JOURNAL OF SOLID STATE CHEMISTRY **90**, 69–78 (1991)

Phase Relationships in the Sm–Ba–Cu–O System at ~950°C

J. CZERWONKA* AND H. A. EICK†

Contribution from Department of Chemistry and Center for Fundamental Materials Research, Michigan State University, E. Lansing, Michigan 48824-1322

Received May 30, 1990

A systematic X-ray powder diffraction study of the Sm_2O_3–$BaCO_3$–CuO system over the temperature range ~920–980°C is presented as a function of cationic molar ratios. In the pseudobinary regions the phases $BaSm_2O_4$, Sm_2CuO_4, and $BaCuO_2$ were observed; in the pseudoternary region Sm_2BaCuO_5, $SmBa_3Cu_2O_z$, $Sm_3Ba_3Cu_6O_y$, and $SmBa_2Cu_3O_y$ were identified. A solid solution region was found in the vicinity of $SmBa_2Cu_3O_y$. Lattice parameters are presented for each compound detected. A pseudoternary phase diagram is presented: subsolidus relationships are indicated. This system is compared with related lanthanoid–barium–copper oxide systems; only the europium system exhibits comparable phases. © 1991 Academic Press, Inc.

Introduction

Discovery of high temperature superconductivity in the pseudoternary region of first the Y–Ba–Cu–O system and then *Ln*–Ba–Cu–O (*Ln* = La–Lu, except Ce, Pr, and Tb) systems (*1*) caused them to become important as well as interesting areas for study. Numerous experiments have demonstrated that the characteristics of the *Ln*–Ba–Cu–O superconducting phases depend greatly upon the preparatory procedure (*2*). Knowledge of phase relationships helps both to improve the properties of these materials and to achieve specimen reproducibility. A number of *Ln*–Ba–Cu–O systems have been examined over the *entire composition range* at temperatures of 900–1000°C in air: *Ln* = Y (*3–7*), La (*8–10*), Pr and Nd (*11*), Eu (*12*), Gd (*13, 14*), Er (*15*), and Tm (*16*). These studies have demonstrated that as the lanthanoid ion is changed the phase relationships vary considerably even at the same temperature. Lanthanoid ion size and basicity appear to be important factors in determining phase stability. From an examination of the phase relationships among the *Ln*–Ba–Cu–O systems it appeared that only the adjacent smaller-lanthanoid Er and Tm systems are identical and that the larger, more basic, lanthanoids exhibit significant differences in their behavior. Understanding these differences requires detailed phase investigations.

The Eu–Ba–Cu–O system (*12*) appeared transitory between the larger and smaller lanthanoid systems since in addition to the compounds characteristic of the larger lanthanoids it exhibited the (*Ln* : Ba : Cu) '211' phase common to the smaller lanthanoids.

---

* On leave from the Faculty of Chemistry, Jagiellonian University, Karasia 3, 30-060 Krakow, Poland.

† To whom correspondence should be addressed.

