

A Thermochemical Study of $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($\text{A} = \text{Ba, Sr, Ca, Pb}$)

JOSEPH DICARLO, JOSEPH BULARZIK,*
AND ALEXANDRA NAVROTSKY

*Department of Geological and Geophysical Sciences and Princeton
Materials Institute, Princeton University, Princeton, New Jersey 08544*

Received April 8, 1991; in revised form July 22, 1991

The compounds $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($\text{A} = \text{Ba, Sr, Ca, Pb}$) were synthesized in their easily accessible single phase regions. High temperature solution calorimetry was performed to determine the enthalpies of formation at 704°C from oxide components. For small values of x ($x \leq 0.1$), the enthalpy of formation for Ba, Sr, and Ca substituted materials becomes progressively more exothermic with x . In contrast, Pb substituted materials show no change in the enthalpy of formation. For higher values of x ($x > 0.1$), the enthalpy of formation of the Ba, Sr, and Ca substituted materials differs significantly. These enthalpy trends are interpreted as a balance of effects due to oxidation, oxygen vacancy formation, and oxygen vacancy ordering. The former depends strongly on the basicity of the divalent cation. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, the enthalpy of oxidation (formation of formal Cu^{3+}) is -129 ± 20 kJ/(mole O_2), the enthalpy of the charge balanced substitution resulting in oxygen vacancy formation is 0 ± 10 , and the enthalpy of oxygen vacancy ordering is -40 ± 10 kJ/(mole O^{2-} vacancy). For $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$, the enthalpy of oxidation is -220 ± 50 kJ/(mole O_2), while the enthalpy of the charge balanced substitution is 0 ± 10 as in the strontium doped system. Apparent phase relationships in the $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($\text{A} = \text{Ba, Sr, Ca, Pb}$) pseudobinary system are interpreted in terms of these thermodynamic properties.

© 1992 Academic Press, Inc.

Introduction

$\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($\text{A} = \text{Ba, Sr, Ca, Pb}$) crystallizes with a K_2NiF_4 -related structure previously found for La_2CuO_4 (1). At room temperature the structures for barium, strontium, and calcium substituted materials go from orthorhombic to tetragonal for $x \geq 0.1$, however, no such change is found in the lead system (2). Superconductivity has been observed in the barium, strontium, and calcium systems, but not in the lead substituted system (3). The substitution of La^{3+} by A^{2+} ($\text{A} = \text{Ba, Sr, Ca, Pb}$) is charge

compensated by a combination of two mechanisms: the creation of Cu^{3+} or (O^-) and the creation of oxygen vacancies (4).

Not much is known about the thermodynamic properties of these systems. Recently a study of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ found that the enthalpy of oxidation was -129 ± 20 kJ/(mole O_2) and the enthalpy of vacancy formation was independent of strontium content (5). The purpose of this study is to further explore the energetics of the $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($\text{A} = \text{Ba, Sr, Ca, Pb}$) system using high temperature solution calorimetry. Enthalpies of solution in molten $2\text{PbO} \cdot \text{B}_2\text{O}_3$ at 704°C were measured and used to determine the enthalpies of formation from component oxides. The enthalpies

*Present Address: Inland Steel Research, 3001 Columbus Dr., East Chicago, IN 46312.

of formation were then used to determine the enthalpy of oxygen vacancy ordering in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ as well as interpret the phase relationships in the doped lanthanum cuprate systems.

Experimental

Preparation of $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$

$A = \text{Ba}$. The compounds $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ were prepared by grinding stoichiometric amounts of La_2O_3 (Aesar 99.99) dried at 700°C prior to use, BaCO_3 (Fischer certified ACS) dried at 400°C prior to use, and CuO (Johnson Matthey Grade 1), then heating in a platinum crucible for 48 hr at 1050°C with intermediate grindings every 12 hr. The materials were then heated at 700°C in air for 24 hr and quenched to room temperature. The oxidized and reduced forms of $\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{4-y}$ were synthesized by annealing the samples in pure oxygen and nitrogen, respectively, at 700°C for 3 hr. $\text{Ba}_2\text{CuO}_{3+x}$ was prepared by dissolving stoichiometric amounts of BaCO_3 , and CuO in 1 : 1 nitric acid, drying on a hot plate, and then heating at 950°C with several intermediate grindings.

$A = \text{Sr}$. The preparation of compounds with $x \leq 1.0$ has been previously described (5). For $x > 1.0$ the samples were prepared by grinding stoichiometric amounts of La_2O_3 (Aesar 99.99) dried at 700°C prior to use, SrCO_3 (Johnson Matthey grade 1) dried at 200°C prior to use, and CuO (Johnson Matthey Grade 1), then heating in a platinum crucible for 24 hr at 1100°C , followed by 48 hr at 1200°C . The samples were ground after each 24 hr heating. The materials were then heated at 700°C for 48 hr and quenched to room temperature.

