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BRIEF COMMUNICATIONS

Phases Observed at 900–1100°C in the Binary *Ln*–Ba–O Systems for *Ln* = Dy, Ho, Er, Tm, and Yb

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The compounds $Ln_2Ba_2O_5$, $Ln_2Ba_4O_7$, and $Ln_4Ba_3O_9$, for *Ln* = Dy, Ho, Er, Tm, and Yb, have been prepared and characterized by X-ray powder diffraction. Phase interrelationships were established as a function of temperature by quenching specimens annealed at 900–1100°C. Comparable *Ln* = Tb phases could not be prepared. Lattice parameters are presented for all phases observed.

Introduction

The report of 90 K superconductivity in the Y–Ba–Cu–O system (*1*) has produced an intensive research effort directed at characterizing this and related ternary oxide systems. Complete characterization requires that the number and composition of all compounds in binary *Ln*–Ba–O (*Ln* = La–Lu) systems be established. Most published work relates specifically to the superconducting region, with minimal emphasis on the binary components; only one detailed study of the *Ln*–Ba–O region could be found (*2*). Lopato and co-workers (*3, 4*) constructed phase diagrams for the *Ln*–Ba–O systems, with *Ln* = Y, Dy, and Yb, over the temperature range 1200–2400°C. They found only the compounds Ln_2BaO_4 and $Ln_4Ba_3O_9$. Later investigations of the Y–Ba–O system (*5, 6*) in the 900–1000°C range disclosed the presence of the additional compounds $Y_2Ba_2O_5$ and $Y_2Ba_4O_7$, and a complete phase diagram which covered the 900–2400°C region was presented in Ref. (*7*). According to Kwestroo *et al.* (*5*) $Y_2Ba_2O_5$ could not be prepared pure; it was present as one of two or three components in specimens heated at 900°C.

These observations suggested that similar phases would be present in related lanthanoid systems. We therefore undertook a systematic study of the *Ln*–Ba–O systems for *Ln* = Dy–Yb to prepare these phases and report herein the results of this study.

Experimental

Reactants were Ln_2O_3 (nominally 99.9%, Research Chemicals, Phoenix, AZ) and

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$BaCO_3$ (reagent grade, J. T. Baker Co., Phillipsburg, NJ). The reactants were examined by X-ray powder diffraction; all were found monophasic. Stoichiometric quantities of the reactants were weighed to an accuracy of ±0.1 mg. On the basis of the report of Kwestroo *et al.* at least three specimens at *Ln*: Ba molar ratios of 1 : 1, 1 : 2, and 1.33 : 1 were prepared for each system investigated. Mixtures of 500 mg each were ground in acetone, dried, confined in alumina boats, and then fired at 900°C for 24 hr. The samples were air-quenched by removing them from the furnace, examined by X-ray diffraction, reground in acetone, and then fired again at a higher temperature. Experiments were continued to a temperature of 1100°C.

Temperatures were determined to an accuracy of ±5°C with Omega stainless-steel-encased type K thermocouples and Doric digital temperature indicators. Products obtained at each stage of reaction were examined by X-ray powder diffraction with monochromatized $CuK\alpha_1$ radiation ($\lambda\alpha_1$ = 1.54050 Å) in a 114.59-mm Guinier-Hägg camera evacuated to 10^{-3} Torr during exposure. NBS-certified Si powder [*a* = 5.43082(3) Å] served as internal standard. Reflection positions were measured with a Supper film reader; intensities were estimated visually. Lattice parameters of the individual compounds were calculated with locally written least-squares programs. X-ray intensity calculations were effected with the program POWD12 (*8*).

Results and Discussion

From the compounds detected in the X-ray diffractograms the phase relationships were determined; they are summarized in Table I. All of the systems behaved similarly and three phases which could be prepared pure were found in each: $Ln_2Ba_2O_5$, $Ln_2Ba_4O_7$, and $Ln_4Ba_3O_9$. Previously unreported powder X-ray diffraction data for these phases are summarized in Tables II–IV. The X-ray powder diffraction patterns of the $Ln_2Ba_2O_5$-type phases were indexed on tegragonal symmetry with lattice parameters close to those reported by Kwestroo *et al.* (*5*) for $Y_2Ba_2O_5$. The observed (*hkl*) values suggest that these compounds have primitive unit cells. The $Ln_2Ba_2O_5$ compounds were found stable only to ~950°C. If the specimens were heated above this temperature $Ln_2Ba_4O_7$-type compounds were observed. At 980°C the phase transformation to $Ln_2Ba_4O_7$ was complete, but pure phases were observed only for specimens mixed at the molar ratio 1 : 2. The X-ray diffraction patterns of $Ln_2Ba_4O_7$ could be indexed on tetragonal symmetry with lattice parameters which agree well with the data of Kovba *et al.* (*6*) for $Y_2Ba_4O_7$. When the samples are fired above 1000°C $Ln_4Ba_3O_9$ phases result. The phase behavior observed for all the systems is in general agreement with the detailed phase diagram reported for the Y–Ba–O system (*7*). Lattice parameters of all the phases prepared in this work are compiled in Table V. A "Tb_4O_7" sample reduced to Tb_2O_3 by hydrogen did not react with BaO under the reaction conditions used.