0022-4596/91 $3.00

TABLE I

PHASES OBSERVED IN THE Sm_2O_3–$BaCO_3$–CuO SYSTEM UNDER VARIOUS PREPARATORY CONDITIONS

Sample no.	Mixed composition[a]	Preparatory conditions Time	 Atmosphere	 Temperature (°C)	Phases observed	Color
2	8:1:1			950	Sm_2BaCuO_5 + Sm_2O_3	Green
3	3:1:0			950	Sm_2BaO_4 + Sm_2O_3	Lt grey
4	7:2:1			950	Sm_2BaCuO_5 + Sm_2BaO_4 + Sm_2O_3	Green
5	7:1:2			950	Sm_2BaCuO_5 + Sm_2CuO_4 + Sm_2O_3	Dk green
6	2:1:0			900	Sm_2BaO_4	Lt grey
6	2:1:0			955	Sm_2BaO_4	Lt grey
6	2:1:0			1030	Sm_2BaO_4	Lt grey
6	2:1:0			1130	Sm_2BaO_4	Lt grey
7	2:0:1			1030	Sm_2CuO_4	Black
8	6:3:1			950	Sm_2BaCuO_5 + Sm_2BaO_4	Green
9	3:1:1			950	Sm_2BaCuO_5 + Sm_2O_3	Green
10	6:1:3			950	Sm_2BaCuO_5 + Sm_2CuO_4	Blk-grn
11	4:3:0			950	Sm_2BaO_4 + BaO	White
12	4:2:1			950	Sm_2BaCuO_5 + Sm_2CuO_4	Lt green
13	1:1:0			900	Sm_2BaO_4 + BaO + $Ba(OH)_2 \cdot H_2O^c$	White
13	1:1:0			955	Sm_2BaO_4 + BaO	White
13	1:1:0			1030	Sm_2BaO_4 + BaO	White
13	1:1:0			1130	Sm_2BaO_4 + BaO	White
14	2:1:1			950	Sm_2BaCuO_5	Green
15	5:3:2			950	Sm_2BaCuO_5 + Sm_2CuO_4 + $Sm_3Ba_3Cu_6O_y$	Green
16	1:0:1			1025	Sm_2CuO_4 + CuO	Brown
17	3:2:2			950	Sm_2BaCuO_5 + $Sm_3Ba_3Cu_6O_y$ + $SmBa_3Cu_2O_z$	Grey-grn
18	2:2:1			950	Sm_2BaCuO_5 + Sm_2BaO_4 + $SmBa_3Cu_2O_z$	Dk green
19	2:1:2			950	Sm_2BaCuO_5 + Sm_2CuO_4 + $Sm_3Ba_3Cu_6O_y$	Black
20	4:1:5			950	Sm_2CuO_4 + CuO + $Sm_3Ba_3Cu_6O_y$	Grey
21	1:2:0			900	Sm_2BaO_4 + BaO + $BaCO_3^c$	White
21	1:2:0			955	Sm_2BaO_4 + BaO	White
21	1:2:0			1030	Sm_2BaO_4 + BaO	White
21	1:2:0			1130	Sm_2BaO_4 + BaO	White
22	1:1:1			950	$SmBa_3Cu_2O_y$ + Sm_2BaCuO_5 + $Sm_3Ba_3Cu_6O_y$	Grn-blk
23	1:0:2			955	Sm_2CuO_4 + CuO	Black
24	3:1:6			950	Sm_2CuO_4 + $Sm_3Ba_3Cu_6O_y$ + CuO	Black
25	1:1:2		O_2	975	$Sm_3Ba_3Cu_6O_y$	Black
25	1:1:2	48 hr	O_2	975	$Sm_3Ba_3Cu_6O_y$	Black
25	1:1:2			950	$Sm_3Ba_3Cu_6O_y$	Black
26	1:8:1			950	Sm_2BaO_4 + $SmBa_3Cu_2O_z$ + BaO	Grey
28	1:3:2			950	$SmBa_3Cu_2O_z$	Black
29	1:2:3			950	$SmBa_2Cu_3O_y$	Black
30	3:5:12			950	$Sm_3Ba_3Cu_6O_y$ + CuO + $SmBa_2Cu_3O_z{}^d$	Black
31	1:1:5			950	$Sm_3Ba_3Cu_6O_y$ + CuO	Black
32	1:8:1			950	BaO + $SmBa_3Cu_2O_z$ + Sm_2BaO_4	Grey
33	1:6:3			950	$BaCuO_2$ + $SmBa_3Cu_2O_z$ + BaO	Black
34	2:9:9			950	$BaCuO_2$ + $SmBa_2Cu_3O_y$ + $SmBa_3Cu_2O_z$	Black
35	1:3:6			950	$BaCuO_2$ + CuO + $SmBa_2Cu_3O_y{}^d$	Black
37	0:3:1			950	$BaCuO_2$ + BaO + $BaCO_3^c$	Grey
42	4:7:9			950	$SmBa_2Cu_3O_y{}^d$ + $SmBa_3Cu_2O_z$ + $Sm_3Ba_3Cu_6O_y$	Black
43	3:8:9			950	$BaCuO_2$ + $SmBa_2Cu_3O_y{}^d$ + $SmBa_3Cu_2O_z$	Black

[a] Sm : Ba : Cu molar ratio.
[b] Heated in air 24 hr unless O_2 indicated; °C.
[c] Trace of substance detected.
[d] Solid solution apparent.

In the *Ln* = Nd system the '211' compound was not observed, but a '311' compound related structurally to the lanthanum '422' phase was reported (*11*, *17*). This study was undertaken to determine if the Sm–Ba–Cu–O system would be similar to either the Eu or Nd system, or exhibit yet different phases. The Sm–Ba–Cu–O compounds and their phase relationships in air at ~950°C are presented herein. The ~950°C temperature was chosen since at lower temperatures it is difficult to attain equilibrium.

