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Energetics of $La_{2-x}Sr_xCuO_{4-y}$ Solid Solutions ($0.0 \leq x \leq 1.0$)

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Compounds in the $La_{2-x}Sr_xCuO_{4-y}$ series have been synthesized in the single phase range $0 \leq x \leq 1$. High temperature solution calorimetry in molten lead borate was used to determine the heats of formation from oxide components. The enthalpy of formation becomes more exothermic with increasing Sr substitution $0 \leq x \leq 0.15$ and then remains approximately constant for $0.15 \leq x \leq 1$. This trend can be explained by the balance between the (formal) substitution $La^{3+} + Cu^{2+} = Sr^{2+} + Cu^{3+}$ and the loss of oxygen, keeping copper formally divalent but creating oxygen vacancies. Using a transposed temperature drop method, the heat of oxidation was determined to be −129 kJ/(mole O_2) by a comparison of samples with the same strontium content but a different oxygen content. © 1991 Academic Press, Inc.

Introduction

The perovskite-related $La_{2-x}Sr_xCuO_{4-y}$ system has generated much interest due to the discovery of its superconducting phase region (*1*). The solid solution has three structural regions, an orthorhombic structure appears for $0.0 \leq x < 0.1$, while for $0.1 \leq x \leq 1.0$ the tetragonal K_2NiF_4 structure is seen (*2*). Upon the substitution of strontium for lanthanum, the La_2CuO_4 structure must compensate for the difference in ionic charge. An oxidation of other species in the structure, such as (formally) Cu^{2+} to Cu^{3+}, or a creation of oxygen vacancies ($y > 0$) can balance the charge. The third structural region for $1.0 \leq x \leq 1.34$ shows additional superstructure due to the ordering of oxygen vacancies in the basal plane of the octahedra (*3*).

The oxygen content, 4-*y*, depends on the Sr content, partial pressure of oxygen, annealing temperature, and cooling rate (*4*). Higher oxygen content can be achieved by annealing the samples under high oxygen pressure. Under 3 kbar of O_2 and at 800°C, $LaSrCuO_4$ was reported to be synthesized with no vacancies (*5, 6*). The oxygen content affects other properties, including T_c (*7*).

Rather little is known about the thermodynamic properties of the $La_{2-x}Sr_xCuO_{4-y}$ series. The heats of formation of La_2CuO_4 and $La_{1.85}Sr_{0.15}CuO_4$ have been measured by acid solution calorimetry (*8*). Several reports give widely different Gibbs free energ-

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ies from solid cell electrochemical measurements on La_2CuO_4 (*9–11*). The purpose of this study is to explore the energetics of the $La_{2-x}Sr_xCuO_{4-y}$ series for $0.0 \leq x \leq 1.0$ using high temperature reaction calorimetry. Measuring the heats of formation throughout the solid solution can determine the effects of Sr doping and reduction on the thermochemistry. Calorimetry of samples with varying oxygen deficiency, y, and constant Sr content, x, is used to determine the heat of oxidation.

Experimental Methods

Sample Synthesis and Analysis

All starting materials were high purity (>99.999%) purchased from AESAR. Lanthanum oxide was dried and CO_2 removed by firing the powder in dense alumina crucibles prior to use; all other reactants were used as received. The preparation of solid solutions in the system $La_{2-x}Sr_xCuO_{4-y}$ has been reviewed by De Leeuw *et al.* (*12*). Powdered La_2O_3, $SrCO_3$, and CuO were mixed at the appropriate stoichiometry, ground, and calcined at 1000°C in air for 24 hr. For $0 \leq x \leq 0.35$, pellets of the calcined mixtures were pressed and fired at 1000°C in air for 72 hr with two intermediate grindings. For compositions $0.4 \leq x \leq 1.0$, the pelletized powders were heated at 1150°C in air to ensure formation of a single phase that was not obtained at 1000°C. All samples were cooled in air at 100°C per hour to 200°C. A portion of the samples with $x = 0.75$ and 1.00 were annealed at 645°C under 1080-bar O_2, cooled to 500°C, held there 24 hr at 900-bar O_2, and cooled 30°C per hour to room temperature.

All the samples were analyzed by X-ray diffraction on a Siemens 500 diffractometer and the cell parameters determined by a least-squares refinement of the diffraction data. Atomic absorption analysis verified the compositions of the compounds within the 2 wt% uncertainty of each component. The samples were stored in a desiccator. The lack of decomposition of the compounds under ambient conditions was verified by comparison of X-ray patterns and the heats of solution in a lead borate solvent after a several-month interval.

The oxygen content was determined by iodometric titration (*13*). Thermogravimetric analysis on several samples confirmed the titration values. The phase purity and oxygen contents of the samples used for calorimetry, as well as the oxidation state of the copper dissolved in the lead borate solvent, are crucial to interpreting the calorimetric data. To determine these parameters, weight loss experiments were done on the samples under several different conditions.

