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Thermochimica Acta 319 (1998) 1–5

thermochimica acta

Synthesis and thermodynamic characteristics of $LaSrNiO_4$

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Received 7 January 1998; received in revised form 21 April 1998; accepted 5 May 1998

Abstract

Samples of $LaSrNiO_4$ were synthesised from La_2O_3, NiO, $Sr(NO_3)_2$ in concentrated nitric acid and investigated by solution calorimetry. Using the present data on the dissolution enthalpy of La_2O_3, NiO, $SrCO_3$ and some literature data, the thermodynamic values of the reaction of $LaSrNiO_4$ formation from: (1) La_2O_3, SrO, NiO; (2) La_2O_3, NiO, $SrCO_3$; (3) $La(OH)_3$, $Sr(OH)_2$, $Ni(OH)_2$; (4) and from La_2O_3, NiO, $Sr(NO_3)_2$ were calculated. The calculated values permitted to conclude that $LaSrNiO_4$ reacted with CO_2 giving a mixture of La_2O_3, NiO, $SrCO_3$ and with H_2O forming metal hydroxides. The formation of $LaSrNiO_4$ from simple oxides is thermodynamically favourable. The dependence of formation enthalpies on the atomic number of transition metals (Cu, Co, Ni) was analysed. The temperatures at which reactions of $LaSrNiO_4$ formation from La_2O_3, NiO, $SrCO_3$ and from La_2O_3, NiO, $Sr(NO_3)_2$ became thermodynamically possible are 1918 K and 1172 K, respectively. This allows a conclusion to be made that La_2O_3, NiO, $Sr(NO_3)_2$ are preferable as starting reagents for the synthesis of $LaSrNiO_4$. © 1998 Elsevier Science B.V.

Keywords: Enthalpy; Calorimetry; La–Sr–Ni–O system

1. Introduction

The paper is devoted to the thermochemical investigation of $LaSrNiO_4$. The interest in La–Sr–Ni–O system is associated with high temperature superconductors. The discovery of superconductivity of phases formed in the La–Sr–Cu–O system raises a question: why only cuprates are superconductors, whereas other transition metal compounds analogous to cuprates are not [1–5]. The investigation of nickel-bearing compounds is interesting from this point of view.

This paper deals with thermodynamic parameters of phases in the La–Sr–Ni–O system. The literature analysis showed there are no thermochemical data on $LaSrNiO_4$ phase in the literature.

2. Experimental

2.1. Preparation of samples

Stoichiometric quantities of La_2O_3, NiO and $Sr(NO_3)_2$ were mixed together and dissolved in concentrated nitric acid by heating. The excess of nitric acid was removed by gradual heating. The powder mixture was tipped into a porcelain crucible, and the

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PII S0040-6031(98)00370-0

nitrous gases were carefully evaporated. The grey product was grounded and heated in air at 1073 K during 12 h. After being cooled and grounded the product was heated again at 1373 K during 12 h. The samples were cooled down to 1073 K in the furnace before being quenched down to the room temperature. Next, they were grounded and pressed into pellets. The pellets were baked in porcelain crucibles in air at 1373 K during 48 h and slowly cooled down to the room temperature. The samples obtained were characterised by X-ray powder diffraction and chemical analyses. According to the results of analyses, the prepared samples were single phases.

2.2. Solution calorimetry

Solution calorimetry was used to obtain experimental data on some reactions with $LaSrNiO_4$. The construction of the calorimeter and the experimental procedure were described elsewhere [6–8]. The thermochemical cycle was designed in such a way that it was possible to compare the dissolution enthalpy of $LaSrNiO_4$ with the dissolution enthalpy of the mixture containing La_2O_3, NiO, $SrCO_3$. A short scheme of the process is given below:

$$1/2La_2O_3(s) + \text{solution I} = \text{solution II} + 1/2\Delta_{sol}H_1 \quad (1)$$

$$NiO(s) + \text{solution II} = \text{solution III} + \Delta_{sol}H_2 \quad (2)$$

$$SrCO_3(s) + \text{solution III} = \text{solution IV} + CO_2 + \Delta_{sol}H_3 \quad (3)$$

$$LaSrNiO_4(s) + \text{solution I} = \text{solution II} + \Delta_{sol}H_4 \quad (4)$$