TABLE II

Phases Observed in the $BaCO_3$–CuO Pseudobinary Region under Various Sintering Conditions

		Preparatory conditions				
Sample no.	Initial composition[a]	Time (hr)	Atmosphere	Temperature (°C)	Phases observed	Color
38	0:2:1	150		600	$BaCO_3$ + CuO + $BaCuO_2$	Lt grey
38	0:2:1	250		700	$BaCO_3$ + CuO + $BaCuO_2$	Grey
38	0:2:1	72	O_2	700	$BaCO_3$ + CuO + $BaCuO_2$	Grey
38	0:2:1	160		800	$BaCO_3$ + CuO + $BaCuO_2$	Grey
38	0:2:1	150	O_2	800	$BaCO_3$ + CuO + $BaCuO_2$	Grey
38	0:2:1	150		975	$BaCO_3$ + CuO + $BaCuO_2$	Black
39	0:1:1	150		600	$BaCO_3$ + CuO + $BaCuO_2$	Lt grey
39	0:1:1	72	O_2	700	$BaCuO_2$	Grey
39	0:1:1	250		700	$BaCuO_2$	Dk grey
39	0:1:1	150	O_2	800	$BaCuO_2$	Dk grey
39	0:1:1	160		800	$BaCuO_2$	Dk grey
39	0:1:1	150		975	$BaCuO_2$	Black
40	0:1:2	150		600	CuO + $BaCO_3$ + $BaCuO_2$	Grey
40	0:1:2	250		700	CuO + $BaCO_3$ + $BaCuO_2$	Grey
40	0:1:2	72	O_2	700	CuO + $BaCO_3$ + $BaCuO_2$	Black
40	0:1:2	150	O_2	800	CuO + $BaCO_3$ + $BaCuO_2$	Black
40	0:1:2	160		800	CuO + $BaCO_3$ + $BaCuO_2$	Black
40	0:1:2	150		975	CuO + $BaCO_3$ + $BaCuO_2$	Black
41	0:1:3			950	$BaCuO_2$ + CuO	Black

[a] Sm : Ba : Cu molar ratio.

[b] Heated in air unless O_2 indicated; °C.

Experimental

Reactants were: Sm_2O_3 (99.9%, Research Chemicals, Phoenix, AZ), $BaCO_3$ (reagent grade, J. T. Baker Co., Phillipsburg, NJ), and CuO (reagent grade, Mallinckrodt, St. Louis, MO). The $BaCO_3$ and CuO were monophasic by X-ray powder diffraction; the Sm_2O_3 diffraction pattern indicated the presence of known polymorphic modifications with the monoclinic form predominant. Reactants were weighed to an accuracy of ±0.1 mg, hand-mixed under acetone with an agate mortar and pestle, dried, and then ground again. The specimens were placed in platinum or alumina crucibles and heated in a tube furnace either in air or under a dynamic 1-bar oxygen atmosphere at 600–1130°C for 24 hr, then in most cases cooled to room temperature at a rate of ~150°C hr^{-1}. Some products were reground and heated again under either air or O_2 for 24 to 120 hr, then cooled slowly to room temperature.

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 ~0.1 Torr during exposure. NBS-certified Si [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 (*18*). Theoretical X-ray powder diffraction intensities were calculated with the program POWD12 (*19*); unless indicated otherwise the following iso-

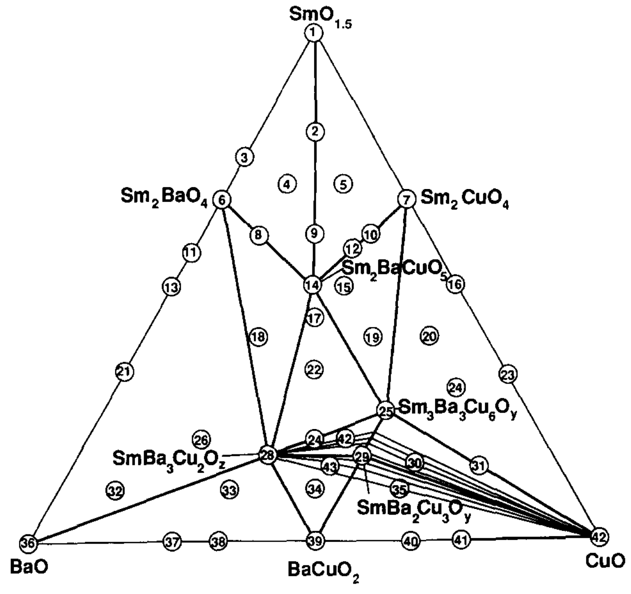

FIG. 1. Subsolidus phase relationships at ~950°C in the Sm–Ba–Cu–O system. The numbers correspond to those listed in Tables I and II. The lined area represents a solid solution region.

tropic thermal parameters were used: Sm, 0.9; Ba and Cu, 1.0; and O, 1.5 Å^2. All calculations were effected on a VAX 11/750 computer.