The first type of weight loss experiment determined the apparent stability of the $La_{2-x}Sr_xCuO_{4-y}$ compounds at 700°C, the temperature of solution calorimetry. Some of the samples were weighed out in small tared platinum capsules. The samples were placed in a muffle furnace at 700°C for several hours to replicate the equilibration conditions in the calorimeter. After air cooling, the weights were recorded. No weight changes greater than 0.02 mg (which is less than 0.1% of the mass of any of the samples and equal to the precision of the balance) were recorded. The constancy of weights confirmed that the samples prepared in the air did not change in oxygen content during equilibration under calorimetric conditions and that the oxidation state of the compounds titrated at room temperature was the same as the oxidation state of the equilibrated compounds at 700°C. X-ray diffraction of a few selected compositions further confirmed the lack of decomposition.

For the samples that were annealed under high oxygen pressure, the weight loss experiments helped determine the oxidation state. Initial heating at 700°C for 1 hr imitated a transposed temperature calorimetric experiment. The weight difference between the original sample and that after heating showed some reduction of the sample under these conditions. During subsequent heating cycles the weight remained constant, showing that the reduction is rapid.

A second method determined the oxidation state of the copper in the lead borate solvent. Powdered 2 PbO · B_2O_3 glass (the calorimetric solvent) was heated in a platinum crucible for 90 min, then cooled at room temperature for 1 hr and weighed. This heating cycle was repeated several times until the weight remained constant within 0.02 mg. Several heating cycles were needed because during the first cycles the weight decreased slightly, presumably due to loss of small amounts of volatile impurities such as water. After the weight no longer changed, a $La_{2-x}Sr_xCuO_{4-y}$ sample was added to the solvent 30 min into the heating cycle. The powdered sample was contained in a small platinum crucible weighted at the bottom with a piece of platinum rod. The sample sank quickly and was covered with solvent, minimizing any reactions at the melt–air interface. Any weight difference between the sample added and the sample in the solvent was due to the oxidation or reduction of the sample upon dissolution. Previous experiments, dissolving PbO in the lead borate solvent with no weight gain, have been performed. Also, when Co_3O_4 is dissolved, both weight loss and heat effect indicate complete conversion to CoO dissolved in the solvent, with no other side reactions (*14*). In addition, both the $La_{2-x}Sr_xCuO_{4-y}$ and the Co_3O_4 dissolution experiments, when done in an open furnace one could look into, showed clear evidence of gas evolution, presumably oxygen. Furthermore, 700°C is probably too high a temperature for thermodynamic stability of Pb^{4+} compounds. These observations argue against any specific coupled reactions forming tetravalent lead, i.e., $Pb^{2+} + 2\,Cu^{3+} = Pb^{4+} + 2\,Cu^{2+}$.

Similar weight loss experiments can determine the solubility of volatile decomposition products as the sample dissolves. Such experiments were done with $SrCO_3$; see below.

Calorimetry

The twin microcalorimeter of the Tian Calvet type and general methods of solution calorimetry and transposed temperature calorimetry are described by Navrotsky (*15*). This calorimeter measures heat flow through a sensitive thermopile which surrounds the sample chamber and separates it from a large alloy block maintained at constant temperature. The thermopile experiment is recorded as a curve of voltage versus time; the area under which is proportional to the heat effect.

Heats of formation for the series $La_{2-x}Sr_x CuO_{4-y}$ were calculated from the heats of solution of the compounds and the component oxides in molten 2PbO · B_2O_3 at 703°C. For solution calorimetry, a sample of 20 to 40 mg was suspended in a platinum sample holder several centimeters above 20–30 g of lead borate solvent in a platinum crucible for at least 8 hr to reach thermal equilibrium. By the use of a long silica manipulation rod, the sample holder was lowered, the sample was stirred into the solvent, and the heat of the solution was recorded. The bottom of the sample holder, a thin platinum foil, was perforated with several pinholes to allow quick contact of the sample with the solvent (without loss prior to the experiment) and for drainage of the solvent (*19*). After the reaction was completed and the calorimetric signal had returned to a steady baseline, a second stirring run was performed. This "stirring effect" determination has two important functions. First, the heat contribution from stirring the empty platinum sample holder is substracted from the experimental heat of reaction to allow the measurement of the heat of solution. In these experiments, the stirring effect was usually 5–10% of the total heat effect observed. Since this stirring effect can be determined to about ±10%, stirring introduces a residual uncertainty of less than 1% in these experiments. Second, a deviation of the stirring effect from the average range of values indicates a problem with the experiment, such as incomplete dissolution of the sample or mechanical difficulty.