$A = \text{Ca}$. The compounds $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ were prepared by grinding stoichiometric amounts of La_2O_3 (Aesar 99.99) dried at 700°C prior to use, CaCO_3 (Aesar 99.99) dried at 130°C prior to use, and CuO (Johnson Matthey Grade 1), and then heating in

a platinum crucible for 48 hr at 1000°C with intermediate grindings every 12 hr. The samples were then heated at 700°C for 24 hr and quenched to room temperature.

$A = \text{Pb}$. The compounds $\text{La}_{2-x}\text{Pb}_x\text{CuO}_{4-y}$ were prepared by grinding stoichiometric amounts of La_2O_3 (Aesar 99.99) dried at 700°C prior to use, PbO (Baker 99.4), and CuO (Johnson Matthey Grade 1), and then transferring the material to a platinum crucible. This crucible was then enclosed in a quartz tube which contained excess PbO to prevent lead loss upon heating. The assembly was heated for 24 hr at 950°C . The material was ground and heated for 24 hr at 700°C and quenched to room temperature.

Characterization of Products

Powder diffraction patterns were obtained with a Scintag PAD V automated diffractometer using monochromatic $\text{CuK}\alpha_1$ radiation ($\lambda = 1.54059 \text{ \AA}$). For qualitative identification of the phases present, the patterns were taken from $20^\circ < 2\theta < 70^\circ$ with a scan rate of $1^\circ(2\theta)/\text{min}$. The scan rate used to obtain X-ray patterns for precision cell constant determination was $0.25^\circ(2\theta)/\text{min}$. Cell parameters were determined by a least-squares refinement program. Sodium chloride was used as an internal standard.

Oxygen content of samples was determined by iodometric titration using the method of Nazzari *et al.* (6). A total of six titrations were done on every sample. Measurements on the same sample were always within 0.01 in oxygen content.

Inductively Coupled Plasma-Atomic Emission Spectroscopy analyses (ICP) were performed using a Perkin-Elmer ICP-5000. Approximately 20–30 mg samples were dissolved in 1 : 1 : 2 HNO_3 : HCl : H_2O solution and diluted 1 : 10. Three runs were performed on each sample, and NBS standards for each element were used to determine concentrations of the various elements.

TABLE I
CHEMICAL ANALYSIS FOR $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}$)

Compound		La ^c (wt%)	Cu ^a (wt%)	A ^a (wt%)	O ^b (wt%)
La_2CuO_4	Theoretical	68.5	15.7	—	
	Found	68.5	15.7 ± 0.2	—	15.8 ± 0.2
$\text{La}_{1.7}\text{Ba}_{.3}\text{CuO}_{3.93}$	Theoretical	58.5	15.7	10.2	
	Found	58.5	16.0 ± 0.07	9.93 ± 0.03	15.6 ± 0.2
$\text{La}_{1.5}\text{Sr}_{.5}\text{CuO}_{3.91}$	Theoretical	55.1	16.8	11.6	
	Found	55.3	16.3 ± 0.37	11.9 ± 0.01	16.5 ± 0.2
$\text{La}_{1.9}\text{Ca}_{.1}\text{CuO}_{3.99}$	Theoretical	66.8	16.1	1.0	
	Found	67.0	15.9 ± 0.11	0.95 ± 0.11	16.2 ± 0.2
$\text{La}_{1.9}\text{Pb}_{.1}\text{CuO}_{3.95}$	Theoretical	64.2	15.4	5.0	
	Found	65.0	15.2 ± 0.19	4.4 ± 0.01	15.4 ± 0.2

^a Weight percents found by ICP, errors are expressed as standard deviation of 3–5 runs.

^b Weight percent found by titration, errors are expressed as standard deviation of 3 runs.

^c Weight percent found by difference (semiquantitatively confirmed by ICP, see text).

Calorimetry

Thermochemical measurements were made using a high temperature Tian Calvet type calorimeter operating at 704°C in air, with molten lead borate ($2\text{PbO} \cdot \text{B}_2\text{O}_3$) as the solvent. Solution calorimetry was performed as previously described (5, 7). It has been found in a lead borate solvent that copper dissolves as Cu^{2+} (5). Compounds that contain formal Cu^{3+} , such as $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, liberate oxygen upon dissolving. The variation of the uncertainties in the enthalpy of solution (expressed as twice the standard deviation of the mean) reflects the small number of experiments, rather than variation in sample quality or ease of dissolution. Therefore, uncertainties for the enthalpy of formations are expressed as the average propagated error (square root of the sum of the squares of the uncertainties) for all samples, which is ± 5 kJ/mole.