Solution I indicates 6 N HCl. Reactions (1)–(3) minus reaction (4) give the following:

$$1/2La_2O_3(s) + NiO(s) + SrCO_3(s) + 0.25O_2(g) = LaSrNiO_4(s) + CO_2(g) + \Delta_R H_5 \quad (5)$$

where

$$\Delta_R H_5 = 1/2\Delta_{sol}H_1 + \Delta_{sol}H_2 + \Delta_{sol}H_3 - \Delta_{sol}H_4$$

The weight of samples used in the calorimetric measurements was about 0.1 g. The volume of the calorimeter vessel was 200 ml.

3. Results

We obtained the following values of dissolution enthalpies of La_2O_3, NiO, $SrCO_3$:

La_2O_3	$\Delta_{sol}H_1$ (323.15 K) = −465.1 ± 2.6 kJ/mol
NiO	$\Delta_{sol}H_2$ (323.15 K) = −51.3 ± 3.0 kJ/mol
$LaSrNiO_4$	$\Delta_{sol}H_3$ (323.15 K) = −525.7 ± 5.0 kJ/mol
$SrCO_3$	$\Delta_{sol}H_4$ (323.15 K) = −13.5 ± 1.0 kJ/mol

Six calorimetric experiments were performed for each value and the uncertainty is given as a standard deviation (95% confidence interval, using the Student coefficient).

The enthalpies of some reactions with the participation of $LaSrNiO_4$ were calculated on the basis of the above given data. Literature data used for the calculation (Tables 1 and Table 2) were taken from Refs. [9,10].

The values of reaction enthalpies calculated from our experimental data are presented below:

$$0.5La_2O_3(s) + NiO(s) + SrCO_3(s) + 0.25O_2(g) = LaSrNiO_4(s) + CO_2(g) \quad (6)$$

$$\Delta_R H_5 = +230.4 \pm 6.2\ \text{kJ/mol}$$

$$0.5La_2O_3(s) + NiO(s) + SrO(s) + 0.25O_2(g) = LaSrNiO_4(s) \quad (7)$$

$$\Delta_R H_6 = -11.0 \pm 6.2\ \text{kJ/mol}$$

$$2LaSrNiO_4(s) + 7H_2O(l) = 2La(OH)_3(s) + 2Sr(OH)_2(s) + 2Ni(OH)_2(s) + 0.5O_2(g) \quad (8)$$

$$\Delta_R H_7 = -139.5\ \text{kJ/mol}$$

$$2LaSrNiO_4(s) + 7H_2O(g) = 2La(OH)_3(s) + 2Sr(OH)_2(s) + 2Ni(OH)_2(s) + 0.5O_2(g) \quad (9)$$

$$\Delta_R H_8 = -440.2\ \text{kJ/mol}$$

$$0.5La_2O_3(s) + NiO(s) + Sr(NO_3)_2(s) = LaSrNiO_4(s) + 2NO_2(g) + 0.25O_2(g) \quad (10)$$

$$\Delta_R H_9 = +457.7\ \text{kJ/mol}$$

The uncertainties of reactions (8)–(10) are not listed because there are no exact data for the uncertainties of

Table 1
Literature data used for calculation of reaction enthalpies

Reaction	Temperature (K)	Thermodynamic values		Ref.
		$\Delta_R H$ (kJ/mol)	$\Delta_R S$ (J/K mol)	
SrO(s)+CO2(g)=$SrCO_3$(g)	298.15	−241.490	−172.054	[10]
	323.15	−241.445	−171.909	[10]

$\Delta_R H$ – Enthalpy of reaction, which, for example, for the reaction SrO + CO_2 = $SrCO_3$ is given by $\Delta_f H(SrCO_3) - \Delta_f H(SrO) - \Delta_f H(CO_2)$.
$\Delta_R S$ – Entropy of reaction.
$\Delta_f H$ – Enthalpy of formation of compounds from elements.
S – Entropy.