Magnetic susceptibilities of two '123' specimens were determined with a Quantum Design SQUID magnetometer over the temperature range 5–100 K in a 500-G magnetic field.

Results and Discussion

Initial Sm : Ba : Cu molar compositions, sample numbers, heating conditions, phases observed, and specimen colors are tabulated in Table I; comparable data on numerous Ba–Cu mixtures are presented in Table II. Phase relationships are presented in Fig. 1. The numbers in the figure are keyed to the sample numbers listed in Tables I and II. Lattice parameters and structure types for all seven phases observed, together with selected literature data, are presented in Table III.

The Pseudobinary Regions

The $BaCO_3$–CuO region. Only the well-characterized cubic *Im*$\bar{3}$*m* $BaCuO_2$ (*20, 21*) was observed.

The Sm_2O_3–$BaCO_3$ region. Only white orthorhombic $BaSm_2O_4$ was found. Its observed lattice parameters agree well with previously reported values (*22*). In Table IV interplanar *d*-spacings, observed intensities, and values calculated with the atomic positional parameters of $CaSc_2O_4$ (*23*) are presented. Attempts to prepare compounds with the Sm : Ba ratios 1 : 1, 4 : 3, and 1 : 2, which have been observed in related systems (*16, 24*), yielded mixtures of Sm_2O_3 and $BaSm_2O_4$ or BaO and $BaSm_2O_4$. Weak X-ray reflections assignable to $Ba(OH)_2 \cdot H_2O$ in a few diffractograms are presumed the result of specimen reaction with atmospheric moisture during transfer to the Guinier camera.

The Sm_2O_3–CuO region. Only Sm_2CuO_4 was observed. The X-ray data were indexed

TABLE III

LATTICE PARAMETER AND SYMMETRY DATA ON COMPOUNDS OBSERVED IN THE Sm_2O_3–$BaCO_3$–CuO SYSTEM

Compound	Symmetry[a]	Lattice parameters a(Å)	b(Å)	c(Å)	Ref.[b]	Notes
$BaCuO_2$	C	18.2848(6)				
		18.2772(2)			(21)	
Sm_2CuO_4	T	5.5379(2)		11.977(1)		
		5.522		11.938	(25)	$a\sqrt{2}$
Sm_2BaO_4	O	10.520(2)	12.344(1)	3.5616(6)		
		10.548	12.332	3.554	(22)	
$SmBa_2Cu_3O_y$	O	3.8818(3)	3.896(1)	11.8015(8)		950°/air
		3.855(2)	3.899(2)	11.721(4)	(1)	O_2
	T	3.884(2)		11.822(8)	(1)	vacuum heat
$Sm_3Ba_3Cu_6O_y$	T	5.4754(7)		11.613(3)		975°/air/24 hr
		5.4717(2)		11.594(1)		950°/O_2/48 hr
Sm_2BaCuO_5	O	12.398(1)	7.272(1)	5.755(1)		
		12.398(3)	7.271(2)	5.759(1)	(30)	
		12.405(3)	7.283(7)	5.74(1)	(31)	
$SmBa_3Cu_2O_z$	T	5.8270(3)		8.0461(7)		
		5.8312(7)		8.048(1)	(32)	

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

[b] This work, except as noted.

with tetragonal lattice parameters slightly larger than previously reported values (*25*). X-ray powder diffraction intensities calculated with the atomic parameters reported for K_2NiF_4-type La_2CuO_4 (*26*) agreed well with observed values. Attempts to prepare $Ln_2Cu_2O_5$- and $LnCuO_3$-type compounds (*27, 28*) met with failure.

The Pseudoternary Region

Four compounds were obtained: $SmBa_2Cu_3O_y$, '123'; Sm_2BaCuO_5, '211'; $Sm_3Ba_3Cu_6O_y$, '336'; and $SmBa_3Cu_2O_z$, '132'.

The '123' phase when prepared in air at 950°C yielded a well-defined monophasic X-ray powder diffraction pattern indexable on orthorhombic symmetry. These parameters lie between literature values (*1*) for vacuum- and O_2-annealed preparations. Several '123' specimens were annealed under different conditions—various heating times, temperatures, and air or O_2 atmospheres; the preparatory conditions, lattice parameters, and unit cell volumes of selected preparations are compiled in Table V. Only a rapidly quenched, oxygen-annealed specimen evidenced tetragonal symmetry. Consistent with previous reports none of the samples annealed in air and quenched showed the Meissner effect at liquid nitrogen temperatures, but the high-T_c version could be produced by cooling O_2-annealed specimens slowly. A plot of χ vs T for two slowly cooled specimens, one heated initially 24 hr at 975°C and then 20 hr at 700°C and the other heated initially 48 hr at 975°C and then 120 hr at 700°C, are presented in Fig. 2. The transition to diamagnetism occurs between 45 and 50 K for the sample heated 20 hr in O_2 and between 85 and 90 K for the specimen heated 120 h. The latter value agrees favorably with the reported midpoint value of 93 K (*1*). In like fashion, the small positive magnetic moment observed at higher tem-

