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Energetics of $La_{2-x}Sr_xCoO_{4-y}$ ($0.5 < x < 1.5$)

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Several compositions in the $La_{2-x}Sr_xCoO_{4-y}$ series were synthesized in air and in argon. The heats of formation of these compounds were calculated from the measured heats of solution using high-temperature drop solution calorimetry in lead borate solvent. The heats of formation become more exothermic with increasing strontium content, consistent with a high heat of oxidation of −400 kJ per mole of O_2 determined from calorimetry of samples with the same strontium content and different oxygen nonstoichiometry. This enthalpy of oxidation is significantly more exothermic than values for the corresponding cuprates and nickelates. © 1994 Academic Press, Inc.

INTRODUCTION

Re_2MO_4 (M = Cu, Ni, Co) oxides, which crystallize in the K_2NiF_4 structure, have been of interest as they span a spectrum of physical properties and offer the possibility of a systematic study of structure–property relations. There has been a tremendous renewal of interest since the discovery of superconductivity in the copper-containing compounds (1). This laboratory has undertaken a systematic study of the energetics of $La_{2-x}A_xMO_{4-y}$, where A = Ba, Sr, Ca, Pb and M = Cu, Ni (2–4). The present work is an extension of this study to the energetics of $La_{2-x}Sr_xCoO_{4-y}$ oxides, which are of interest in applications as catalysts and as cathodes in fuel cells (5, 6). The thermodynamic stability and the energetics of oxidation of these compounds must be known to understand their behavior under both oxidizing and reducing conditions associated with these applications.

EXPERIMENTAL

Stoichiometric amounts of La_2O_3 (heated to 700°C prior to use), $SrCo_3$, and Co_3O_4 were ground in an agate mortar and calcined at 1300°C for 16 hr. This procedure was repeated four or five times and finally the powders were pressed into pellets and heated at 1320°C for 12 hr in air or in argon and slowly cooled to 800°C. The air-treated samples were maintained at 800°C for 16 hr and quenched to room temperature, while the argon-treated samples were slowly cooled to room temperature.

Powder X-ray diffraction was performed on a Scintag PAD V diffractometer using CuK_α radiation.

The oxidation state of the cobalt ion and hence the oxygen content were determined by iodometric titrations. About 50–80 mg of each sample was dissolved in 10 ml of 1 N $HClO_4$ and approximately 1.16 g of KI was added. The solution was titrated with a standard thiosulfate solution. The oxidation state of Co determined by this method (see Table 1) was similar to that of earlier reports for these compounds (5).

CALORIMETRY

Thermochemical measurements were performed in air in a high-temperature twin calorimeter operating at 704°C using molten lead borate ($2PbO \cdot B_2O_3$) as the solvent. The details of drop solution calorimetry have been described previously (7). For these experiments, about 30 g lead borate in a platinum crucible was equilibrated overnight (approximately 16 hr) at 704°C. Small chunks of 20–30 mg were broken from the sintered pellets and dropped into the solvent in the calorimeter. At least six runs were performed on each composition. The measured heat effect was the sum of the heat content of the compound from room temperature to 704°C and the heat of solution of the compound in the lead borate solvent at 704°C.

Heats of formation of the compounds were calculated from the measured heat of drop solution of the compound and the component oxides.

For proper interpretation, the oxidation state of the cobalt must be known both for the sample being dropped and for the final dissolved state. The former was determined by iodometric titrations described above and the latter by weight loss measurements as follows. Co_3O_4 of known weight was added to lead borate glass in a platinum cup. The lead borate glass had been previously equilibrated at 700°C for 48 hr to constant weight. The mixture was heated at 704°C in air for 70 min (which is the approximate duration of a drop solution experiment) and cooled to room temperature. The weight was measured again (to ±0.01 mg) and any difference was attributed to oxygen loss. The measured weight loss showed that cobalt dissolves in lead borate as Co^{2+}, with any formal Co^{3+} evolv-