The CuO (Johnson Matthey grade 1) and $La_{2-x}Sr_xCuO_{4-y}$ samples all remain unchanged at 700°C and dissolve readily in the lead borate solvent; therefore, heats of solution were determined by using the solution calorimetry method on the powders. The La_2O_3 (Aesar 99.99% AAS grade) powder formed a lanthanum borate precipitate during calorimetry; a white solid in the sample cup was seen and identified by X-ray diffraction. Because no precipitate formed either during the dissolution of the lanthanum cuprate powders or during calorimetry of lanthanum-bearing glasses, each giving final dissolved lanthanum concentrations comparable with those using La_2O_3, we suspect that the precipitate is formed metastably by local saturation of the solvent as the La_2O_3 grains are dissolving. Large "stirring effect" values and "baseline shifts" suggested slow dissolution of the lanthanum borate upon further contact with the lead borate solvent.

The original powder appeared quite dense, with few air spaces between grains. Suspecting that sample morphology may affect dissolution kinetics, we prepared La_2O_3 by an aqueous precipitation route. The La_2O_3 powder was dissolved in nitric acid. The solution was heated to dryness on a hot plate and then gently heated with a flame to drive off NO_2. The solid was heated overnight at 700°C. The weight change during this process was consistent with the final product being La_2O_3 rather than a hydroxide or carbonate. X-ray diffraction confirmed single phase A type La_2O_3, the same as the starting material. Visual examination under a low power binocular microscope showed the sample to be a porous mass of loosely interconnected small grains, with large air spaces between them. Although this sample certainly has smaller particle size than the original, its X-ray diffraction pattern was as sharp as that of the starting material, and we believe that surface energy effects are unlikely to be large enough to affect the heat of solution. This sample dissolved readily during solution calorimetry. To further check the effects of morphology, the solid was again ground into powder and used in solution calorimetry. A precipitate formed during solution calorimetry with the same apparent heat of reaction as the original powder, but the heat was significantly more exothermic than the heat of solution of the sample which dissolved completely, again indicative of compound formation in the former case. These results indicate that the morphology of the sample controls the kinetics of dissolution. The enthalpy of solution listed in Table III is that of the sample which dissolved completely.

Because SrO is highly reactive with H_2O and CO_2, its stoichiometry is difficult to maintain. The heat of solution of SrO was determined from a thermodynamic cycle based on the heat of solution of $SrCO_3$ (Johnson Matthey grade 1); see Fig. 1. When $SrCO_3$ dissolves in lead borate, CO_2 is evolved. Weight loss experiments determined that all of the CO_2 is expelled upon dissolution. For an average sample of 20 mg of $SrCO_3$ a weight change of about 6 mg is recorded for CO_2 loss. The ±0.02 mg precision of the balance gives an uncertainty of less than ±0.5% of the CO_2 loss. Initial calorimetry using a static air atmosphere in the calorimeter always resulted in significant baseline shifts, much larger than any seen during normal solution calorimetry of samples which did not evolve gas. The volume of CO_2 evolved would be approximately sufficient to fill the sample chamber within the calorimeter, and, if this gas, denser than air, did not rapidly diffuse away, the final state in the calorimter could be slightly different

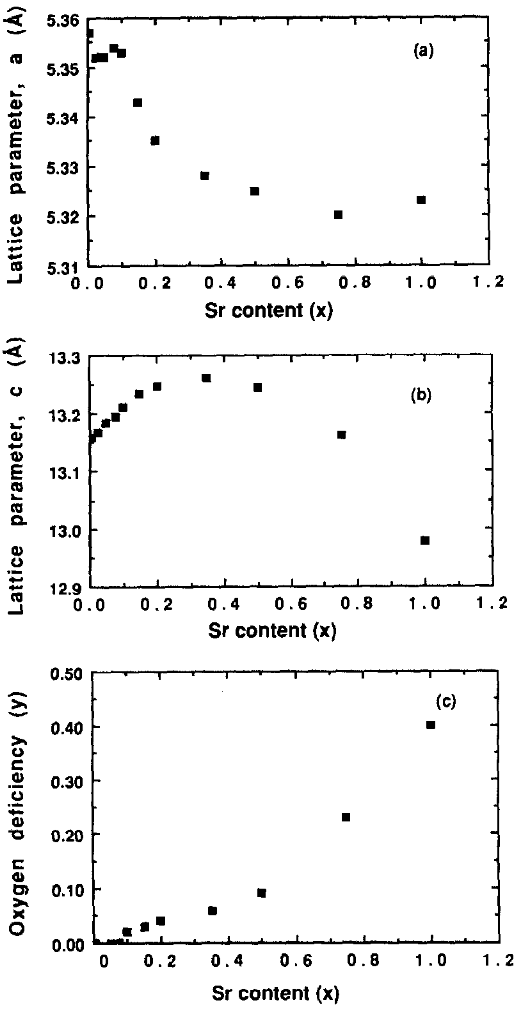

FIG. 1. (a) Lattice parameters, a, versus Sr content, x, for $La_{2-x}Sr_xCuO_{4-y}$. (b) Lattice parameter, c, versus Sr content, x, for $La_{2-x}Sr_xCuO_{4-y}$. (c) Oxygen deficiency, y, versus Sr content, x, for $La_{2-x}Sr_xCuO_{4-y}$. All samples annealed in air at 700°C.

from the original in terms of the atmosphere's heat capacity and thermal conductivity. This change could be responsible for the baseline shift. We confirmed this hypothesis by two sets of experiments. First, experiments run in a flowing argon or CO_2 atmosphere (flow rate of several cm^3/sec on both sides of the calorimeter) eliminated the baseline shift, probably because the evolved gas was carried away with the flowing gas. Second, a static CO_2 atmosphere also resulted in no baseline shifts, presumably because the gas atmosphere in the calorimeter did not change during the experiment.