TABLE IV

MILLER INDICES AND OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS AND INTENSITIES FOR $BaSm_2O_4$

h k l	d_0 (Å)	d_c (Å)	I_0[a]	I_c[b]
2 0 0		5.264		4
2 2 0	3.999	4.003	w	8
0 1 1	3.418	3.422	w	10
1 1 1	3.253	3.254	w	10
0 4 0	3.086	3.086	s	44
3 2 0	3.049	3.049	s	100
1 4 0	2.957	2.961	s	7
1 2 1		2.960		70
2 0 1		2.950		33
2 1 1	2.868	2.868	w	5
1 3 1	2.609	2.609	s	22[c]
3 1 1	2.449	2.449	m	8
4 2 0	2.418	2.420	vw	4
2 3 1	2.397	2.397	vw	1
1 4 1	2.276	2.277	w	8[c]
3 3 1	2.131	2.135	m	10
2 4 1		2.132		31
4 0 1	2.115	2.116	m	22
4 1 1	2.085	2.085	vw	11
0 5 1	2.023	2.029	vw	6
2 6 0	1.893	1.916	vw	11
2 5 1		1.893		4
0 0 2	1.7814	1.7808	m	19
3 6 0	1.7743	1.7745	m	15
1 6 1	1.7558	1.7565	m	17
6 0 0		1.7534		12
4 4 1	1.7451	1.7450	m	21
5 4 0	1.7394	1.7392	w[c]	4
5 2 1		1.7382		15
2 6 1	1.6875	1.6874	vw	6
5 3 1	1.6585	1.6580	vw	2
4 5 1	1.6099	1.6065	vw	3
1 7 1	1.5627	1.5628	vw	3
0 4 2	1.5428	1.5424	w	14
3 2 2	1.5382	1.5377	w	32
6 4 0	1.5248	1.5245	w	12

[a] Estimated from Guinier film.

[b] Intensities calculated with $CaSc_2O_4$ atomic parameters (*23*) and the isotropic thermal parameters: Sm, 0.9; Ba, 1.0; O, 1.5 Å^2.

[c] Superposition with $BaCO_3$ reflection.

peratures is consistent with the moment of 0.8 B.M. expected for Sm^{3+} (*1*).

The data presented in Table V show the influence of temperature, O_2 atmosphere, and heating time on the '123' lattice parameters. Specimens heated at 950°C in both air and O_2 yielded identical lattice parameters. Only extended heat treatments in O_2 at lower temperatures led to smaller lattice parameters and presumably concomitant copper(II) oxidation. Refined lattice parameters of the superconducting phase are only slightly smaller than those of the nonsuperconducting analogue (see Table V); the unit cell volume decreases from 178.480(3) Å^3 for specimens annealed in air and cooled slowly to 177.469(4) Å^3 for the specimen annealed 120 hr in oxygen and quenched by removal from the hot furnace. This 1.01 Å^3 volume change compares with 1.43 Å^3 for the Nd (*11*), 1.33 Å^3 for the Eu (*12*), and 1.24 Å^3 for the Tm (*16*) '123' compound. The unit cell volume decrease observed for $YBa_2Cu_3O_{7-\delta}$ (*29*) upon reheating in a dynamic oxygen atmosphere was attributed principally to oxidation of the copper ion. The small volume decrease in the samarium '123' compound upon annealing in oxygen is difficult to understand, but may reflect a lower degree of copper oxidation.

The "green" '211' compound exhibits orthorhombic symmetry; its lattice parameters (see Table III) agree well with literature values (*30, 31*) and observed intensities agree well with those calculated using the positional parameters in (*30*).