Results and Discussion

All materials in the $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ system ($A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}$) crystallized with a K_2NiF_4 -related structure. Copper and di-

valent compositions were found to be within 1 wt% of the nominal composition (Table I). Lanthanum concentrations measured by ICP were lower than the nominal concentrations by 1 to 4 wt%. We believe this difference reflects a possible systematic problem with lanthanum standards. Since the oxygen contents were measured by iodometric titrations, the lanthanum concentrations in Table I have been calculated by difference. When this is done, all analyzed lanthanum concentrations are within 1 wt% of theoretical values, and the nominal compositions are used in all further discussions.

Lattice parameters and oxygen contents for these samples reported in Table II indicate that at room temperature the structures of Ba, Sr, and Ca substituted materials change from orthorhombic to tetragonal at $x \geq 0.1$. Johnston *et al.* reported that La_2CuO_4 undergoes a second order orthorhombic to tetragonal phase transformation between 233 and 263°C (8). Oxygen contents obtained by iodometric titration for samples equilibrated in air at 704°C are shown in Fig. 1. For Ba, Sr, and Ca substituted materials, initial substitution retains the stoichiometric oxygen content ($y < 0.02$ for $x < 0.10$), but

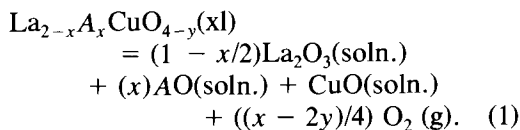
TABLE II
LATTICE PARAMETERS AND OXYGEN CONTENTS FOR
 $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ (A = Ba, Sr, Ca, Pb)

x	y	a(Å)	b(Å)	c(Å)	Cell volume (Å ³) ^a
Ba = 0.0	0.005.357(2)	5.400(2)	13.160(5)	380.7	
Ba = 0.05	0.015.358(2)	5.384(2)	13.199(5)	380.8	
Ba = 0.10	0.013.792(2)		13.245(5)	380.9	
Ba = 0.15	0.033.792(2)		13.251(5)	381.1	
Ba = 0.20	0.033.789(2)		13.296(5)	381.7	
Ba = 0.30	0.073.783(2)		13.353(5)	382.2	
Sr = 0.05	0.005.352(2)	5.382(2)	13.184(5)	379.8	
Sr = 0.10	0.023.785(2)		13.213(5)	378.7	
Sr = 0.15	0.033.778(2)		13.235(5)	377.9	
Sr = 0.20	0.043.772(2)		13.248(5)	377.2	
Sr = 0.35	0.063.767(2)		13.261(5)	376.5	
Sr = 0.50	0.093.765(2)		13.244(5)	375.6	
Sr = 0.75	0.233.761(2)		13.162(5)	372.5	
Sr = 1.00	0.403.764(2)		12.976(5)	367.7	
Sr = 1.10	0.493.758(2)		12.953(5)	365.8	
Sr = 1.20	0.563.750(2)		12.922(5)	363.5	
Sr = 2.00	0.953.502(2)	3.912(2)	12.709(5)	348.2	
Ca = 0.05	0.015.352(2)	5.387(2)	13.156(5)	379.3	
Ca = 0.10	0.033.790(2)		13.165(5)	378.2	
Ca = 0.15	0.043.784(2)		13.168(5)	377.0	
Ca = 2.00	1.003.258(2)	3.778(2)	12.238(5)	301.3	
Pb = 0.05	0.025.354(2)	5.388(2)	13.183(5)	380.3	
Pb = 0.10	0.055.353(2)	5.380(2)	13.196(5)	380.0	

^a All volumes are expressed in terms of the orthorhombic La_2CuO_4 structure.

further substitution causes oxygen deficiency, presumably by oxygen vacancy formation. Lead substitution results in oxygen loss for all values of x , to the extent that no formal oxidation states greater than Cu^{2+} (and Pb^{2+} , O^{2-}) are detected. The Ba, Sr, and Ca samples show oxygen contents intermediate between those expected for complete vacancy formation (all formal Cu^{2+}) and for no vacancy formation (oxidation to formal Cu^{3+} valence state), confirming that both charge balance mechanisms are operating for samples quenched in air from 700°C.

Table III shows the enthalpies of solution for the systems $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ (A = Ba, Sr, Ca, Pb) and for the constituent oxides. Since solution calorimetry was performed at 704°C, the data obtained pertain to the tetragonal K_2NiF_4 structure for all samples with $x < 2.0$. Enthalpies of solution are represented by the reaction (at 704°C)



From these values the enthalpy of formation at 704°C can be calculated,

$$\begin{aligned} \Delta H_f = (1 - x/2) \cdot \Delta H_s(\text{La}_2\text{O}_3) \\ + x \cdot \Delta H_s(\text{AO}) + \Delta H_s(\text{CuO}) \\ - \Delta H_s(\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}). \quad (2) \end{aligned}$$

Figure 2 shows the enthalpy of formation (Eq. 2) of $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ (A = Ba, Sr, Ca, Pb) at 704°C as a function of divalent substitution, x . At small x values ($x < 0.10$), the enthalpy of formation for Ba, Sr, and Ca substituted materials become more exothermic to about the same extent with increasing x . However, the Pb compounds show no significant change in ΔH_f up to $x = 0.10$. At $x > 0.1$, each system behaves somewhat differently. These differences are discussed in detail later.