TABLE I

PHASES OBSERVED AS A FUNCTION OF TEMPERATURE IN THE SYSTEMS Ln_2O_3–$BaCO_3$ (*Ln* = Dy, Ho, Er, Tm, AND Yb)

Ln/Ba ratio	Phase expected	Phases observed at temperature (°C) indicated[a] 900	920	940	960	980	1020	1100
1 : 1	$Ln_2Ba_2O_5$	*ABC*	$A^{t}B^{t}C$	*C*	*ACD*	*AD*	*DEF*	*EF*
1 : 2	$Ln_2Ba_4O_7$	*ABC*	$B^{t}C$	*CF*	*CDE*	*D*	*DEF*	*EF*
1.33 : 1	$Ln_4Ba_3O_9$	*ABC*	$AB^{t}C$	*AC*	*ACD*	*AD*	*ADE*	*E*

[a] *A*, Ln_2O_3; *B*, $BaCO_3$; *C*, $Ln_2Ba_2O_5$; *D*, $Ln_2Ba_4O_7$; *E*, $Ln_4Ba_3O_9$; *F*, BaO; t, trace.

The X-ray data for the $Ln_4Ba_3O_9$ phases are of concern. All observed diffraction reflections from $Ln_4Ba_3O_9$ phases (when in

TABLE II

Observed Interplanar *d*-Spacings (Å) and Relative Intensities for Tetragonal $Ln_2Ba_2O_5$ (*Ln* = Dy, Ho, Er, Tm, and Yb)

	Dy		Ho		Er		Tm		Yb	
h k l	$I_0{}^a$	d_0	$I_0{}^a$	d_0	$I_0{}^a$	d_0	$I_0{}^a$	d_0	$I_0{}^a$	d_0
0 0 1	w	11.92	m	11.90	s	11.88	m	11.87	s	11.92
0 0 2	w	5.962	m	5.947	m	5.923	m	5.929	m	5.953
1 0 0			w	4.377	w	4.361				
1 0 1	w	4.115	m	4.107	m	4.092	m	4.091	m	4.063
0 0 3					x	3.954				
1 0 2	m	3.535	m	3.521	m	3.514	m	3.512	m	3.497
1 1 0	vs	3.101	vs	3.092	vs	3.084	vs	3.082	vs	3.057
1 1 1			vw	2.993	w	2.983	vw	2.983		
1 0 3	s	2.948	vs	2.935	vs	2.929	vs	2.928	vs	2.923
1 1 2	x	2.752			vw	2.736	vw	2.735	vw	2.719
1 1 3	w	2.446	m	2.436	m	2.432	w	2.430	m	2.423
0 0 5	w	2.388	m	2.374	m	2.371	vw	2.372	w	2.381
2 0 0	s	2.194	vs	2.186	vs	2.181	s	2.179	vs	2.163
1 0 5	m	2.097	w	2.087	x	2.083	vw	2.083	w	2.085
2 0 2	w	2.059	w	2.051			vw	2.045	w	2.033
0 0 6	m	1.9898	m	1.9790	m	1.9758	m	1.9764	m	1.9845
1 1 5	w	1.8916	w	1.8834	vw	1.8789	vw	1.8797	w	1.8787
2 1 2	w	1.8641	w	1.8570	vw	1.8525			w	1.8397
2 0 4	w	1.7672								
1 2 3	s	1.7603	vs	1.7531	s	1.7488	vs	1.7482	vs	1.7395
1 1 6	m	1.6751	vs	1.6667	s	1.6636	m	1.6638	s	1.6648
2 0 5	vw	1.6155			w	1.6049	x	1.6039	m	1.6011
2 2 0					w	1.5425	w	1.5423		
1 2 5							x	1.5060		
2 0 6	w	1.4737	w	1.4668	w	1.4642	m	1.4641	w	1.4623
3 0 0							x	1.4524		

[a] Estimated from Guinier films: v, very; s, strong; m, medium; w, weak; x, extremely weak.