Reactants in the molar ratio Sm : Ba : Cu = 1 : 1 : 2 produced a black compound isostructural with $La_3Ba_3Cu_6O_{14.1}$ (*8*). This phase was indexed on tetragonal lattice parameters (see Table III) by comparing its powder X-ray diffraction pattern with those of other '336' phases. As expected, lattice parameters of this '336' specimen are slightly smaller than those of the praseodymium and neodymium analogues (*11*). Calculated and observed interplanar *d*-spacings and intensities are presented in Table VI. The model $La_3Ba_3Cu_6O_{14.1}$ structure was determined from X-ray powder diffraction data and agreement between calculated and observed intensities was marginal. Calcu-

TABLE V

LATTICE PARAMETERS AND UNIT CELL VOLUMES OF $SmBa_2Cu_3O_y$ COMPOUNDS PREPARED UNDER VARIOUS CONDITIONS

Preparatory conditions				Lattice parameters				
Time (hr)	Atmosphere	Temperature (°C)[a]	Symmetry	a(Å)	b(Å)	c(Å)	Volume (Å^3)	Notes[b]
24	air	1025	O	3.872(1)	3.9037(7)	11.805(2)	178.434(4)	
24	air	950	O	3.8818(3)	3.896(1)	11.8015(8)	178.480(3)	
24	O_2	950	O	3.880(4)	3.8972(3)	11.797(1)	178.38(1)	
72	O_2	950	O	3.889(5)	3.900(1)	11.755(7)	178.29(3)	
24	O_2	975 +	}O	3.8588(8)	3.9161(3)	11.752(2)	177.590(4)	
20	O_2	700[c]						
48	O_2	975 +	}O	3.8575(5)	3.9171(8)	11.745(1)	177.469(4)	
120	O_2	700[c]						
140	O_2	975[d]	T	3.877(8)		11.770(1)	176.92(2)	
				3.884(2)		11.822(8)	178.34(3)	(*1*)[e]

[a] Sample cooled in furnace unless indicated otherwise; the + indicates successive heating conditions.

[b] This work, except as noted.

[c] Removed from hot furnace and cooled in laboratory atmosphere.

[d] Rapid quench.

[e] Vacuum annealed.

lated and observed intensity agreement for this Sm compound is also marginal and suggests positional parameter inaccuracies. The unit cell volume decreased 1.14 Å^3 after the specimen was heated 48 hr in an O_2 atmosphere, suggestive of copper ion oxidation. In contrast to the behavior observed in the Eu–Ba–Cu–O system (*12*) where an orthorhombic '336' modification was formed upon annealing in O_2, only the tetragonal form was identified in specimens heated in both air and O_2 and then quenched.

The black '132' $SmBa_3Cu_2O_z$ phase observed in the $BaCO_3$(BaO)-rich ternary region was indexed on tetragonal lattice parameters (see Table III) close to those reported previously for this and other smaller lanthanoids (*32*). This phase could not be prepared pure; traces of $BaCuO_2$ and Sm_2BaCuO_5 were always present. The observed X-ray powder diffraction intensities are in good agreement with those reported (*32*) for the gadolinium analog. This phase was not identified in the initial study of the Eu–Ba–Cu–O system (*12*); its presence was probably masked by $BaCuO_2$. A recent report suggests that in the Y system '132' is actually a mixture of '152' and '253' phases (*4*).

Attempts to prepare phases that other lanthanoid systems suggest might be present, e.g., $Sm_2Cu_2O_4$, Sm_3BaCuO_5, and $Sm_2Ba_4O_7$ (*24, 16*), the latter of which is actually a carbonate (*7*), met with failure. Although the Sm and Nd systems might be expected to be similar, the '311' phase found with Nd (*11*), a phase which appears identical to lanthanum '422' (*33*), is not present in this system and the '211' phase observed herein was absent in the Nd system.

The Sm–Ba–Cu–O phase diagram is identical to that of Eu (*12, 32*) and similar subsolidus compatabilities are expected. Reported compatability differences probably stem from different preparatory conditions. The Sm system evidences solid solution in the vicinity of the '011'–'123'–'336' tie line as do its larger congeners. Two specimens of

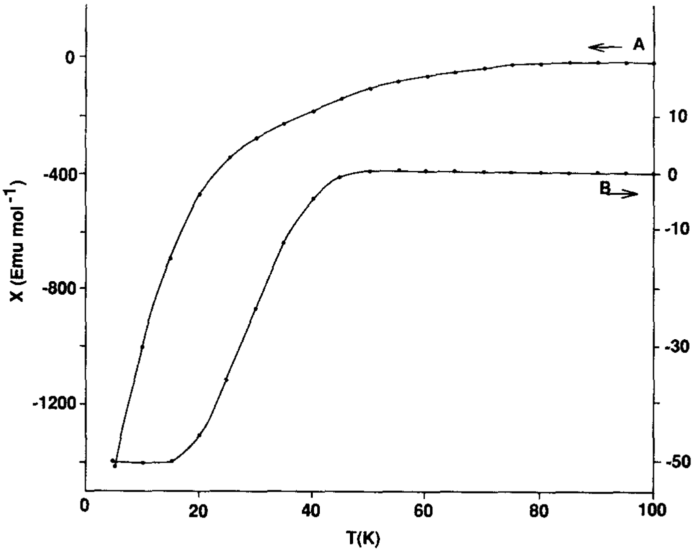

FIG. 2. The temperature dependence of the magnetization at 500 G for orthorhombic $SmBa_2Cu_3O_y$ (A, left scale) heated initially 48 hr at 975°C and then 120 hr at 700°C and (B, right scale) heated initially 24 hr at 975°C and then 20 hr at 700°C.

