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The Energetics of $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr)

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The enthalpy of formation of the solid solution series $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr; $0 \le x \le 0.7$ and $-0.18 \le y \le 0.04$) has been measured using high-temperature reaction calorimetry. As barium or strontium is substituted for lanthanum, the enthalpy of formation from the oxides becomes more exothermic. The enthalpy of formation from the component oxides and the enthalpy of oxidation for the barium- and the strontium-doped material for a given value of x is the same within the experimental uncertainty. From the measurements of the enthalpy of oxidation for the oxygen interstitial regime ($y < 0$) and the oxygen vacancy regime ($y > 0$), the oxygen Frenkel energy for the lanthanum nickelates has been found to be 43 ± 20 kJ/(mole O). Based on the oxidation enthalpy measurements, we argue that the excess holes in lanthanum nickelate are predominantly in Ni $3d$-type bands. © 1993 Academic Press, Inc.

Introduction

RE_2MO_4 oxides (RE = rare earth, M = transition metal), which crystallize in the K_2NiF_4 structure, are of interest both from the point of view of general solid-state chemical systematics and because of their physical properties. Some of the rare earth cuprates are superconducting (*1*), while other members of this group have been studied as possible catalytically active materials (*2, 3*). Also, as the K_2NiF_4 structure is relatively simple, it offers a unique opportunity to investigate the effects of chemical composition and oxidation state on structure, thermodynamics, and physical properties in a systematic way. A basic question in the field of high-temperature superconductivity is why cuprates superconduct whereas the other transition metal analogues generally do not. One of the objectives of this paper is to investigate the chemical differences between the hole states in the cuprates and the nickelates and thus provide direct energetic evidence for the crystal-chemical factors relevant to superconductivity and normal state and ionic conductivity.

Recently the thermochemistry of the systems $La_{2-x}A_xCuO_{4-y}$ (A = Ba, Sr, Ca, Pb) has been studied by high-temperature reaction calorimetry (*4*). The energetics of alkaline earth substitution, with compensating oxygen vacancy formation, oxygen vacancy ordering, and oxidation could be isolated, to some extent, as separate thermochemical effects. The purpose of the present study is to determine analogous thermochemical parameters for the $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr) system so that the crystal chemistry of

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the K_2NiF_4 structure can be understood in more detail.

Experimental

Sample Preparation

Stoichiometric amounts of La_2O_3 (Aesar 99.99%; dried at 700°C prior to use), $BaCO_3$ (Aesar 99.99%; dried at 400°C prior to use), $SrCO_3$ (Aesar 99.99%; dried at 130°C prior to use) and NiO (Aesar 99.999%) were ground in an agate mortar and heated in a platinum crucible at 1100°C for 12 hr. The samples were then well ground and heated at 1250°C for 24 hr and then annealed at 704°C in air for 24 hr and quenched to room temperature. For the barium compounds the platinum crucible was annealed at 1250°C with a lanthanum barium-containing nickelate with an identical composition to the material to be synthesized. This minimized any further reaction between the sample and the crucible.

Samples used to determine the enthalpy of oxidation were sintered into small pellets (100–150 mg) at 1250°C. The pellets were enclosed in platinum capsules. The capsules were annealed at 1100°C in air for an hour and dropped into a brass cup held at room temperature.

Characterization

Powder X-ray diffraction patterns were obtained on a Scintag PAD V automated diffractometer using CuK_α radiation. For determining the lattice parameters, diffraction patterns were obtained from $20° < 2\theta < 70°$ at scan rate of 1° 2θ per min and a chopper increment of 0.03° 2θ. NaCl was used as an internal standard. Before determining the peak positions, background was substract from the diffraction pattern and the peaks due to $K_{\alpha 2}$ were removed. The lattice parameters for tetragonal cell (*I4/mmm*) were refined using a least-squares procedure.