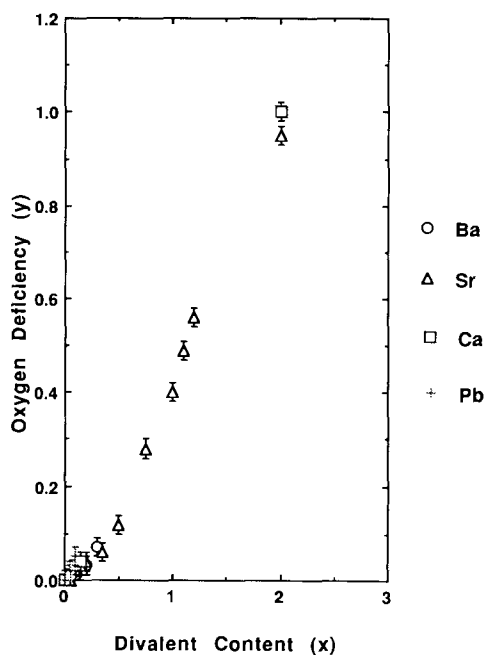


FIG. 1. Oxygen deficiency, y , versus divalent oxide content, x , for $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ (A = Ba, Sr, Ca, Pb).

TABLE III
THERMODYNAMIC DATA FOR $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ (A = Ba, Sr, Ca, Pb)

Compound	ΔH_f (704°C) ^c (kJ/mol)	ΔH_f (704°C) ^d (kJ/mol)
CuO	+33.3 ± 0.4(10) ^a	—
La_2O_3	-126 ± 4.4(7)	—
La_2CuO_4	-73.2 ± 1.6(20)	-19.5
BaO^b	-127 ± 2.2(6)	—
Ba = 0.05	-73.0 ± 4.2(6)	-22.9
Ba = 0.10	-73.5 ± 4.8(6)	-25.6
Ba = 0.15	-69.5 ± 3.8(6)	-32.8
Ba = 0.20	-71.1 ± 4.0(6)	-34.4
Ba = 0.30	-75.6 ± 4.4(6)	-36.3
SrO	-93.6 ± 2.0(17)	—
Sr = 0.05	-73.4 ± 1.8(6)	-20.7
Sr = 0.10	-71.6 ± 4.1(6)	-24.2
Sr = 0.15	-67.3 ± 2.2(6)	-30.0
Sr = 0.20	-70.4 ± 2.5(6)	-28.4
Sr = 0.35	-74.2 ± 4.3(6)	-29.2
Sr = 0.50	-76.8 ± 2.6(6)	-31.2
Sr = 0.75	-86.0 ± 4.0(6)	-29.7
Sr = 1.00	-96.8 ± 0.9(6)	-26.5
Sr = 1.10	-99.7 ± 4.3(6)	-26.7
Sr = 1.20	-104 ± 4.0(6)	-25.4
Sr = 2.00 ^e	-95.6 ± 4.8(6)	-58.3
CaO^b	-58.9 ± 1.4(8)	—
Ca = 0.05	-72.3 ± 3.8(6)	-20.2
Ca = 0.10	-69.0 ± 3.2(6)	-23.3
Ca = 0.15	-73.0 ± 3.2(7)	-19.1
Ca = 2.00 ^e	-73.7 ± 3.6(6)	-10.8
PbO	+18.3 ± 0.8(6)	—
Pb = 0.05	-65.6 ± 2.8(6)	-23.0
Pb = 0.10		

^a Uncertainty is 2 s.d. of mean, value in () is number of experiments.

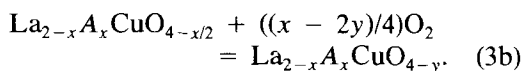
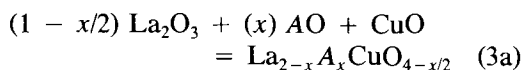
^b Values obtained from Ref. (11).

^c Enthalpy of solution in molten $2\text{PbO} \cdot \text{B}_2\text{O}_3$.

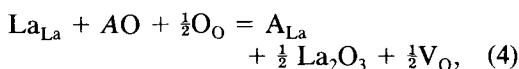
^d Enthalpy of formation from component oxides.

^e Ordered A_2CuO_3 structure.