mixed composition '479' and '389' both evidenced this solubility. The solid solution region is lined in Fig. 1.

This system apparently constitutes the upper limit of lanthanoid-containing barium–copper '211' compounds. This phase has been observed in every *Ln*–Ba–Cu–O system studied to date with *Ln* radius smaller than that of Nd.

The experimental results permit construction of the phase diagram projection on the Gibbs triangle of composition as shown in Fig. 1. The phase subsolidus compatabilities in air near the investigation temperature of 950°C as determined by the seven phases described previously divide the diagram into 12 ternary regions. The samarium system, like that of europium, is transitory between those of the larger and the smaller lanthanoids.

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, Tm) is presented in Table VII. These data demonstrate the diversity of the phase relationships in these systems. This diversity probably results from changes in the lanthanoid (III) electronic structure and ionic radii,

TABLE VI

MILLER INDICES AND OBSERVED AND CALCULATED INTERPLANAR *d*-SPACINGS AND INTENSITIES FOR $Sm_3Ba_3Cu_6O_z$

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]
0 0 1	11.587	11.594	w	1	3 1 0	{ 1.730 }	1.730	vw}	3
0 0 2	5.796	5.797	vw	0	2 2 3		1.730		2
1 1 0	{ 3.871}	3.869	m }	13	1 1 4		1.729		3
0 0 3		3.864		2	0 0 7	1.656	1.656	vw	1
1 1 1	3.669	3.670	vw	0	3 1 3	{1.579 }	1.579	s	43
1 1 2	3.219	3.218	vw	1	2 0 6		1.578		7
2 0 0	{ 2.735}	2.736	vs }	40	1 1 7	1.523	1.523	vw	1
1 1 3		2.734		100	3 1 4	{1.4858}	1.4857	vw}	2
2 0 2	2.475	2.474	vw	0	2 2 5		1.4855		2
1 1 4	2.319	2.320	vw	3	2 0 7	1.4167	1.4169	vw	1
2 0 3	2.233	2.233	w	16	4 0 0	{1.3677}	1.3678	m }	9
2 0 4	1.990	1.990	vw	1	2 2 6		1.3672		15
2 2 0	{ 1.933}	1.934	w }	29	3 3 0	{1.2896}	1.2897	vw}	1
0 0 6		1.932		12	4 0 3		1.2896		1
2 0 5	1.769	1.769	vw	1	3 1 6		1.2890		3
					2 2 7	1.2577	1.2582	vw	1

[a] Estimated from Guinier film.

[b] Intensities calculated with $La_3Ba_3Cu_6O_{14.1}$ atomic parameters (*8*) and the isotropic thermal parameters: Sm, 0.9; Ba, 1.0; Cu, 1.0; O, 1.5 Å^2.

TABLE VII

COMPARISON OF PHASES OBSERVED *IN AIR* AT ~950°C in the *Ln*-Ba-Cu-O (*Ln* = LANTHANOID) SYSTEMS

	Phases present														
Ln	011	240[a]	220[a]	430	210	201	202	123	132	211	212	336	'422'	415	XP
La	+				+	+		+			+	+	+	+	+[b]
Pr	+				+[c]	+		+				+			+[d]
Nd	+				+	+		+				+	+[e]		
Sm	+				+	+		+	+	+		+			
Eu	+				+	+		+	+	+		+			
Y	+	+	+		+[f]		+	+	+[g]	+					
Gd[h]	+	+			+	+		+	+						
Er	+	+[i]	+	+			+	+	+[i]	+					
Tm	+	+	+	+			+	+	+	+					

Note. The digits represent the *Ln* : Ba : Cu ratio. A '+' indicates the phase has been reported.

[a] 240 is actually $Ln_2Ba_4O_7 \cdot CO_2$ (*7, 14*); 220 is probably $Ln_2Ba_2O_5 \cdot CO_2$ (*7*).

[b] XP = $La_{2-x}Ba_xCuO_{4-(x/2)+\delta}$ according to (*10*).