pure form—the 1.33 : 1 preparations) could be indexed on hexagonal symmetry with lattice parameters close to those which are based on the $Sc_4Ba_3O_9$ structure and are reported by Lopato (*2*). Our interplanar *d*-values for *Ln* = Tm agreed very well with those reported by Spitsyn *et al.* (*9*) and consequently are omitted from Table IV. Kovba and Paromova determined the structure of $Sc_4Ba_3O_9$ from powder X-ray data and report the space group to be $R\bar{3}m$ (*10*). Consistent with this space group assignment, Blanchard *et al.* in a spectroscopic study of Eu^{3+}-doped $Lu_4Ba_3O_9$ determined that the dopant was equally distributed over two sites of rhombohedral symmetry (*11*). X-ray powder diffraction intensities were calculated for $Dy_4Ba_3O_9$ with the positional parameters reported for $Sc_4Ba_3O_9$ and with thermal parameters estimated as 0.95, 1.0, and 1.5, respectively, for Dy, Ba, and O. An examination of these intensity data (see Table IV) reveals that while the strong reflections match reasonably well, agreement among the weaker reflections is less satisfactory. Three weak reflections in the *Ln* = Dy data set, 6.333, 1.9520, and 1.9435 Å, two in the *Ln* = Ho set, 6.318 and

TABLE III

OBSERVED INTERPLANAR d-SPACINGS (Å) AND RELATIVE INTENSITIES FOR TETRAGONAL $Ln_2Ba_4O_7$ (Ln = Dy, Ho, Er, Tm, AND Yb)

	Dy		Ho		Er		Tm		Yb	
$h\,k\,l$	I_0^a	d_0	I_0^a	d_0	I_0^a	d_0	I_0^a	d_0	I_0^a	d_0
0 0 2	vw	14.35	w	14.28	w	14.38	x	14.40	w	14.43
0 0 4	s	7.168	s	7.157	s	7.189	m	7.201	vs	7.215
1 0 1	m	4.316	m	4.307	m	4.300	vw	4.268	m	4.253
1 0 3	m	3.978	w	3.964	m	3.958	vw	3.936	s	3.927
0 0 8	vw	3.587	w	3.582	w	3.592			vw	3.614
1 0 5	s	3.482	m	3.468	s	3.467	m	3.454	s	3.451
1 1 0	vs	3.093	vs	3.083	vs	3.074	vs	3.053	vs	3.043
1 0 7	vs	2.996	vs	2.985	vs	2.983	vs	2.976	vs	2.979
1 1 3			x	2.935	vw	2.926	vw	2.912		
1 1 4	w	2.841	vw	2.831	m	2.826	x	2.812	m	2.805
1 0 9	m	2.578	m	2.572	m	2.573	vw	2.572	m	2.575
0 0 12	m	2.395	m	2.389	m	2.396	w	2.399	m	2.410
1 1 8	s	2.343	s	2.337	s	2.334	m	2.328	s	2.328
1 0 11	s	2.243	s	2.237	s	2.239	m	2.239	s	2.244
2 0 0	vs	2.189	vs	2.180	vs	2.172	vs	2.159	vs	2.152
2 0 2					x	2.148			vw	2.128
2 0 4	m	2.092	m	2.085	m	2.079	w	2.068		
0 0 14	m	2.054	m	2.048	m	2.054	m	2.059	s[b]	2.064
2 1 1	vw	1.9523	m	1.9450	w	1.9381				
2 1 3			vw	1.9107	vw	1.9044	w	1.8942		
1 1 12	m	1.8941	m	1.8886	m	1.8886	vw	1.8887	m	1.8896
2 0 8	x	1.8689	w	1.8624	w	1.8583			x	1.8498
2 1 5	m	1.8527	m	1.8459	m	1.8406	vw	1.8320	m	1.8262
1 1 13	vw	1.7988	w	1.7939	w	1.7944				
2 1 7	vs	1.7669	vs	1.7609	vs	1.7563	vs	1.7489	vs	1.7450
1 1 14	s	1.7111	s	1.7064	s	1.7068	m	1.7074	s	1.7098
2 1 9	w	1.6691	w	1.6630	w	1.6598				
2 0 12	s	1.6157	m	1.6107	m	1.6087	vw	1.6067	m	1.6057
2 1 11	s	1.5667	m	1.5616	s	1.5589	m	1.5548	s	1.5534
2 2 0	s	1.5475	s	1.5416	s	1.5357	m	1.5253	s	1.5218

[a] Estimated from Guinier films: v, very; s, strong; m, medium; w, weak; x, extremely weak.
[b] Broad reflection.