For transposed temperature calorimetry in air, a sample (either a pellet or pressed powder or a powder enclosed in a platinum capsule) was dropped at room temperature through a hollow silica rod into an empty Pt crucible in the hot calorimeter. The atmosphere in the calorimeter is in dynamic equilibrium with air through the silica tubes. The measured heat effect is a combination of the heat contents of the platinum and the sample plus the enthalpy of any reactions or phase changes which occur rapidly at calorimetric temperature. Once these changes have occurred, a second drop of the same sample gives heat content terms only. The difference between the first and second drops gives the enthalpy of reaction (at room temperature). To determine the heat of oxidation of the $La_{2-x}Sr_xCuO_{4-y}$ samples, transposed temperature drop calorimetry was performed on the samples prepared under high oxygen pressure. Because the samples quickly equilibrated to lower oxygen contents at 703°C, the difference between the first drop and subsequent drops was used to determine the heat of oxidation (see Fig. 2).

Results and Discussion

X-Ray Diffraction

The lattice parameters for the $La_{2-x}Sr_xCuO_{4-y}$ compounds with $0 \leq x \leq 1$ are given in Table I and Figs. 1a and 1b. The diffraction data indicate that all the samples are single phase. The unit cell is orthorhombic for $x \leq 0.075$ and tetragonal for $x \geq 0.1$. The a axis decreases as the amount of Sr increases, with the largest change at low Sr concentrations. The c axis initially increases up to $x = 0.35$ and then decreases (see Fig. 1). Both trends were previously reported

Heat of Solution of SrO

$SrO\ (s, 295\ K) + CO_2\ (g, 295\ K) \rightarrow SrCO_3\ (s, 295\ K)$
$SrO\ (s, 975\ K) \rightarrow SrO\ (s, 295\ K)$
$CO_2\ (g, 975\ K) \rightarrow CO_2\ (g, 295\ K)$
$SrCO_3\ (s\ 295) \rightarrow SrCO_3\ (s\ 975)$
$SrCO_3\ (s, 975\ K) \rightarrow SrO\ (soln, 975\ K) + CO_2\ (g, 975\ K)$

$SrO\ (s, 975\ K) \rightarrow SrO\ (soln, 975\ K)$

Heat of Formation of $La_{2-x}Sr_xCuO_{4-y}$
all steps at 975 K

$CuO\ (s) \rightarrow CuO\ (soln)$
$(x)\ SrO\ (s) \rightarrow (x)\ SrO\ (soln)$
$(1-x/2)\ La_2O_3\ (s) \rightarrow (1-x/2)\ La_2O_3\ (soln)$
$CuO\ (soln) + (x)\ SrO\ (soln) + (1-x/2)\ La_2O_3\ (soln)$
$+ (0.25x - 0.5y)\ O_2\ (g) \rightarrow La_{2-x}Sr_xCuO_{4-y}\ (s)$

$CuO\ (s) + (x)\ SrO\ (s) + (1-x/2)\ La_2O_3\ (s) + (0.25x - 0.5y)\ O_2\ (g)$
$\rightarrow La_{2-x}Sr_xCuO_{4-y}\ (s)$

Heat of Oxidation of $La_{2-x}Sr_xCuO_{4-y}$

$La_{2-x}Sr_xCuO_{4-y'}\ (s, 975K) + (y'-y)/2\ O_2\ (g, 975K)$
$\rightarrow La_{2-x}Sr_xCuO_{4-y}\ (s, 298K)$
$La_{2-x}Sr_xCuO_{4-y'}\ (s, 298K) \rightarrow La_{2-x}Sr_xCuO_{4-y'}\ (s, 975K)$
$(y'-y)/2\ O2\ (g, 298K) \rightarrow (y'-y)/2\ O2\ (g, 975K)$

$La_{2-x}Sr_xCuO_{4-y'}\ (s, 298K) + (y'-y)/2\ O_2\ (g, 298K)$
$\rightarrow La_{2-x}Sr_xCuO_{4-y}\ (s, 298K)$

FIG. 2. Thermochemical cycles used in calculations.

(*12*). The variation of the lattice parameters is due to both the substitution of Sr for La and the corresponding change in the copper oxidation state and/or oxygen content.