The formation of $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ from component oxides may be separated into two steps,



Reaction (3a) incorporates the coupled substitution



where subscripts denote type of site in the La_2CuO_4 structure; V represents a vacancy.

Thus the enthalpy of formation (Eq. 3) may be considered as a balance of two terms, one arising from coupled substitution involving vacancy formation and the second involving formal oxidation of Cu^{2+} to Cu^{3+} and reintroduction of oxygen. The enthalpy of each step is expected to vary with the nature of the divalent cation, and the contribution of the oxidation term will depend on the extent of oxidation ($0 < y < x/2$), which will be a function of composition, temperature, and oxygen fugacity.

Available data are insufficient to quantitatively ascertain thermodynamic parameters associated with reactions (3a) and (3b) for all the systems studied, but partial analysis and some qualitative comparisons can be made.

For $x = 0.1$, the oxygen deficiency, y , is 0.01, 0.02, 0.03, and 0.05 for Ba, Sr, Ca, and Pb, respectively. This demonstrates a trend toward less complete oxidation (vacancy formation dominating over oxidation) as the main substitution mechanism with decreasing basicity of the divalent cation, consistent with electrostatic considerations relating the stabilization of high oxidation states to the nature of the other cation (9). Such an argument would imply that the enthalpy of oxidation becomes more exothermic, and the extent of oxidation more complete, in the sequence Pb, Ca, Sr, Ba. A previous study (5) determined the enthalpy of oxidation of the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ series (Eq. 3b) to be -129 ± 20 kJ/(mole O_2) by comparing transposed temperature drop calorimetric data for samples having the same amount of Sr (same x value) but differing oxygen deficiency, y . Also, the enthalpy of formation of the nonoxidized compounds, La_{2-x}

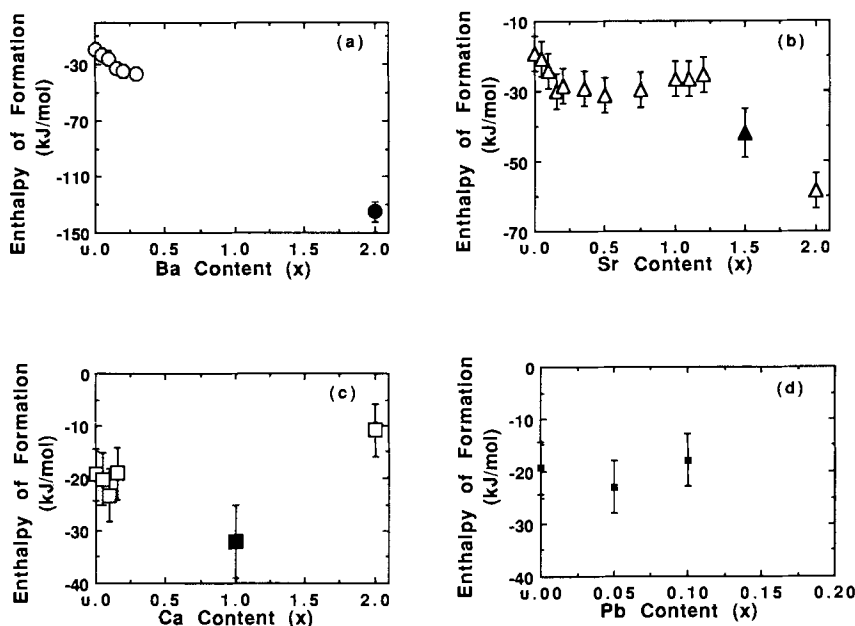


FIG. 2. Enthalpy of formation at 704°C for compounds with y values as specified in Table II, namely values representing equilibrium in air at 704°C: (a) $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$; (b) $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$; (c) $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$; (d) $\text{La}_{2-x}\text{Pb}_x\text{CuO}_{4-y}$. Darkened symbols indicate multiphase materials. Error bars are displayed or are smaller than symbol size.

$\text{Sr}_x\text{CuO}_{4-x/2}$ (Eq. 3a) was determined to be approximately independent of x for $0 \leq x \leq 1$. This constancy implies that the enthalpy of the coupled substitution involving vacancy formation (Eq. 4) is essentially zero. The present work extends these data to $x = 1.2$, and confirms the relatively constant value of the enthalpy of formation (Eq. 2) of about -22 ± 3 kJ/mole for the nonoxidized Sr-series.