The oxygen stoichiometry, for each dopant composition quenched from 704°C in air, was determined by a programmed temperature reduction cycle using a Cahn system 113 thermal balance (at Brown University). Samples (~100 mg) were loaded in a TGA bucket and the TGA system was purged at room temperature in a stream of 15% H_2 in Ar until a constant weight was reached. The flow rate of the gas mixture was 50 sccm. The temperature was then increased to 900°C at a rate of 200°C/hr and held at 900°C for 1 h. The reaction products were determined from X-ray analysis to be Ni metal and La, Ba/Sr oxides. The oxygen stoichiometry of the sample was ascertained from the weight loss on reduction.

Calorimetry

Thermochemical measurements were performed in air using a high-temperature Tian Calvet twin calorimeter operating at 704°C. Molten lead borate ($2PbO * B_2O_3$) was used as a solvent for solution calorimetry (details of the measurement techniques and thermochemical cycles employed are given elsewhere (*5*)). The final oxidation state of Ni in the solvent was determined from weight loss analysis to be +2 regardless of its formal oxidation in the starting material.

Enthalpies of oxidation were determined using transposed temperature drop calorimetry (described in detail elsewhere (*6*)). Samples quenched from 1100°C in air were dropped into a calorimeter at 704°C, where they quickly oxidized. The enthalpy for the first drop consisted of the heat content plus the oxidation enthalpy. The samples were retrieved from the calorimeter and weighed. After determining the weight gain (and hence the amount of oxidation), they were dropped for a second time. The heat effect for the second drop consisted of only the heat content of the sample. From the difference between the heat effect of the first and the second drop, enthalpy of oxidation for

TABLE I

UNIT CELL PARAMETERS AND OXYGEN CONTENTS FOR $La_{2-x}A_xNiO_{4-y}$ A = (Ba, Sr)

x	y	a(Å)	b(Å)	c(Å)	Cell volume (Å^3)
Ba = 0.0	−0.18	3.866(2)		12.668(5)	189.3
Ba = 0.10	−0.06	3.857(2)		12.714(5)	189.1
Ba = 0.30	0.00	3.849(2)		12.825(5)	190.0
Ba = 0.50	0.03	3.848(2)		12.893(5)	190.9
Ba = 0.70	0.03	3.855(2)		12.915(5)	191.9
Sr = 0.10	−0.06	3.850(2)		12.696(5)	188.2
Sr = 0.30	0.02	3.830(2)		12.717(5)	186.5
Sr = 0.50	0.04	3.814(2)		12.734(5)	185.2

that sample was determined. The enthalpy of oxidation thus determined is an average over the stoichiometry change that the sample underwent in the calorimeter. As the stoichiometry change in the oxidation measurement is small (usually $\delta y \sim 0.04$), the measured average oxidation enthalpy is a good approximation to the partial molar enthalpy of oxidation at a fixed average oxygen stoichiometry.

TABLE II

ENTHALPY OF SOLUTION AND FORMATION FROM THE OXIDES AT 704°C FOR $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr)

Compound	ΔH_{sol}(704°C) (kJ/mole)	ΔH_f(704°C) (kJ/mole)
NiO	+34.0 ± 0.8(7)[a]	—
La_2O_3	−126 ± 4.4(7)	—
$La_2NiO_{4.18}$	−75.0 ± 3.6(6)	−17.0
BaO	−127 ± 2.2(6)	—
SrO	−93.6 ± 2.0(17)	—
Ba = 0.1	−67.8 ± 3.4(6)	−30.6
Ba = 0.3	−66.8 ± 3.6(6)	−44.4
Ba = 0.5	−61.9 ± 3.1(6)	−62.1
Ba = 0.7	−53.5 ± 1.1(6)	−83.3
Sr = 0.1	−65.8 ± 2.1(6)	−29.3
Sr = 0.3	−57.7 ± 1.8(6)	−43.5
Sr = 0.5	−47.5 ± 2.6(6)	−59.8

[a] Uncertainty is two standard deviations of mean; value in ( ) is number of experiments.