Oxygen Content Analysis

Iodometric titrations determined the oxygen content (see Table I). The standard deviation of the oxygen content from three runs was always ± 0.01 or less. The oxygen content up to $x = 0.35$ agrees with data reported by Nguyen *et al.* (*2*, *3*), who determined the value by reducing the compounds with hydrogen in a TGA. For $x \geq 0.50$, the oxygen contents determined in this study are higher, which is expected from the lower heating temperature used here. The variation of oxygen deficiency, y, with Sr content, x, is shown in Fig. 1c. No oxygen deficiency ($y = 0$) is detectable for $x < 0.10$. For $0.10 \leq x \leq 1.00$ the oxygen deficiency increases with the addition of Sr. For our samples, no direct correlation exists between the change in the c axis (with a maximum value around $x = 0.3$) and the onset of oxygen vacancy formation ($y = 0$) as previously reported, nor does the compound with the greatest nominal amount of Cu^{3+} correspond to the compound with the largest c axis (*16*).

This study does not address where holes reside in the crystal, and whether Cu^{3+}, O_2^{2-}, O^- or other ionic species exist. We adopt the convention that the formal valence shall be balanced by referring to Cu^{3+}, without implying anything about speciation, band occupancy, or covalency. The iodometric titration results determine a nearly linear increase in the amount of Cu^{3+} as Sr increases at $0.00 \leq x \leq 0.50$, then a decrease at $0.50 \leq x \leq 1.00$ (see Table I).

Weight Loss Experiments

The weight of the $La_{2-x}Sr_xCuO_{4-y}$ samples did not change when heated in air to 700°C. Also the sample exposed to air at 22°C and 60% humidity did not change weight after several days. The $La_{2-x}Sr_xCuO_{4-y}$ samples lost weight when dissolved in lead borate at 700°C. These losses correspond to the reduction of the sample in the solvent to La_2O_3, and CuO with a loss of O_2 gas. Weight experiments indicate that all the copper in the solvent is divalent, because no weight change results from dissolving CuO and a weight gain results from dissolving Cu_2O.

The samples annealed under 1 kbar of oxygen lost weight when heated to 700°C in air. For four experiments at each composition, the weight loss was 0.47 ± 0.06% for $x = 0.75$ and 0.71 ± 0.04% for $x = 1.00$.

TABLE I

LATTICE PARAMETERS AND OXYGEN CONTENTS FOR $La_{2-x}Sr_xCuO_{4-y}$

Sr content (x)	a (Å)	b (Å)	c (Å)	Volume (Å^3)	Oxygen deficiency (y)	Mole fraction formal Cu^{3+} ($x - 2y$)
0.000[a]	5.357	5.400	13.160	380.7	0.00	0.00
0.025[a]	5.352	5.395	13.167	380.2	0.00	0.02
0.050[a]	5.352	5.382	13.184	379.8	0.00	0.04
0.075[a]	5.352	5.367	13.196	379.1	0.00	0.08
0.100[a]	5.353[c]		13.213	378.7	0.02	0.06
0.150[a]	5.343		13.235	377.9	0.03	0.09
0.200[a]	5.335		13.248	377.2	0.04	0.12
0.350[a]	5.328		13.261	376.5	0.06	0.22
0.500[a]	5.325		13.244	375.6	0.09	0.32
0.750[a]	5.319		13.162	372.5	0.23	0.28
1.000[a]	5.323		12.976	367.7	0.40	0.20
0.750[b]					0.14	0.47
1.000[b]					0.24	0.52

[a] Oxygen contents by iodometric titration.

[b] Prepared under 1 kbar oxygen pressure.

[c] Cell constants expressed in terms of the lanthanum cuprate unit cell.

The uncertainty in this weight loss is estimated to be ± 10% of this value. The gravimetric oxygen loss equaled that determined by iodometric titration (see Table IV).

Calorimetry

The heats of solution in the lead borate solvent of the $La_{2-x}Sr_xCuO_{4-y}$ series are given in Table II. The dissolution reaction is written with all the copper dissolving as Cu^{2+} and O_2 gas evolving from the solvent as determined by the weight loss experiments.

$$\begin{aligned} La_{2-x}Sr_xCuO_{4-y}\,(s) &= (x)SrO(soln) \\ &+ (1 - x/2)La_2O_3(soln) \qquad (1) \\ &+ CuO(soln) + ((x - 2y)/4)O_2\,(g). \end{aligned}$$

Six calorimetry experiments were performed at each composition and the uncertainty is given as twice the standard deviation of the mean. The variation of the uncertainties (±0.9 to ± 4.4 kJ/mole) reflects the small number of experiments, rather than a variation in sample quality or ease of dissolution. The average uncertainty is ±2.6 kJ/mole, which is about 3% of the heat of solution, a typical uncertainty for this method of calorimetry.

The heats of solution of La_2O_3 and CuO from solution calorimetry experiments are also given in Table II. The heat of solution of SrO was not directly measured but calculated from a thermochemical cycle involving $SrCO_3$ (see Fig. 2). The heat of formation of $SrCO_3$ and the heat contents of SrO, and $SrCO_3$, taken from the tabulations of Robie *et al.* (*16*), were used in this computation. The measured heat of solution of $SrCO_3$ and the calculated heat of solution of SrO are given in Table II.