The above analysis of the Sr substitution was made possible by the large range of solid solution ($0 \leq x \leq 1.2$) and the significant variation of y values obtainable by annealing in atmospheres of different oxygen fugacity. For the Ca and Pb systems, x is too small ($x \leq 0.15$) to allow y to be determined with sufficient accuracy to detect its variation with annealing history. For Ba, it was possible to vary the oxygen content for the sample with $x = 0.30$ from $y = 0.10$, when

annealed in nitrogen, to $y = 0.07$ in air, and to $y = 0.05$ in oxygen. The enthalpy of oxidation obtained from these samples was -220 ± 50 kJ/(mole O_2) (Tables III, IV). This value is close to the enthalpy of oxidation of -190 ± 5 kJ/(mole O_2) found for the $\text{YBa}_2\text{Cu}_3\text{O}_x$ ($6 < x < 7$) series (10). The thermodynamic cycle for oxidation is shown in Table V. Thus the value obtained for the

TABLE IV
TRANSPosed TEMPERATURE DROP CALORIMETRY OF
 $\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}$ and $\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.95}$

Compound	ΔH_{obs} (kJ/mol)
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}$	109 ± 1.7 (6) ^a
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.95}$	115 ± 1.6 (6)

^a Uncertainty is 2 s.d. of mean, value in () is number of experiments.

TABLE V
THERMODYNAMIC CYCLE FOR OXIDATION
OF $\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{4-y}$

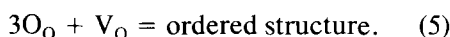
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}(\text{s}, 25^\circ\text{C}) \rightarrow \text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}(\text{s}, 700^\circ\text{C})$
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}(\text{s}, 700^\circ\text{C}) + 0.015 \text{O}_2(\text{g}, 700^\circ\text{C}) \rightarrow \text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.93}(\text{s}, 700^\circ\text{C})$
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.93}(\text{s}, 700^\circ\text{C}) + 0.01 \text{O}_2(\text{g}, 700^\circ\text{C}) \rightarrow \text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.95}(\text{s}, 25^\circ\text{C})$
$0.025 \text{O}_2(\text{g}, 25^\circ\text{C}) \rightarrow 0.025 \text{O}_2(\text{g}, 700^\circ\text{C})$
$\text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.90}(\text{s}, 25^\circ\text{C}) + 0.025 \text{O}_2(\text{g}, 25^\circ\text{C}) \rightarrow \text{La}_{1.7}\text{Ba}_{0.3}\text{CuO}_{3.95}(\text{s}, 25^\circ\text{C})$

enthalpy of oxidation for $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ is significantly more exothermic than the value obtained for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, consistent with the oxide basicity arguments above (Table VI). The values for the enthalpies of oxidation suggest that the enthalpy of oxidation depends more strongly on the nature of the divalent cation (Sr vs. Ba) than on the details of crystal structure (K_2NiF_4 vs. defect perovskite type).

In an attempt to better understand the phase relationships in the $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$

($A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}$) system, the end member compounds $\text{A}_2\text{CuO}_{3+y}$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$) were prepared. Only $\text{Sr}_2\text{CuO}_{3+y}$ and $\text{Ca}_2\text{CuO}_{3+y}$ could be prepared as single phase materials (Table II). The compound $\text{Ba}_2\text{CuO}_{3+y}$ was prepared and appeared single phase to X rays; however, optical microscopy showed additional phases to be present to the extent of a few percent. At $x > 0.1$ for $\text{La}_{2-x}\text{Pb}_x\text{CuO}_{4-y}$, an impurity phase of $4\text{PbO} \cdot \text{La}_2\text{O}_3$ was found.

$\text{A}_2\text{CuO}_{3+x}$ ($A = \text{Ba}, \text{Sr}, \text{Ca}$) compounds crystallize with a K_2NiF_4 -related structure; however, there is an ordered oxygen vacancy distribution in the copper plane yielding the stoichiometry A_2CuO_3 rather than A_2CuO_4 (II). As discussed earlier, the change in the enthalpy of formation with strontium content in nonoxidized compounds up to $x = 1.2$ (Eq. 3a) was small, thus the difference between the enthalpy of formation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, ($x = 0, y = 0$) and ($x = 2, y = 1$) can be attributed to oxygen vacancy ordering represented by the equation



The enthalpy of this ordering was calculated to be approximately $-40 \pm 10 \text{ kJ}/(\text{mol O}^{2-})$

TABLE VI
THERMODYNAMIC PROPERTIES AND RELATIVE BASICITY OF SOME PEROVSKITE-RELATED COMPOUNDS

Ion	Radius (Å)	Electroneg.	Compound	ΔH_{ox} (kJ/mol)	ΔH_{sub} (kJ/mol)	ΔH_{ord}^e (kJ/mol)
Ba^{2+}	1.52 ^c	1.0	$\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$	-190 ± 5	—	—
Ba^{2+}	1.47 ^d	1.0	$\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$	-220 ± 50	0.0 ± 10	$(-110 \pm 20)^d$
Sr^{2+}	1.31 ^d	1.0	$\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$	-129 ± 20	0.0 ± 10	-40 ± 10
Ca^{2+}	1.18 ^d	1.0	$\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$	—	0.0 ± 10	$+8.0 \pm 10^b$
Pb^{2+}	1.35 ^d	1.6	$\text{La}_{2-x}\text{Pb}_x\text{CuO}_{4-y}$	not favorable	—	structure type absent

^a Value obtained using value of $-135 \text{ kJ}/\text{mol}$ for Ba_2CuO_3 .