Results and Discussion

All samples prepared in this study crystallized in the K_2NiF_4 structure. Lattice parameters based on the tetragonal cell ($I4/mmm$) and oxygen contents for these samples are reported in Table I. For samples with $x > 0.5$ for Sr and $x > 0.7$ for Ba, high quality X-ray diffraction analysis (step counting with step size of 0.02° for 2θ and counting time of 10 sec per step) revealed small extra peaks which could not be indexed on the convention K_2NiF_4 cell. We are currently exploring the structure of these samples in more detail.

Tables II and III show the thermochemical data for the single phase samples. The enthalpy of formation expressed by the equation

$$\mathrm{NiO(s)} + \left(1 - \frac{x}{2}\right) \mathrm{La_2O_3(s)} + x A\mathrm{O(s)} + \left(\frac{x - 2y}{4}\right) \mathrm{O_2\,(g)} \Rightarrow \mathrm{La}_{2-x}A_x\mathrm{NiO}_{4-y}\mathrm{(s)} \quad (1)$$

is shown in Fig. 1. The enthalpy of formation progressively and almost linearly becomes more exothermic with increasing alkaline earth substitution. There is no observable difference between the Ba-substituted and the Sr-substituted materials for a given value of x ($x \leq 0.5$). This is in sharp contrast to the more complex behavior observed for

TABLE III

ENTHALPY OF OXIDATION FOR $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr)

x	δy (avg.) (mole)	1st Drop (avg.) (J/g)	2nd Drop (avg.) (J/g)	$\Delta H_{ox}(O_2)$[a] (kJ/mol)
0.0	0.034(6)	294.4 ± 2.0(6)	304.4 ± 2.1(6)	−108 ± 14
Ba = 0.1	0.037(6)	292.2 ± 2.5(6)	303.0 ± 2.5(6)	−106 ± 32
Ba = 0.3	−0.010(2)	—	—	(See text)
Ba = 0.5	−0.007(4)	—	—	(See text)
Ba = .07	−0.029(6)	284.0 ± 2.0(6)	295.4 ± 2.7(6)	−148 ± 18
Sr = 0.1	0.026(6)	296.7 ± 1.8(6)	304.2 ± 3.0(6)	−100 ± 18
Sr = 0.3	0.002(2)	—	—	(See text)
Sr = 0.5	−0.004(4)	—	—	(See text)

[a] Uncertainties are expressed as two standard deviations of mean; values in ( ) are the number of measurements. For each set of transposed temperature drops (one first drop and one second drop, see text), an enthalpy of oxidation was determined. The enthalpies of oxidation shown in this table are obtained as a statistical average of six such sets.

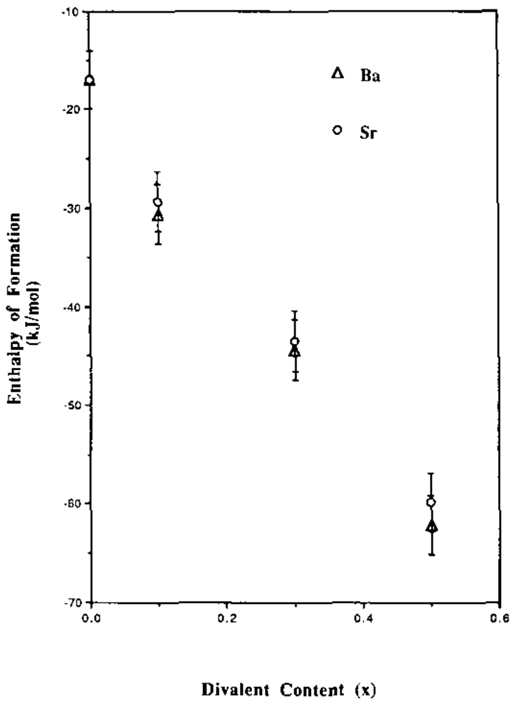

FIG. 1. Enthalpy of formation versus divalent content (x) at 704°C for $La_{2-x}A_xNiO_{4-y}$ (A = Ba, Sr). Oxygen contents (y) for samples quenched from 704°C are listed in Table I.

the alkaline-earth-doped lanthanum cuprates (*4*) which show a minimum in ΔH_f.