To calculate the heats of formation of the $La_{2-x}Sr_xCuO_{4-y}$ series from the component oxides, the heats of solution of the compounds and their oxide components are needed (see Fig. 2). Table II shows enthalpy values for the formation reaction.

TABLE II

THERMODYNAMIC DATA FOR $La_{2-x}Sr_xCuO_{4-y}$

Compound	ΔH_{sol} (kJ/mole)	ΔH_f (kJ/mole)		
		Observed[a]	Oxidized[b]	Reduced[c]
CuO	33.3 ± 0.4 (10)[d]			
La_2O_3	−126.0 ± 4.4 (7)			
$SrCO_3$	135.4 ± 1.0 (17)			
SrO	−93.6 ± 2.0			
$x = 0.00,\ y = 0.00$	−73.4 ± 1.6 (6)	−19.3	−19.3	−19.3
$x = 0.05,\ y = 0.00$	−73.4 ± 1.8 (6)	−20.7	−20.7	−19.1
$x = 0.075,\ y = 0.00$	−73.0 ± 2.4 (6)	−20.2	−20.2	−17.6
$x = 0.10,\ y = 0.02$	−71.6 ± 4.1 (6)	−24.2	−25.5	−22.3
$x = 0.15,\ y = 0.03$	−67.3 ± 2.2 (6)	−30.0	−31.9	−27.1
$x = 0.20,\ y = 0.04$	−70.4 ± 2.5 (6)	−28.4	−31.0	−24.5
$x = 0.35,\ y = 0.06$	−74.2 ± 4.3 (6)	−29.2	−33.1	−21.8
$x = 0.50,\ y = 0.09$	−76.8 ± 2.6 (6)	−31.2	−37.0	−20.9
$x = 0.75,\ y = 0.23$	−86.0 ± 4.0 (6)	−29.7	−44.5	−20.3
$x = 1.00,\ y = 0.40$	−96.8 ± 0.9 (6)	−26.5	−52.3	−20.0

[a] Formation from oxides plus O_2 sample with given y value, reaction (2).

[b] Formation from oxides plus O_2 of oxidized compound, $y = 0$.

[c] Formation from oxides of reduced compound, $y = 0.5x$.

[d] Uncertainty is 2 SD of mean; value in () is number of experiments.

$$(1 - x/2)La_2O_3(s) + (x)SrO(s) + CuO(s) + ((x - 2y)/4)O_2(g) = La_{2-x}Sr_xCuO_{4-y}(s). \quad (2)$$

The heat of formation at 703°C of La_2CuO_4 is −193. ± 4.7 kJ/mole, within the error limits of −28 ± 11 kJ/mole determined by Morss *et al.* at 25°C (*8*). Because C_p of $La_{2-x}Sr_xCuO_{4-y}$ cannot readily be measured from room temperature to 700°C (the sample could undergo changes in y on heating in a DSC), the data are unavailable for making an $\int \Delta C_p\, dt$ correction to compare the heats of formation at room temperature and at 700°C. We believe it unlikely that this term is larger than about 6 kJ/mole in magnitude.

TABLE III

TRANSPOSED TEMPERATURE DROP CALORIMETRY OF $La_{2-x}Sr_xCuO_{4-y}$ PREPARED UNDER ~kbar OXYGEN PRESSURE[a]

x	ΔH_{obs} (kJ/mole)		ΔH_{ox} (kJ/(mole O_2)
	First drop	Subsequent drops	
0.75	123.2 ± 0.1	116.4 ± 0.1	−129
1.00	122.0 ± 1.4	109.9 ± 1.0	−129

[a] Experiments done under flowing Ar gas.

An initial exothermic trend is followed by a reasonably constant value for the heats of formation with the addition of Sr (see Fig. 3). The uncertainty of these values is calculated from the uncertainty of the heats of solution, using an average of ±2.6 kJ/mole. The trends are well outside this uncertainty.

Transposed temperature calorimetry experiments were run on the $La_{2-x}Sr_xCuO_{4-y}$ compounds with $x = 0.75$ and 1.00 that had been annealed under a kilobar of oxygen. The samples were enclosed in a platinum capsule, with the top crimped closed to contain the powder, but not sealed to allow gas exchange. The heat effect of the initial drop (after the heat content of the platinum capsule is subtracted) is a sum of the heat content of the oxide and the heat of reduction of the oxide as it loses oxygen and equili-

TABLE IV

OXYGEN CONTENTS OF SAMPLES PREPARED UNDER 1 kbar OXYGEN PRESSURE

x	Heating	Oxygen deficiency, y	Iodometric titration (corresponding % mass change[a]	Weight loss (%)	TGA (corresponding % mass change[b]
0.75	645°C in O_2	0.14		1.06	
	703°C in air	0.23	0.40	0.67	0.39
1.00	645°C in O_2	0.24		1.26	
	703°C in air	0.40	0.72	0.52	0.74

[a] Change corresponding to reduction to y value for 700°C, air.