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TABLE 1
Thermochemical Data for $La_{2-x}Sr_xCoO_{4-y}$

Compound		$\Delta H_{dropsol}$[a] (kJ/mol)	ΔH[b] (kJ/mol)
CoO		57.80 ± 0.77	—
La_2O_3		-39.50 ± 4.56	—
SrO		-58.59 ± 2.00	—
x	$4 - y$ in $La_{2-x}Sr_xCoO_{4-y}$		
0.6	4.0	83.63 ± 2.79	-85.4
0.6	3.98	80.20 ± 2.64	-81.6
0.75	4.0	94.16 ± 2.31	-101.0
0.75	3.95	74.21 ± 3.32	-81.5
1.0	3.99	102.35 ± 3.33	-117.6
1.0	3.83	67.92 ± 2.89	-84.9
1.25	3.96	101.93 ± 1.08	-125.8
1.25	3.67	42.76 ± 1.06	-69.8
1.4	3.92	104.33 ± 4.50	-133.7
1.4	3.59	39.30 ± 2.49	-72.2
1.5	3.87	99.31 ± 2.65	-132.5
1.5	3.52	25.36 ± 2.08	-62.4

[a] $\Delta H_{dropsol}$ is enthalpy of drop solution (Eq. [1]).
[b] ΔH_f is enthalpy of formation from the oxides (Eq. [2]).

ing oxygen gas upon dissolution. This result agreed with previous work in this laboratory (8).

To determine the heats of oxidation, the heats of formation of two compounds of similar composition but different oxygen stoichiometry obtained by processing in air and argon were measured as described above. From these data, the heat of oxidation for each composition was determined.

The calorimetric methodology used here depends on the oxides dissolving (as ionic species) in the lead borate melt at the limit of infinite dilution (Henry's Law) behavior. This means that the observed molar enthalpy of solution of a given oxide depends neither on the amount of that oxide present nor on the presence of other dissolved oxides. This dilute solution behavior has been verified in both this work and many previous studies (for example, 2–4, 7) by varying the weights of solutes and the order in which they are dissolved.

RESULTS AND DISCUSSION

All the compositions, for processing in both air and argon, crystallized in the tetragonal K_2NiF_4 structure. The oxygen contents and the formal cobalt oxidation number are given in Fig. 1. For each composition, the value reported is the average of three titrations. The error, as given by twice the standard deviation of the mean, was always less than ±0.01 in (y). The nonstoichiometry (y) is plotted as a function of the strontium content (x) in Fig. 1. As the strontium content increases, the difference in oxygen content for samples annealed in air and argon increases.

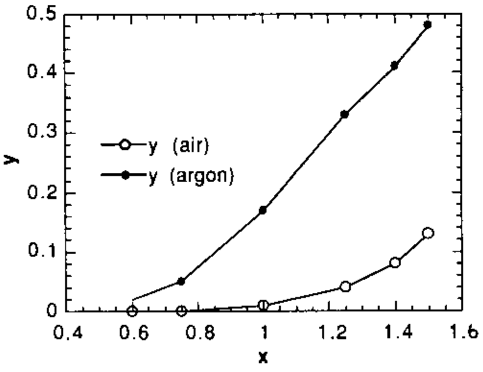

FIG. 1. The oxygen nonstoichiometry (y) in $La_{2-x}Sr_xCoO_{4-y}$ for different strontium contents, for samples synthesized in air and argon.

The thermochemical cycles used to determine the heat of formation and the heat of oxidation at room temperature for each composition are shown in Fig. 2. The reaction is written such that all the Co ions are in the 2+ valence state in the solvent and any samples with formal Co^{3+} dissolve with the evolution of oxygen (see discussion above). The heats of solution of SrO, CoO, and La_2O_3 used are those determined in this laboratory previously (2, 8). The heat contents of SrO, La_2O_3, CoO, and O_2 are

Heat of formation of $La_{2-x}Sr_xCoO_{4-y}$

(1-x/2) La_2O_3 (s, 22 °C) --> (1-x/2) La_2O_3 (soln, 704 °C)