Also for the lanthanum cuprates the enthalpy of formation (as well as the enthalpy of oxidation) is strongly dependent on the chemical nature of the dopant. The enthalpy of formation in the cuprates was modeled by three competing energetic factors: (a) enthalpy for the alkaline earth substitution (without oxidation) given by the reaction,

$$2La_{La} + 2AO + O_O \Rightarrow 2A'_{La} + La_2O_3 + V_O^{\cdot\cdot} \quad (2)$$

(defect reactions are represented in the Kroger–Vink notation (*10*)) (b) enthalpy of oxidation (oxygen vacancy filling) represented by the defect reaction

$$V_O^{\cdot\cdot} + \frac{1}{2}O_2 \Rightarrow O_O + 2h^{\cdot}, \quad (3)$$

and (c) effects of oxygen vacancy ordering. The energetic effect due to cation substitution (reaction (2)) was found to be independent of the degree of substitution. The constancy of the substitution reaction implied that there was no significant interaction between cation defects, and hence the cations were thought not to order in the material.

Further the enthalpy for reaction (2) was found to be very close to zero. The enthalpy of oxidation for the Sr doped compound was strikingly different from the Ba doped compounds (−65 ± 10 kJ/mole versus −110 ± 25 kJ/mol (*4*, *9*)) and at high oxygen vacancy concentrations, the vacancies were found to order in the lanthanum cuprates with an ordering energy of −40 ± 10 kJ/mole for Sr-doped materials and −110 ± 20 kJ/mole for Ba-doped materials (*4*).

The lanthanum nickelates differ in several important respects from the cuprates. First, the oxygen vacancy concentration for all the samples investigated is small, making the energetic effects of oxygen vacancy ordering far less important. The second important difference is in the oxidation mechanisms. All the nickelates studied are in highly oxidized states (at 701°C, the formal nickel valence >2.3). Consequently, samples with lower levels of doping ($x \leq 0.1$) have significant concentration of interstitial oxygen. So for the lanthanum nickelate one has to consider an additional oxidation mechanism: oxidation through incorporation of interstitials

$$V_I + \frac{1}{2}O_2 \Rightarrow O_I'' + 2h^{\cdot} \qquad (4)$$

Third, the enthalpy of oxidation in nickelates, unlike cuprates, does not depend on whether the substitutional cation is Ba or Sr; suggesting that the nature of hole states is different in the nickelates than in the cuprates.

The difference between the p-type oxidation in which oxygen vacancies are filled (reaction (3)) and the p-type oxidation in which oxygen interstitials are generated is the oxygen Frenkel reaction given by

$$V_I + O_O \Rightarrow V_O^{\cdot\cdot} + O_I''. \qquad (5)$$

As the enthalpy of oxidation and the enthalpy of formation are the same within experimental uncertainty for the corresponding Ba-doped and Sr-doped lanthanum nickelates ($x \leq 0.7$), we invoke the simplifying hypothesis that the alkaline earth cations play only the role of aliovalent dopants and contribute little to the energetics of oxidation (and by inference most other defect reactions). Thus as a first approximation, the oxygen Frenkel energy (enthalpy for reaction (5)) is independent of the amount or the chemical nature of alkaline earth dopants in lanthanum nickelates.