[b] Change corresponding to weight loss in TGA, Ar.

brates in air atmosphere at 703°C. The subsequent drops measured only the heat content of the equilibrated oxide. The heat effects of the second and third drops were the same within experimental error, and no further weight loss occurred. Thus all reduction occurred during the first drop experiment. The heat of reduction of the $x = 0.75$ and 1.00 samples are 6.8 ± 0.1 and 12.1 ± 1.7 kJ/mole of compound, respectively (see Table III). The heat of oxidation is, of course, just the negative of the heat of reduction.

The oxygen contents were determined by iodometric titrations for the sample annealed under oxygen pressure (see Table IV) and for the samples that had been dropped into the calorimeter at 703°C. The oxygen contents of the latter were the same as those of the samples synthesized in air (see Table I). The measured weight losses of the samples after the first calorimetric drop matched the weight loss calculated from the oxygen loss determined by the titrations (see Table IV). The percentage weight losses calculated from the iodometric titrations for the $x = 0.75$ and 1.00 samples were 0.40 and 0.72%, respectively. The relative difference in the oxygen content of the samples before and after a calorimetric run was also determined by thermogravimetry. The samples were heated to 1000°C in flowing Ar in the TGA. The percentage weight losses calculated from TGA experiments for $x = 0.75$ and 1.00 were 0.39 and 0.74%, respectively. Within the error of the TGA experiments, the oxygen differences determined from iodometric titrations are confirmed. The differences in the oxygen content between the oxygen annealed samples and the dropped samples are 0.09 for $x = 0.75$ and 0.16 for $x = 1.00$. Dividing the heat of reduction, corrected for the heat content of oxygen (see Fig. 2), by the moles of oxygen lost in reduction for the $x = 0.75$ and 1.00 samples gives a heat of oxidation of −64.5 kJ/(mole oxygen atom). This corresponds to heats of oxidation (see Fig. 2) for thermochemical cycle used in calculation- of −129 ± 20 kJ/(mole O_2). The estimated uncertainty incorporates the standard deviations of both the calorimetric measurements and the oxygen content determination, which are about ± 10% of their respective values. We suggest that a heat of oxidation of −129 ± 20 kJ/(mole O_2) is associated with the reaction

$$La_{2-x}Sr_xCuO_{4-y} + (y' - y)/2)O_2 = La_{2-x}Sr_xCuO_{4-y'}. \quad (3)$$

The two measurements indicate that the heat of oxidation is approximately indepen-

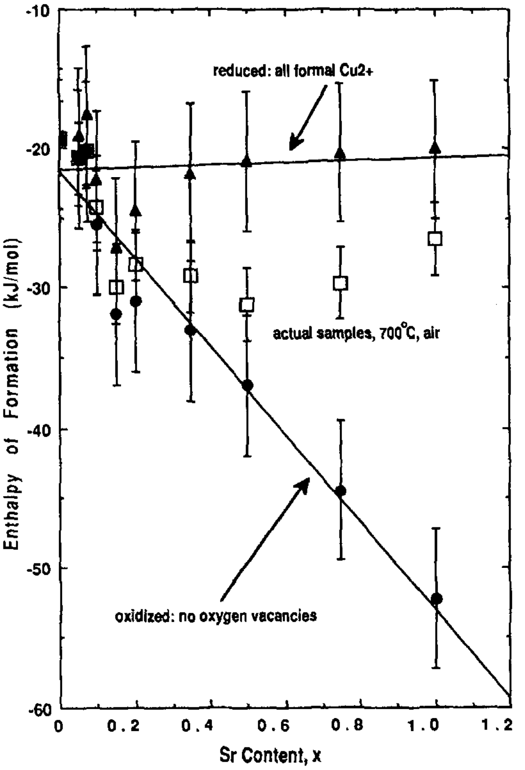

FIG. 3. Enthalpy of formation from the oxides (reaction (2)). Open squares represent samples with observed y values, characteristics of 700°C in air. Estimated errors are ± 2.6 kJ/mole; see text. Solid circles represent calculated values for fully oxidized ($y = 0$). Error estimate is ±5 kJ/mole. Solid triangles represent calculated values for maximally reduced samples ($y = 0.5x$). Error estimate is ±5 kJ/mole.

dent of the strontium content, x, and the oxygen deficiency, y, throughout the $La_{2-x}Sr_xCuO_{4-y}$ series. Its value is significantly less exothermic than the value reported for the $YBa_2Cu_3O_x$ series ($6 \leq x \leq 7$), -190 ± 5 kJ/(mole O_2) (*17*).

