R. ASHBURN, C. J. TORNG, P. H. HOR, R. L. MENG, L. GAO, Z. J. HUANG, Y. Q. WANG, AND C. W. CHU, *Phys. Rev. Lett.* **58,** 908 (1987).
2. J. M. TARASCON, W. R. MCKINNON, L. H. GREENE, G. W. HULL, AND E. M. VOGEL, *Phys. Rev. B* **36,** 226 (1987).
3. F. ZUO, B. R. PATTON, D. L. COX, S. I. LEE, Y. SONG, J. P. GOLBEN, X. D. CHEN, S. Y. LEE, Y. CAO, Y. LU, J. R. GAINES, J. C. GARLAND, AND A. J. EPSTEIN, *Phys. Rev. B* **36,** 3603 (1987).
4. Y. LEPAGE, T. SIEGRIST, S. A. SUNSHINE, L. F. SCHNEEMEYER, D. W. MURPHY, S. H. ZAHURAK, J. V. WASZCZAK, W. R. MCKINNON, J. M. TARASCON, G. W. HULL, AND L. H. GREENE, *Phys. Rev. B* **36,** 3617 (1987).
5. A. R. MOODENBAUGH, M. SUENAGA, T. ASANO, R. N. SHELTON, H. C. KU, R. W. MCCALLUM, AND P. KLAVINS, *Phys. Rev. Lett.* **58,** 1885 (1987).
6. P. H. HOR, R. L. MENG, Y. Q. WANG, L. GAO, Z. J. HUANG, J. BECHTOLD, K. FORSTER, AND C. W. CHU, *Phys. Rev. Lett.* **58,** 1891 (1987).
7. See, for example: Y. ZHANG, W. K. 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).
8. 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); 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).

9. G. Wang, S.-J. Hwu, S. N. Song, J. B. Ketterson, L. D. Marks, K. R. Poeppelmeier, and T. O. Mason, *Adv. Ceram. Mater.* **2,** 313 (1987).
10. W. Reichelt, H. Wilhelm, G. Försterling, and H. Oppermann, *Cryst. Res. Technol.* **24,** K26 (1989).
11. R. S. Roth, K. L. Davis, and J. R. Dennis, *Adv. Ceram. Mater.* **2,** 303 (1987).
12. K. G. Frase and D. R. Clarke, *Adv. Ceram. Mater.* **2,** 295 (1987).
13. D. M. DeLeeuw, C. A. H. A. Mutsaers, C. Langereis, H. C. A. Smoorenburg, and P. J. Rommers, *Physica C* **152,** 39 (1988).
14. F. Abbattista, M. Vallino, and D. Mazza, *Mater. Chem. Phys.* **21,** 521 (1989).
15. L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, *J. Solid State Chem.* **37,** 151 (1981).
16. 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).
17. D. Klibanow, K. Sujata, and T. O. Mason, *J. Am. Ceram. Soc.* **71,** C267 (1988).
18. S. A. Hodorowicz, J. Czerwonka, and H. A. Eick, *J. Solid State Chem.* **88,** 391 (1990).
19. J. Czerwonka and H. A. Eick, *J. Solid State Chem.* **90,** 69 (1991).
20. S. A. Hodorowicz, A. Lasocha, W. Lasocha, and H. A. Eick, *J. Solid State Chem.* **75,** 270 (1988).
21. J. K. Liang, X. T. Xu, G. H. Rao, S. S. Xie, X. Y. Shao, and Z. G. Duan, *J. Phys. D.: Appl. Phys.* **20,** 1324 (1987).
22. S. A. Hodorowicz, A. Chodorowicz-Bak, J. Czerwonka, E. Hodorowicz, W. Lasocha, and H. A. Eick, *J. Solid State Chem.* **92,** 480 (1991).
23. S. A. Hodorowicz, A. Lasocha, W. Lasocha, A. Chodorowicz, and H. A. Eick, *Acta Phys. Pol. A* **75,** 437 (1989).
24. E. Hodorowicz, S. A. Hodorowicz, and H. A. Eick, *Physica C* **158,** 127 (1989).
25. Z. Yiling, L. Jingkui, C. Xiangrong, R. Guanghui, L. Hongbin, N. Yongming, Z. Dongnin, and X. Sishen, *J. Less-Common Met.* **146,** 121 (1989).
26. 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).
27. C. H. MacGillavry and G. R. Rieck (Eds.), "International Tables for X-Ray Crystallography," Vol. 3, p. 213, Kynoch Press, Birmingham, England (1968); J. A. Ibers and W. C. Hamilton (Eds.), "International Tables for X-Ray Crystallography," Vol. 4, p. 71, Kynock Press, Birmingham, England (1974).