1.9354 Å, and the 2.633 and 2.623 Å d-values in the Er and Tm sets, respectively, violate the $(-h + k + l)$ rhombohedral constraint. Since the phases were prepared by rapid quenching, the extra reflections might belong to another phase. A search of the ASTM powder diffraction file for probable impurity reflections, e.g., Dy_2O_3 BaO, $BaCO_3$, or BaO_2, did not reveal any likely candidate (*12*). From the Dy_2O_3 and BaO unit cell volumes the $Dy_4Ba_3O_9$ molar volume can be estimated as 3 V(BaO) + 2V(Dy_2O_3) = 275 Å^3. For hexagonal indices z must then equal 3.

The largest data set, that of $Dy_4Ba_3O_9$, was submitted to the indexing program TREOR (*13*). The best fit was obtained when the three reflections mentioned above were omitted: a monoclinic cell with the figure-of-merit: $M(20) = 73$ (*14*) and refined lattice parameters: $a = 8.6045(7)$, $b = 3.0550(4)$, $c = 5.268(4)$ Å, $\beta = 101.85(8)°$.

TABLE IV

OBSERVED INTERPLANAR *d*-SPACINGS (Å) AND RELATIVE INTENSITIES FOR RHOMBOHEDRAL $Ln_4Ba_3O_9$ (Ln = Dy, Ho, Er, AND Yb)

	Dy			Ho		Er		Yb	
h k l	$I_0{}^a$	$I_c{}^b$	d_0	$I_0{}^a$	d_0	$I_0{}^a$	d_0	$I_0{}^a$	d_0
—	w	—	6.333	x	6.318				
0 1 2	s	5	4.891	m	4.874	m	4.856	s	4.814
0 1 5	s	2	3.659	s	3.647	m	3.635	s	3.602
1 1 0	vs	100	3.066	vs	3.055	vs	3.041	vs	3.019
1 0 7	vs	80	2.985	vs	2.975	vs	2.961	vs	2.939
1 1 3	w	—	2.882						
0 0 9	vw	1	2.807			x	2.786	w	2.762
—						vw	2.633		
0 2 1								w	2.600
2 0 2	w	3	2.597						
2 0 5	w	4	2.350	m	2.342	w	2.332	m	2.312
—				x	2.327				
1 0 10	x	1	2.281	vw	2.271				
0 2 7	vs	31	2.139	vs	2.131	vs	2.121	vs	2.105
0 0 12	w	2	2.105	w	2.096	x	2.089	w	2.071
1 1 9	s	14	2.070	s	2.062	m	2.054	s	2.038
1 2 2	w	2	1.9520					w	1.9505
—	w	—	1.9435	vw	1.9354				
1 2 5	w	1	1.8650	w	1.8586	x	1.8505	vw	1.8362
3 0 0	vs	24	1.7700	vs	1.7642	vs	1.7556	vs	1.7419
2 1 7	vs	39	1.7538	vs	1.7477	vs	1.7398	vs	1.7265
1 1 12	s	6	1.7356	m	1.7286	m	1.7224	m	1.7080
0 1 14	s	7	1.7085	s	1.7020	m	1.6955	s	1.6816
2 2 0	s	20	1.5324	vs	1.5275	s	1.5206	vs	1.5089

[a] Estimated from Guinier films: v, very; s, strong; m, medium; w, weak; x, extremely weak.

[b] See text.

The 135-Å^3 volume of this monoclinic cell is just about half the expected volume, half that of the rhombohedral cell, and typical of a cell, one edge of which needs to be doubled. Other cells selected by the indexing program accounted for all reflections and had figure-of-merit values of $\sim$5, and unit cell volumes of $\sim$1000 Å^3, but there was no apparent justification for selecting any particular one.

Data on $Nd_4Sr_3O_9$ were found in the CRYSTDAT data base (*15*, *16*). This similar high-temperature crystalline modification was assigned to space group C_s^4-*Cc* with a = 11.474, b = 7.238, c = 13.246 Å, β = 115.6°, and a cell volume of 992.1 Å^3. With the positional and thermal parameters reported for this phase and with estimated lattice parameters a theoretical powder pattern was calculated for $Dy_4Ba_3O_9$. Although the two strongest reflections match, the calculated and observed patterns in general disagree. It appears that the true symmetry of the $Ln_4Ba_3O_9$ phases studied in this work must be determined by single-crystal techniques.