The formation of $La_{2-x}Sr_xCuO_{4-y}$ from component oxides (reaction (2) may be separated into two steps:

$$(1 - x/2)La_2O_3 + (x)SrO + CuO = Sr_xLa_{2-x}CuO_{4-x/2} \quad (4)$$

$$Sr_xLa_{2-x}CuO_{4-x/2} + 0.5(y - x/2)O_2 = Sr_xLa_{2-x}CuO_{4-y}. \quad (5)$$

Reaction (4) incorporates the coupled substitution

$$2La^{3+} + O^{2-} = 2Sr^{2+} + \text{oxygen vacancy} \quad (6)$$

and does not involve any oxidation. Reaction (5) is the oxidation to the equilibrium vacancy concentration, y, and formal Cu^{3+} concentration, $x - 2y$, and may also be written as

$$2Cu^{2+} + \text{oxygen vacancy} + \tfrac{1}{2}O_2 = 2Cu^{3+} + O^{2-}. \quad (7)$$

It represents oxidation and its enthalpy may be taken as that of reaction (3), namely -129 ± 20 kJ(mole O_2). We may then calculate the enthalpy of reaction (4), since $\Delta H_4 = \Delta H_2 - \Delta H_5$. The results are shown in Table II and Figure 3. ΔH_4, the enthalpy of formation from the oxides of a maximally reduced phase having no formally trivalent copper but with charge balance achieved by the required stoichiometric number of oxygen vacancies, is virtually independent of strontium content, at approximately -20.4 ± 3 kJ/mole (see Fig. 3). This suggests that the enthalpy of the coupled substitution, reaction (6), does not change with x.

We calculate the enthalpy of formation of the fully oxidized phase, $La_{2-x}Sr_xCuO_4$ similarly:

$$(1 - x/2)La_2O_3 + (x)SrO + CuO + (x/4)O_2 = La_{2-x}Sr_xCuO_4. \quad (8)$$

This reaction incorporates the substitution:

$$La^{3+} + Cu^{2+} = Sr^{2+} + Cu^{3+}. \quad (9)$$

By reasoning analogous to that above, $\Delta H_8 = \Delta H_2 - 64.5\,y$. The enthalpy of formation of the fully oxidized solid solution series (see Table II and Fig. 3) becomes more exothermic in an approximately linear manner with x, for $0 \leq x \leq 1$. The data calculated for the fully oxidized compounds are fit by the equation: $\Delta H_8 = -21.6 - 31.4x$. From Eq. (8), if oxidation were the only factor influencing the composition dependence of the enthalpy of formation of the fully oxidized series, the slope should be 0.25 (−129) kJ/mole = −32.2 kJ/mole, in excellent agreement with the average obtained from the data.

We conclude that the complex form of the enthalpy of formation of the series with y values characteristic of equilibration in air at 700°C reflects the competition of the two charge-balancing substitution mechanisms, reactions (6) and (9). The exothermic trend, with increasing Sr content for $x \leq 0.2$, is due essentially to the increasing contribution of the exothermic enthalpy of oxidation. At $x < 0.1$, $y = 0$ and the enthalpy of formation approximately follows the line with a strongly negative slope for fully oxidized samples. At $x \geq 0.2$, when further Sr substitution causes predominantly oxygen vacancy formation rather than oxidation, the enthalpy of formation, ΔH_2, levels off.

Even with the large exothermic enthalpy of oxidation, the fully oxidized compounds are presumably not the most stable in terms of Gibbs free energy at 700°C in air. The stable compounds with Sr content greater than 0.075, when synthesized in air, are partly reduced. This is due to a negative entropy of oxidation, a typical value for transition metal oxides being about −92 J/(mole O) · K (*18*). This negative entropy compensates for the negative enthalpy of oxidation, and an intermediate state, containing both oxygen vacancies and formally trivalent copper, is the state of lowest free energy. This delicate balance responds to changes in oxygen fugacity and temperature, resulting in a significant variation of y with x, T, and p, (O_2). Creating oxygen vacancies in the structure may also be entropically favorable. If these vacancies are randomly distributed over oxygen sites, a significant configurational entropy of mixing may ensue. However, the existence of superstructures related to vacancy ordering at $x \geq 1$ may suggest that, even at lower values of x, considerable short-range order may decrease the configurational entropy.

Conclusions

A single-phase solid solution in the series $La_{2-x}Sr_xCuO_{4-y}$ for $0 \leq x \leq 1$ was synthesized. Compared with other studies, the different synthesis conditions affect the lattice parameters very slightly but can change the oxygen content significantly.

The heats of formation of $La_{2-x}Sr_xCuO_{4-y}$ from the component oxides are always at least 19 kJ/mole exothermic. The variations in the heats of formation is determined by two competing effects, the large exothermic enthalpy of oxidation and an approximately constant enthalpy of about −20 kJ/mole for the formation of the compound with all copper(II). The exothermic enthalpy of oxidation (−129 ± 20 kJ(mole O_2)) is in turn balanced by a strongly negative entropy of oxidation of the order of −90 J/(mole O) · K. This balance makes the oxygen deficiency, y, depend strongly on x, T, and p (O_2) and causes the enthalpy of formation of the compounds stable at 700°C in air to vary in a complex manner with Sr content, x.

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