28. T. Suzuki, *Acta Crystallogr.* **13,** 279 (1960).
29. R. Kipka and H. Müller-Buschbaum, *Z. Naturforsch. B* **32,** 121 (1977).
30. M. T. Weller and D. R. Lines, *J. Solid State Chem.* **82,** 21 (1989).
31. C. L. Teske and H. Müller-Buschbaum, *Z. Naturforsch. B* **27,** 296 (1972).
32. K. G. Frase, E. G. Liniger, and D. R. Clarke, *J. Am. Ceram. Soc.* **70,** C204 (1987).
33. K. Borowiec, J. Przyluski, and K. Kolbrecka, *Eur. J. Solid State Inorg. Chem.* **27,** 333 (1990).
34. A. Bertinotti, J. Hammaun, D. Luzet, and E. Vincent, *Physica C* **160,** 227 (1989).
35. N. Kimizuka, E. Takayama, S. Horiuchi, Y. Yamamoto, and T. J. Fujita, *J. Solid State Chem.* **42,** 322 (1982).
36. H. R. Freund and Hk. Müller-Buschbaum, *Z. Naturforsch. B* **32,** 609 (1977).
37. H. Fjellvåg, P. Karen, and A. Kjekshus, *Acta Chem. Scand. Ser. A* **42,** 144 (1988).
38. R. Famery and F. Queyroux, *Mater. Res. Bull.* **24,** 275 (1989).
39. R. Troc, J. Klamut, Z. Bukowski, R. Horyn, and J. Stepien-Damm, *Physica B* **154,** 189 (1989).
40. L. M. Lopato, *Ceramurgia Int.* **2,** 18 (1976).
41. W. Kwestroo, H. A. M. Van Hal, and C. Langereis, *Mater. Res. Bull.* **9,** 1631 (1974).
42. E. V. Antipov, L. N. Lykova, and L. M. Kovba, *Russ. J. Inorg. Chem.* **29**(6), 932 (1984).
43. L. A. Klinkova, I. V. Soikina, I. I. Zver'kova, S. A. Zver'kov, S. A. Shevchenko, and N. I. Ganovich, *Inorg. Mater.* **25**(12), 1719 (1989).
44. E. Hodorowicz, S. A. Hodorowicz, and H. A. Eick, *J. Solid State Chem.* **84,** 401 (1990).
45. C. Michel and B. Raveau, *J. Solid State Chem.* **43,** 73 (1982).
46. R. M. Hazen, L. W. Finger, R. J. Angel, C. T. Prewitt, N. L. Ross, H. K. Mao, C. G. Hadidiacos, P. H. Hor, R. L. Meng, and C. W. Chu, *Phys. Rev. B* **35,** 7238 (1987).
47. F. Abbattista, M. Vallino, D. Mazza, P. Brovetto, and A. Delumas, *in* "Proceedings, European Workshop on High T_c Superconductors, Genoa, 1987," p. 279.
48. M. A. Rodriguez and R. L. Snyder, *AIP Conf. Proc.* **219,** 610 (1991).

49. K. Osamura and W. Zhang, *Jpn. J. Appl. Phys.* **26,** L2094 (1987).
50. H. Fjellvåg, P. Karen, A. Kjekshus, and J. K. Grepstad, *Acta Chem. Scand. Ser. A* **42,** 171 (1988).
51. S. A. Hodorowicz, E. Hodorowicz, A. Chodorowicz, and H. A. Eick, *Cryst. Res. Technol.* **24,** K71 (1989).
52. P. Karen and A. Kjekshus, *J. Solid State Chem.* **94,** 298 (1991).
53. C. N. Pieczulewski, J. E. McAdams, and T. O. Mason, *J. Am. Ceram. Soc.* **28,** 3088 (1990).
54. K. Osamura, W. Zhang, T. Yamashita, S. Ochiai, and B. Predel, *Z. Metallkd.* **79,** 693 (1988).
55. 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).
56. W. I. F. David, W. T. A. Harrison, R. M. Ibberson, M. T. Weller, J. R. Grasmeder, and P. Lanchester, *Nature (London)* **328,** 328 (1987).
57. C. U. Segre, B. Dabrowski, D. G. Hinks, K. Zhang, J. D. Jorgensen, M. A. Beno, and I. K. Schuller, *Nature (London)* **329,** 227 (1987).
58. S. A. Sunshine, L. F. Schneemeyer, J. V. Waszczak, D. W. Murphy, S. Miraglia, A. Santoro, and F. Beech, *J. Cryst. Growth* **85,** 632 (1987).
59. J. M. Longo and P. M. Raccah, *J. Solid State Chem.* **6,** 526 (1973).
60. B. Grande, H. Müller-Buschbaum, and M. Schweizer, *Z. Anorg. Allg. Chem.* **428,** 120 (1977).
61. H. Müller-Buschbaum and W. Wollschläger, *Z. Anorg. Allg. Chem.* **414,** 76 (1975).
62. C. Michel, L. Er-Rakho, and B. Raveau, *J. Solid State Chem.* **39,** 161 (1981).
63. F. Mizuno, H. Masuda, I. Hirabayashi, S. Tanaka, M. Hasegawa, and U. Mizutani, *Nature (London)* **345,** 788 (1990).
64. R. D. Shannon, *Acta Crystallogr. Sect A* **32,** 751 (1976).