(x) SrO (s, 22 °C) --> (x) SrO (soln, 704 °C)

CoO (s, 22 °C) --> CoO (soln, 704 °C)

(0.25x-0.5y) O_2 (g, 22 °C) --> (0.25x-0.5y) O_2 (g, 704 °C)

(1-x/2) La_2O_3 (soln, 704 °C) + (x) SrO (soln, 704 °C) +

CoO (soln, 704 °C)+(0.25x-0.5y)O_2 (g, 704 °C) --> $La_{2-x}Sr_xCoO_{4-y}$ (s, 22 °C)

(1-x/2) La_2O_3 (s, 22 °C) + x SrO (s, 22 °C) + CoO (s, 22 °C) +

(0.25x-0.5y) O_2 (g, 22 °C) --> $La_{2-x}Sr_xCoO_{4-y}$ (s, 22 °C)

Heat of oxidation of $La_{2-x}Sr_xCoO_{4-y}$

(1-x/2)La_2O_3(soln, 704 °C) + (x)SrO(soln, 704 °C) + CoO(soln, 704 °C) +

(0.25x-0.5y')O_2(g, 704 °C)+(y'-y)/2 O_2(g, 704 °C)=$La_{2-x}Sr_xCoO_{4-y}$(s, 704 °C)

$La_{2-x}Sr_xCoO_{4-y'}$(s, 22 °C)=(1-x/2)La_2O_3(soln, 704 °C)+(x)SrO(soln, 704 °C)

+ CoO(soln, 704 °C) + (0.25x-0.5y')O_2(g, 704 °C)

(y'-y)/2 O_2 (g, 22 °C) = (y'-y)/2 O_2 (g, 704 °C)

$La_{2-x}Sr_xCoO_{4-y'}$(s, 22 °C)+(y'-y)/2 O_2(g, 22 °C)-->$La_{2-x}Sr_xCoO_{4-y}$(s, 22 °C)

FIG. 2. Thermochemical cycles used to determine the heat of formation and the heat of oxidation of $La_{2-x}Sr_xCoO_{4-y}$.

TABLE 2
Enthalpy of Oxidation for $La_{2-x}Sr_xCoO_{4-y}$

Compound	$(y'-y)$ δy (mole)	ΔH_{ox} (kJ/mole)
Sr = x		
0.6	0.013	−506.7 ± 3.8 (±500)
0.75	0.05	−776.3 ± 4.0 (±300)
1.0	0.16	−408.6 ± 4.4 (±50)
1.25	0.29	−386.3 ± 1.5 (±10)
1.4	0.33	−372.4 ± 5.1 (±10)
1.5	0.35	−400.8 ± 3.4 (±10)

Note. Uncertainty represents two standard deviations of the mean. Errors arising from uncertainty in $y'-y'$ are in parentheses.

taken from a standard tabulation (9). All these data, along with the heats of drop solution for the various compositions, are given in Table 2. The heat of drop solution represents the reaction

$$\begin{aligned} La_{2-x}Sr_xCoO_{4-y}&(s, 22°C) \\ &= (1 - x/2)La_2O_3(soln, 704°C) \\ &\quad + (x)SrO(soln, 704°C) \\ &\quad + CoO(soln, 704°C) \\ &\qquad + (0.25x - 0.5y)O_2(g, 704°C). \end{aligned} \quad [1]$$

Six drop solution experiments were performed for each composition and the uncertainty reported (twice the standard deviation of the mean) ranges from ±1 to ±4.5 kJ/mole. The average uncertainty is about ±2.6 kJ/mole, which is about 3% of the heat of drop solution, a typical error for this type of calorimetry.

The heat of drop solution becomes more exothermic initially with increasing strontium content and then stabilizes around 100 kJ/mole for the compositions annealed in air. For the samples processed in argon, the heat of solution becomes less exothermic with increasing strontium content.