^b Value obtained assuming value of 0.0 for coupled substitution.

^c Coordination number is 10.

^d Coordination number is 9.

^e ΔH_{ox} = enthalpy of oxidation (Eq. 3b), ΔH_{sub} = enthalpy of the coupled substitution (Eq. 4), ΔH_{ord} = enthalpy of ordering of oxygen vacancies (Eq. 5).

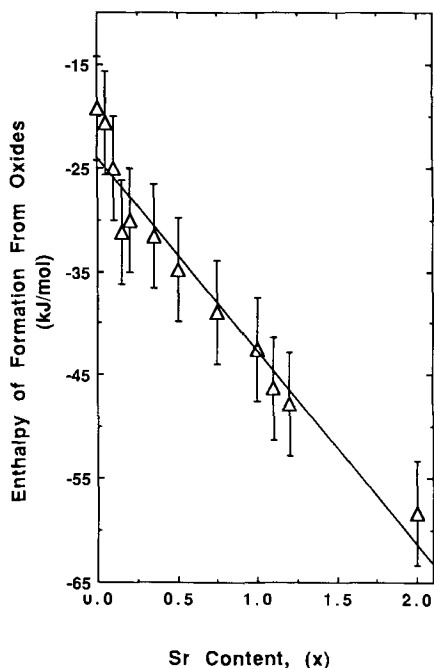


FIG. 3. Calculated enthalpy of formation at 704°C for $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ with hypothetical ordering of oxygen vacancies as in the Sr_2CuO_3 structure, with y values characteristic of 704°C in air as specified in Table II.

vacancy) for Sr-doped materials. If the enthalpies of formation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ (Table III) are corrected by an increment of $-40y$, the calculated enthalpies of formation at 704°C of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ with the Sr_2CuO_3 ordering of oxygen vacancies is obtained. This quantity (Fig. 3) varies linearly with x and suggests that the sharp change in the enthalpy of formation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ between $x = 1.2$ and $x = 2$ (Fig. 2b) is caused by the ordering of oxygen vacancies.

In this study the only phases found to exist under our methods of preparation of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ were the orthorhombic La_2CuO_4 structure for $0.00 \geq x > 0.1$, the tetragonal K_2NiF_4 structure for $0.1 \geq x \geq 1.2$, the Sr_2CuO_3 structure for $x = 2.0$, and a mixture of the tetragonal K_2NiF_4 and

Sr_2CuO_3 structures for $1.2 < x < 2.0$. Virtually no lanthanum could be substituted into Sr_2CuO_3 under our methods of preparation. The enthalpies of formation for the complete series of $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ are shown in Fig. 2b. As Sr is doped into La_2CuO_4 the enthalpy of formation initially becomes more exothermic due to an exothermic enthalpy of oxidation. As x becomes greater the degree of oxidation remains relatively constant, as does the enthalpy of formation. At $x > 1.2$ a second phase of Sr_2CuO_3 becomes evident in X-ray patterns and the enthalpy of formation becomes more exothermic due to the oxygen vacancy ordering in the Sr_2CuO_3 structure.

Figure 2a shows the enthalpies of formation for the $\text{La}_{2-x}\text{Ba}_x\text{CuO}_{4-y}$ system at 704°C. As Ba is doped into La_2CuO_4 there is an exothermic change in the enthalpy of formation greater than that seen for Sr. This is due to a more exothermic enthalpy of oxidation found for the Ba system. At $x > 0.3$, a second phase of $\text{Ba}_2\text{CuO}_{3+y}$ is seen in the X-ray powder patterns. The enthalpy of formation of $\text{Ba}_2\text{CuO}_{3+y}$, derived by drop solution calorimetry, is -135 ± 10 kJ/mol. This value is much more exothermic than the -58 ± 5 kJ/mol found for Sr_2CuO_3 , which may explain why the solubility limit of Ba is less than that of Sr in La_2CuO_4 , namely, that the competing ordered A_2CuO_3 phase is much more energetically favorable for Ba than for Sr. This trend continues for Ca and Pb. The ordered Ca_2CuO_3 phase appears energetically similar to the extrapolation for disordered phases. The corresponding Pb_2CuO_3 is absent, with other structures in the ternary $\text{PbO-La}_2\text{O}_3\text{-CuO}$ system occurring instead (Table VI).