For the samples with low dopant content, i.e., $La_2NiO_{4.18}$, $La_{1.9}Ba_{0.1}NiO_{4.06}$, and $La_{1.9}Sr_{0.1}NiO_{4.06}$, the enthalpy of oxidation corresponds to oxidation through oxygen interstitials (reaction (4)) and is −105 ± 5 kJ/mole. For samples with intermediate dopant content ($0.3 \leq x \leq 0.5$), the partial molar enthalpy of oxidation becomes very difficult to measure, as the change in the oxygen stoichiometry between the sample quenched from 1100°C and the sampled annealed at 704°C is too small to be reliably measured (see Table III). We could construct several plausible models to explain the very small temperature dependence of oxygen stoichiometry in air for these samples. However, we feel that without a more detailed understanding of the defect chemistry of the system, it is impossible to select the most appropriate model for the oxidation mechanism for this compositon range. However, the enthalpy of oxidation for the highly doped samples ($x > 0.5$) can be easily measured. The enthalpy of oxidation for $La_{1.3}Ba_{0.7}NiO_{3.96}$, corresponding to oxidation through filling of oxygen vacancies (reaction (3)), is −148 ± 18 kJ/mole. The difference between the enthalpies for the two types of oxidation mechanisms, namely the oxygen Frenkel energy, is 43 ± 20 kJ/mole (reaction (5)). We point out that this is probably the first direct calorimetric determination of a Frenkel defect energy.

The cuprates and the nickelates, now, can be meaningfully compared. Figures 2a and 2b show one such comparison, namely, of

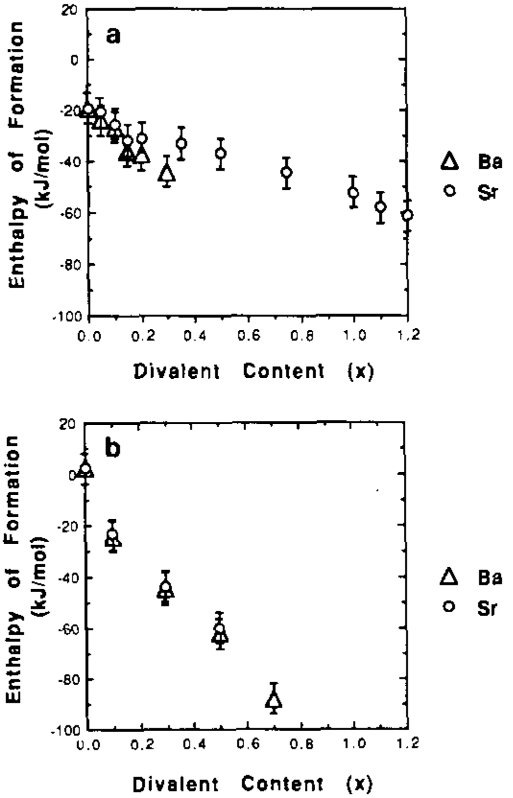

FIG. 2. Enthalpy of formation of $La_{2-x}A_xCuO_{4.00}$ (A = Ba, Sr) compound versus dopant content (x) at 704°C. Data taken from Ref. (*1*). (b) Enthalpy of formation of $La_{2-x}A_xCuO_{4.00}$ (A = Ba, Sr) compound versus dopant content (x) at 704°C.