The heat of formation from binary oxides is given by the equation

$$\begin{aligned} (1 - x/2)&La_2O_3(s, 22°C) + x\,SrO(s, 22°C) \\ &+CoO(s, 22°C) \\ &+ (0.25x - 0.5\,y)\,O_2(g, 22°C) \\ &\qquad = La_{2-x}Sr_xCoO_{4-y}(s, 22°C). \end{aligned} \quad [2]$$

The cycle shown in Fig. 2 is used to determine the heats of formation.

The heat of formation becomes more exothermic with increasing strontium content for the air-annealed samples. For the argon-annealed samples, the trend is toward a less exothermic heat of formation with increasing strontium content.

The heat of oxidation determined by the cycle shown in Fig. 2 is given by the reaction

$$\begin{aligned} La_{2-x}Sr_xCoO_{4-y}{}'(s, 22°C) + (y' - y)/2\, o_2(g, 22°C) \\ \rightarrow La_{2-x}Sr_xCoO_{4-y}(s, 22°C). \end{aligned} \quad [3]$$

While the heat of oxidation is −506 and −776 kJ/mol O_2 for strontium contents of 0.6 and 0.75, respectively, it has a nearly constant value of −400 kJ/mole O_2 for the other four compositions with higher strontium content. One reason for this apparent variation is the small value of difference in oxygen content $(y' - y)$ for the first two compositions. Thus the uncertainty in the enthalpy of oxidation is magnified because the difference in enthalpy of the drop solution of samples with the same x but different y is small, and the difference in oxygen content $(y' - y)$ is also small.

However, the molar enthalpy of oxidation may differ for these samples for another reason related to oxygen content and defect chemistry. Nitadori *et al.* (5) have reported that for compositions processed in air, two different regimes can be established, one for strontium content $0 < x < 0.8$ and another for $0.8 < x < 1.5$. The first regime corresponds to an oxygen content greater than 4.0 marked by the presence of oxygen interstitials (analogous to $La_{2-x}Sr_xNiO_{4+y}$) and the second regime corresponds to an oxygen content less than 4.0 marked by the presence of oxygen vacancies. The values of oxygen nonstoichiometry (y) measured in the present study are positive (suggesting vacancies) whereas Nitadori *et al.* report a negative value of y (suggesting interstitials) for $x = 0.6$ and 0.75. However, the values of nonstoichiometry are very small in both studies, and $y = 4.00 \pm 0.01$ for $x = 0.6$ and 0.75 in our work. Thus it is not clear if these samples are in the oxygen-excess or the oxygen-deficient region, and a change in dominant defect regime could affect the enthalpy of oxidation. Similar effects are seen in the Ba- and Sr-doped lanthanum nickelates (4). For the other four compositions, $x > 0.8$, the oxygen content determined by titrations and the associated uncertainties indicates unambiguously the presence of oxygen vacancies. The data suggest a constant heat of oxidation of −400 kJ/mole O_2 independent of strontium content in the oxygen-deficit regime.

The heat of formation from the binary oxides at room temperature, reaction [2], can be broken into two steps,

$$(1 - x/2)La_2O_3 + xSrO + CoO = La_{2-x}CoO_{4-x/2} \quad [4]$$

and

$$La_{2-x}Sr_xCoO_{4-x/2} + 0.5(x/2 - y)O_2 = La_{2-x}Sr_xCoO_{4-y}. \quad [5]$$

Reaction [4] incorporates the coupled substitution (where $V_{\ddot{o}}$ is an oxygen vacancy, and Kröger–Vink defect notation is used):

$$2SrO + O_O + 2La_{La} = 2Sr'_{La} + V_o^{\cdot\cdot} + La_2O_3. \qquad [6]$$

It does not involve any oxidation. Reaction [5] is the oxidation to the equilibrium vacancy concentration and formal Co^{3+} concentration ($x - 2y$) given by the reaction

$$2Co_{Co} + V_o^{\cdot\cdot} + 0.5O_2 = 2Co'_{Co} + O_o. \qquad [7]$$

Reaction [7] represents oxidation to formal Co^{3+} and the heat of oxidation is given by reaction [3], −400 kJ/mole O_2.