The data obtained in this work suggest a composition-dependent reaction path. Reactants transform to $Ln_4Ba_3O_9$ according to Eq. (1)–(3):

$$2\,Ln_2O_3\ (s) + 4\ BaCO_3\ (s) \xrightarrow{900\text{–}940^\circ C} 2\,Ln_2Ba_2O_5\ (s) + 4\ CO_2\ (g) \xrightarrow{950\text{–}1000^\circ C} Ln_2Ba_4O_7\ (s) + Ln_2O_3\ (s) \xrightarrow{1020\text{–}1100^\circ C} Ln_4Ba_3O_9\ (s) + BaO\ (s) \quad (1)$$

$$2\,Ln_2O_3\ (s) + 8\ BaCO_3\ (s) \xrightarrow{900\text{–}940^\circ C} 2\,Ln_2Ba_2O_5\ (s) + 4\cdot BaO\ (s) + 8\ CO_2\ (g) \xrightarrow{950\text{–}1000^\circ C} 2\,Ln_2Ba_4O_7\ (s) \xrightarrow{1020\text{–}1100^\circ C} Ln_4Ba_3O_9\ (s) + 5\ BaO\ (s) \quad (2)$$

$$8\,Ln_2O_3\ (s) + 12\ BaCO_3\ (s) \xrightarrow{900\text{–}940^\circ C} 6\,Ln_2Ba_2O_5\ (s) + 2\,Ln_2O_3\ (s) + 12\ CO_2\ (g) \xrightarrow{950\text{–}1000^\circ C} 3\,Ln_2Ba_4O_7\ (s) + 5\,Ln_2O_3\ (s) \xrightarrow{1020\text{–}1100^\circ C} 4\,Ln_4Ba_3O_9\ (s) \quad (3)$$

These reactions are reversible and if the quenching procedure was not sufficiently rapid, small amounts of the lower temperature phases were also present in the X-ray diffraction patterns. The transformation rate was found to vary from sample to sample, but since its rate could not be quantified it was not investigated systematically. Generally speaking, all of the compounds obtained are metastable at room temperature.

In summary, phase relationships were determined in the temperature interval 900–1100°C in the Ln_2O_3–$BaCO_3$ system for Ln = Dy, Ho, Er, Tm, and Yb and for initial mixtures of the molar ratios Ln : Ba = 1 : 1, 1 : 2, and 1.33 : 1. Diffraction patterns

TABLE V

LATTICE PARAMETERS AND CELL SYMMETRIES OF $Ln_2Ba_2O_5$, $Ln_2Ba_4O_7$, AND $Ln_4Ba_3O_9$ COMPOUNDS FOR Ln = Dy, Ho, Er, Tm, AND Yb

Compound			Lattice parameters[b]			
Formula	*Ln*	Symmetry[a]	*a* (Å)	*c* (Å)	Cell vol. (Å^3)	Color
	Dy		4.3879(6)	11.939(2)	229.87	Grey
	Ho		4.3711(7)	11.870(2)	226.79	Cream
$Ln_2Ba_2O_5$	Er	T	4.3617(5)	11.853(2)	225.49	Pink
	Tm		4.3587(5)	11.857(1)	225.26	Beige
	Yb		4.3263(6)	11.908(2)	222.88	Grey
	Dy		4.3776(8)	28.755(8)	551.04	Grey
	Ho		4.3607(5)	28.681(4)	545.39	Tan
$Ln_2Ba_4O_7$	Er	T	4.3436(6)	28.742(6)	542.27	Pink
	Tm		4.3203(8)	28.834(8)	538.19	Grey
	Yb		4.3051(6)	28.937(7)	536.31	Grey
	Dy		6.1307(4) 6.132[c]	25.263(2) 25.29	822.25	Grey
	Ho		6.1105(6) 6.109[c]	25.158(3) 25.15	813.34	Tan
$Ln_4Ba_3O_9$	Er	H(R)	6.082(5) 6.087[c]	25.072(3) 25.07	803.21	Pink
	Tm		6.0558(4) 6.063[c]	24.989(2) 24.95	793.99	Beige
	Yb		6.0352(5) 6.038[c]	24.861(3) 24.86	784.27	Tan

[a] T, tetragonal; H(R), rhombohedral, on hexagonal indices.

[b] The estimated standard deviations (in parentheses) refer to the last digit indicated.

[c] Ref. (*2*).

are in good qualitative agreement with those reported for the yttrium analogs. The $Ln_2Ba_2O_5$ phases were found stable only below 950°C; above this temperature they transform to $Ln_2Ba_4O_7$. These $Ln_2Ba_4O_7$ phases are stable between 950 and 1000°C; above 1000°C $Ln_4Ba_3O_9$ was stable.

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