the enthalpy of formation of the y = 0.00 compounds relative to the component oxides. There are several noticeable similarities between these enthalpies. However, one salient difference is in the enthalpy of formation (from oxides) of the two end-members. The enthalpy of formation for $La_2NiO_{4.00}$ is very close to zero (2.2 ± 5 kJ/mole), whereas $La_2CuO_{4.00}$ is substantially exothermic (−19 ± 5 kJ/mole). The close to zero enthalpy of formation of $La_2NiO_{4.00}$ and the strongly exothermic enthalpy of oxidation may explain why this phase, under normally synthesized conditions, is highly oxygen rich ($La_2NiO_{4.18}$ at 704°C in air) and is very difficult to synthesize stoichiometric. The difference in stability of the end-member compounds can be rationalized in terms of a model proposed by Goodenough and Manthiram (*7*). The K_2NiF_4 (e.g., La_2CuO_4) structure can be viewed as a monolayer epitaxial sandwich of the rocksalt-like La–O layers and the perovskite-like $LaCuO_3$ layers. Goodenough and Manthiram propose that if the lattice parameters of the two ideal layers match, the structure is very favorable and stable. However, in La_2CuO_4, the Cu–O distances (*8*) are too long to perfectly match the lattice parameters of the rocksalt La–O layers. This interlayer lattice mismatch strains the structure. The Ni–O distances are even longer than the Cu–O distances and hence the La_2NiO_4 structure should be even more strained. The strain destabilizes the compound as clearly seen in the enthalpy of formation. This model would also explain the low temperature (<1000°C) relative stability of $LaNiO_{3-\delta}$ perovskite (and La_2O_3) over La_2NiO_4. The "epitaxial strain" argument would further suggest that La_2CoO_4 and La_2FeO_4 would be even more unstable relative to the component oxides and thus would be much harder to synthesize. The effect of excess oxygen on this "strain" would depend on the exact positions of the interstitial oxygen and this is still controversial.

Some conclusions can also be drawn from the fact that the oxygen Frenkel energy for La_2NiO_4 is small. Frenkel energy is the sum of the energy required to create an interstitial and a vacancy defect. Point defects in a lattice are deviations from the energetically most stable arrangement of atoms, i.e., the reference structure. Thus creation of a defect is an endothermic process. A small oxygen Frenkel energy for lanthanum nickelate implies that the creation of either an oxygen interstitial or an oxygen vacancy in La_2NiO_4 each individually has low energetic cost. The p-type oxidation reactions (reactions (3) and (4)) involve creation/consumption of oxygen ionic defects and creation of mobile holes. As the energy for creation/consumption of an oxygen defect is small in La_2NiO_4, one can conclude that the predominant contribution to the enthalpy of oxidation comes from stabilization of a hole. One can, thus, estimate that a hole in La_2NiO_4 is stabilized by an energy of the order of 50–100 kJ/mole.

On the other hand, the process of oxidation (reaction (3)) in $La_{2-x}A_xCuO_{4-y}$ (A = Ba, Sr) depends on the chemical nature of the dopant cation. It was further shown that energetically the process is similar to the oxidation of the corresponding oxide, AO, to the peroxide, AO_2 (*9*). It has been proposed that the holes in high oxidation cuprates are located in predominantly oxygen p type bands and possibly even in "peroxide-like" bonding states (*9*) represented by

$$O^{-2} + h^{\cdot} \Rightarrow \frac{1}{2}(O - O)^{-2}. \qquad (6)$$

The enthalpy for the oxidation involving oxygen interstitials (reaction (4)) for La_2CuO_4 is nearly zero (*11*). If one assumes that the oxygen Frenkel energies for the lanthanum cuprates and the lanthanum nickelates are similar, one can estimate the energetics for stabilization of a hole (enthalpy for reaction (6)) in La_2CuO_4 to be small (less exothermic than 20 kJ/mole). The low hole stabilization energy is what is expected for "peroxide-like" states, especially in light of the aging phenomena found in some high oxidation-state cuprates (see Ref. (*9*)).

The much larger magnitude of the hole stabilization energy (of the order of 50–100 kJ/mole) for the lanthanum nickelates suggests that the process of oxidation in the nickelates involve very different hole states. We argue that the holes in lanthanum nickelates probably occupy predominantly Ni 3*d*-type band and could be chemically described as "Ni^{+3}" species. Further, the large hole stabilization energy and the relatively small energy to create an oxygen interstitial in lanthanum, nickelate delineates the driving mechanism for the highly oxidized state of the samples and the occurrence of large concentration of oxygen interstitials.

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