Figure 2c shows the enthalpies of formation for the $\text{La}_{2-x}\text{Ca}_x\text{CuO}_{4-y}$ system at 704°C. As Ca is doped into La_2CuO_4 there is an exothermic change in the enthalpy of formation smaller than that for Sr. This is thought to be due to an enthalpy of oxidation of Ca less than that of Sr, however, its value

could not be obtained. At $x = 1$ for Ca, the X-ray patterns reveal phases that are neither La_2CuO_4 nor Ca_2CuO_3 . Although these phases could not be identified, it is apparent that their enthalpies of formation relative to the component oxides are more exothermic than values located along a hypothetical ideal solid solution line between La_2CuO_4 and Ca_2CuO_3 (Fig. 2c).

Conclusions

Members of the series $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}$) have been synthesized and their enthalpies of formation have been investigated. In order to interpret enthalpies of formation from component oxides, the enthalpies of oxidation, vacancy formation, and vacancy ordering were studied. Only in the $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$ system was it possible to determine all these thermodynamic parameters accurately, since this system had the most extensive range of solid solution. For $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-y}$, the enthalpy of oxidation, vacancy formation and vacancy ordering were determined to be -129 ± 20 kJ/(mole O_2), 0 ± 10 kJ/(mole O^{2-} vacancy) and -40 ± 10 kJ/(mole O^{2-} vacancy), respectively. Figure 2b, which shows the dependence of the heat of formation at 700°C with strontium content, can be interpreted using these thermodynamic properties. From $x = 0$ to $x = 1.2$, the curvature in Fig. 2b is caused by a differing degrees of oxidation in these compounds (Table II). The more exothermic values for the enthalpies of formation for Sr concentrations greater than $x = 1.2$ reflects oxygen vacancy ordering resulting in the formation of Sr_2CuO_3 . Figure 3 indicates that the major energetic difference between the Sr_2CuO_3 and La_2CuO_4 structures is the ordering of the oxygen vacancies.

Differences in the enthalpies of formation in $\text{La}_{2-x}\text{A}_x\text{CuO}_{4-y}$ ($A = \text{Ba}, \text{Sr}, \text{Ca}, \text{Pb}$)

were found to be consistent with the differences in the relative basicity of the A^{2+} cation. Figure 2 shows that the enthalpies of formation become more exothermic in the order Pb, Ca, Sr, and Ba. It was also found that the degree of oxidation (Table II) was greater, and the enthalpy of oxidation became more exothermic in the same order. Thus, we conclude that our results confirm that more basic A-site cations tend to energetically stabilize high oxidation states of B-site cations in these perovskite related materials.

Acknowledgments

This work was supported by the U.S. Department of Energy (Grant DE-FG02-89ER45394). We thank Maria Borscik for performing the ICP measurements.

References

1. J. M. LONGO AND P. M. RACCAH, *J. Solid State Chem.* **6**, 526 (1973).
2. J. GOPALAKRISHNAN, M. A. SUBRAMANIAN, C. C. TORARDI, J. P. ATTFIELD, AND A. W. SLEIGHT, *Mater. Res. Bull.* **24**, 321 (1989).
3. D. U. GUBSER, R. A. HEIN, S. H. LAWRENCE, M. S. OSOFSKY, K. J. SCHRODT, L. E. TOTH, AND S. A. WOLF, *Phys. Rev. B.* **35**(10), 5350 (1987).
4. N. NGUYEN, J. CHOISNET, M. HERVIEU, AND B. RAVEAU, *J. Solid State Chem.* **39**, 120 (1981).
5. J. BULARZIK, A. NAVROTSKY, J. DICARLO, J. BRINGLEY, B. SCOTT, AND S. TRAIL, *J. Solid State Chem.*, in press.
6. A. I. NAZZAL, V. Y. LEE, E. M. ENGLER, R. D. JACOWITZ, Y. TOKURA, AND J. B. TORRANCE, *Phys. C* **153-156**, 1367 (1988).
7. A. NAVROTSKY, *Phys. Chem. Miner.* **2**, 89 (1977).
8. D. C. JOHNSTON, J. R. STOKES, D. P. GOSHORN, AND J. T. LEWANDOWSKI, *Phys. Rev. B.* **36**(7), 4007 (1987).
9. M. YOSHIMURA, T. NAKAMURA, AND T. SATA, *Bull. Tokyo Inst. Technol.* **120**, 13 (1974).
10. M. PARKS, A. NAVROTSKY, K. NOCALA, E. TAKAYAMA-MUROMACHI, A. JACOBSON, AND P. DAVIES, *J. Solid State Chem.* **79**, 53 (1989); **83**, 218 (1989), Errata.
11. H. MULLER-BUSCHBAUM, *Angew. Chem. Int. Ed. Engl.* **16**, 674 (1977).
12. Z. ZHOU AND R. RAPP, Private Communication.