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

[d] XP = $BaPrO_3$.

[e] Designated '311' in (*11*); '422'-like structure (*33*).

[f] According to (*24*) and (*34*) this phase exists above 1000°C.

[g] According to (*4*) '132' is absent; '253' and '152' are present instead.

[h] From (*14*).

[i] Our unpublished data.

and the concomitant basicity variation that follows from these. On the basis of the occurrence of compounds found in these Ln_2O_3–$BaCO_3$–CuO systems, they must be divided into three subgroups: the first characteristic of La, Pr, and Nd, the second specific for Sm and Eu, and the third common to the smaller lanthanoids, the Y-type elements, with some variation within the groups. Because of its ability to exhibit multiple valency, the praseodymium system remains unique.

Acknowledgment

J.C. acknowledges support of the Polish Academy of Sciences, Program CPBP 01.12.

References

1. J. M. TARASCON, W. R. MCKINNON, L. H. GREENE, G. W. HULL, AND E. M. VOGEL, *Phys. Rev.* **B36**, 226 (1987).

2. 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 (London)* **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).

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); 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. Amer. 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).
9. S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, *Japan. J. Appl. Phys.* **26,** L1 (1987); H. Takagi, S. Uchida, K. Kitazawa, and S. Tanaka, *Japan. J. Appl. Phys.* **26,** L123 (1987).
10. D. Klibanow, K. Sujata, and T. O. Mason, *J. Amer. Ceram. Soc.* **71,** C267 (1988).
11. S. A. Hodorowicz, J. Czerwonka, and H. A. Eick, *J. Solid State Chem.* **88,** in press.
12. S. A. Hodorowicz, A. Lasocha, W. Lasocha, and H. A. Eick, *J. Solid State Chem.* **75,** 270 (1988).
13. 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).
14. S. A. Hodorowicz, A. Chodorowicz-Bak, J. Czerwonka, E. Hodorowicz, W. Lasocha, and H. A. Eick, to be submitted.
15. S. A. Hodorowicz, A. Lasocha, W. Lasocha, A. Chodorowicz, and H. A. Eick, *Acta Phys. Pol.* **A75,** 437 (1989).
16. E. Hodorowicz, S. A. Hodorowicz, and H. A. Eick, *Physica C* **158,** 127 (1989).
17. S. A. Hodorowicz, J. Czerwonka, and H. A. Eick, to be published.
18. D. W. Appleman, D. S. Handwerker, and H. T. Evans, "Program X-Ray," Geological Survey, U.S. Department of the Interior, Washington, DC (1966).
19. 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).
20. R. Kipka and H. Müller-Buschbaum, *Z. Naturforsch.* **B32,** 121 (1977).
21. M. T. Weller and D. R. Lines, *J. Solid State Chem.* **82,** 21 (1989).
22. L. M. Lopato, *Ceramurgia Int.* **2,** 18 (1986).
23. H. Müller-Buschbaum and H. G. Schnering, *Z. Anorg. Allg. Chem.* **336,** 295 (1965).
24. W. Kwestroo, H. A. M. van Hal, and C. Langereis, *Mater. Res. Bull.* **9,** 1631 (1974).
25. Powder Diffraction File, JCPDS: International Centre for Diffraction Data, 1601 Park Lane, Swarthmore, PA 19801, Data 1983, File No. 24-998.
26. J. M. Longo and P. M. Raccah, *J. Solid State Chem.* **6,** 526 (1973).
27. N. Kimizuka, E. Takayma, S. Horiuchi, A. Yamamoto, and T. Fujita, *J. Solid State Chem.* **42,** 322 (1982).
28. M. Arjomand and D. J. Machin, *J. Chem. Soc. Dalton Trans.,* 1061 (1975).
29. C. N. R. Rao, *J. Solid State Chem.* **74,** 147 (1988).
30. C. Michel and B. Raveau, *J. Solid State Chem.* **43,** 73 (1982).
31. S. Schiffler and H. Müller-Buschbaum, *Z. Anorg. Allg. Chem.* **540/541,** 243 (1986).
32. S. A. Hodorowicz, E. Hodorowicz, A. Chodorowicz, and H. A. Eick, *Cryst. Res. Technol.* **24,** K71 (1989).
33. F. Mizuno, H. Masuda, I. Hirabayashi, S. Tanaka, M. Hasegawa, and U. Mizutani, *Nature (London)* **345,** 788 (1990).
34. L. M. Kovba, L. N. Lykova, and E. V. Antipov, *Russ. J. Inorg. Chem.* (Engl. Translation) **28(3),** 409 (1983).