We now calculate the enthalpy of formation of the fully reduced $La_{2-x}Sr_xCoO_{4-x/2}$ from the binary oxides, reaction [4], $\Delta H_4 = \Delta H_2 - \Delta H_5$ (see Fig. 3). This calculation suggests a constant enthalpy of formation of the fully reduced compound with no formal trivalent cobalt is about −15 kJ/mole independent of strontium content in the region $0.8 < x < 1.5$. This suggests that the enthalpy of the coupled substitution, reaction [6], does not change with strontium content. This value is similar to the enthalpy of formation of the fully reduced $La_{2-x}Sr_xCuO_{4-x}$ compounds in the oxygen vacancy region, namely −20 kJ/mole (2).

Using similar reasoning, the enthalpy of formation of the fully oxidized phase, $La_{2-x}Sr_xCoO_4$ can be calculated from the reaction

$$La_{2-x}Sr_xCO_{4-x/2} + 0.5(x/2)\,O_2 = La_{2-x}Sr_xCoO_4. \qquad [8]$$

This reaction incorporates the coupled substitution

$$La^{3+}_{La} + Co^{2+}_{Co} \rightarrow Sr^{2+}_{La} + Co^{3+}_{Co} \qquad [9a]$$

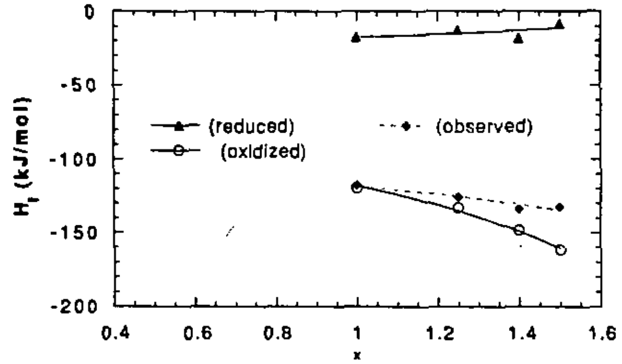

FIG. 3. The enthalpy of formation of the fully reduced ($y = x/2$), fully oxidized ($y = 0$), and air-processed samples of $La_{2-x}Sr_xCoO_{4-y}$ with varying strontium content.

or

$$La_{La} + Co_{Co} = Sr'_{La} + Co'_{Co}.$$

The heat of formation of reaction [8] is given by

$$\Delta H_8 = \Delta H_2 - 0.5y\,\Delta H_{ox}, \qquad [10]$$

where ΔH_{ox} is the enthalpy of oxidation for each composition determined earlier. The enthalpy of formation of the fully oxidized phase becomes more exothermic with increasing strontium content (see Fig. 3). The actual oxygen content for any composition reflects the competition between the two charge-balancing mechanisms. The high heat of oxidation of −400 kJ/mole results in oxygen contents close to 4.0 (when processed in air) even for samples with very high strontium contents. This can be compared to the analogous $La_{2-x}Sr_xCuO_{4-y}$ series [2], where a lower heat of oxidation of −129 kJ/mole results in far greater oxygen nonstoichiometry for similar strontium contents.

The equilibrium oxygen content also reflects the effect of vacancy disordering and its contribution to the free energy through the configurational entropy. For a given nonstoichiometry, the configurational entropy and its contribution to the free energy are fixed, however, and it can be expected to play a relatively larger role when the heat of oxidation is small. Hence for the $La_{2-x}Sr_xCoO_{4-y}$ series, the configurational entropy plays a smaller role in determining the final oxygen content than in the $La_{2-x}Sr_xCuO_{4-y}$ series due to the much higher heat of oxidation in the former. Because the oxygen deficiency (y) is smaller for the cobalt system than for the copper and nickel ones, the cobalt system contains fewer vacancies and there is no evidence of their ordering.

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