Table 2
Literature data used for calculation of reaction enthalpies

Compounds	Temperature (K)	$\Delta_f H$ (kJ/mol)	S (J/K mol)	Ref.
La_2O_3 (s)	323.15	−1793.903		[9]
CoO (s)	323.15	−237.133		[9]
NiO (s)	323.15	−239.599		[9]
SrO (s)	323.15	−590.897	59.258	[9]
CuO (s)	323.15	−61.906		[9]
H_2O (l)	323.15	−85.040		[10]
H_2O (g)	323.15	−242.075		[10]
$Sr(OH)_2$	323.15	−964.156		[10]
$Ni(OH)_2$	323.15	−532.034		[10]
$La(OH)_3$	323.15	−1309.600		[10]
CO_2 (g)	323.15	216.709		[10]
$SrCO_3$ (s)	323.15		104.058	[10]
O_2 (g)	323.15		207.409	[10]
$Sr(NO_3)_2$	323.15	−991.572		[10]
NO_2 (g)	323.15	34.032		[10]

$\Delta_f H$ – Enthalpy of formation of compounds from elements.
S – Entropy of compounds.

formation enthalpies of $La(OH)_3$, $Ni(OH)_2$, $Sr(OH)_2$, $Sr(NO_3)_2$.

The analysis of calculated data shows that $LaSrNiO_4$ reacts with CO_2 and water, but it does not decompose into binary oxides.

4. Discussion

It is not possible to compare our experimental data on $LaSrNiO_4$ with literature data because there is no literature data for this compound.

The first problem which we are going to discuss in the paper is an attempt to find the correlations between thermodynamic values and structural parameters. Specifically, we will analyse $LaSrMeO_4$ phases where Me = Cu, Ni.

We will assume that the crystal network of $LaSrCuO_4$ ($LaSrNiO_4$) is an epitaxial structure built from La_2O_3, SrO and CuO(NiO) layers. It is possible to suppose, as done by Goodenough and Manthram [11], that if the lattice parameters of two layers match, the structure is very favourable and stable.

The relative difference of lattice parameters of two layers (La_2O_3 and CuO layers), namely, $(a_1-a_2)/[(a_1+a_2)/2]\times 100$, is 14.5%. The same value for La_2O_3 and NiO is 29%. The data for lattice parameters were taken from Ref. [12]. The formation enthalpy of $LaSrCuO_4$ from simple oxides is −26.5 kJ/mol [1]. The same value for $LaSrNiO_4$ is −11.0 kJ/mol (this paper). It is worth noting that the increase in the formation enthalpy from simple oxides in the absolute value correlates with the decrease in the relative

Table 3
Formation enthalpies, atomic numbers and ionic radii

Compound	$\Delta_f H$ (kJ/mol)	Atomic number	Ionic radius (nm)	Ref.
$LaSrCuO_4$	−1676.3	29	0.080 (Cu^{2+})	[12]
$LaSrNiO_4$	−1738.4	28	0.074 (Ni^{2+})	[12]
$LaSrCoO_4$	−1809.9	27	0.078 (Co^{2+})	[12]

difference of lattice parameters. It is also necessary to say that the decomposition of $LaSrCuO_4$ into the mixture of simple oxides requires more energy (26.5 kJ/mol) than the same process with $LaSrNiO_4$ (11.0 kJ/mol). It implies that $LaSrCuO_4$ is more stable than $LaSrNiO_4$.

Our data, the data from Refs. [1–4], and literature data of Tables 1 and 2 provide a possibility to calculate the standard formation enthalpies for $LaSrNiO_4$, $LaSrCuO_4$, $LaSrCoO_4$ as follows:

$$\Delta_f H\ (LaSrNiO_4,\ 298.15\,K) = -1738.4\,kJ/mol$$

$$\Delta_f H\ (LaSrCuO_4,\ 298.15\,K) = -1676.3\,kJ/mol$$

$$\Delta_f H\ (LaSrCoO_4,\ 298.15\,K) = -1809.9\,kJ/mol$$

These data can be used for obtaining extrapolated values of $\Delta_f H$ for all transition elements from Sc up to Zn. Data of (Table 3) show that for obtaining high accurate data it is better to use dependence of $\Delta_f H$ on the atomic number of elements rather than that on the ionic radius. In order to extrapolate data for $\Delta_f H$ for unknown compounds ($LaSrMeO_4$, where Me-transition elements from Sc up to Zn), we have constructed three relations between $\Delta_f H$ (see, Table 3) and the element atomic number (x), namely, (1) $\Delta_f H = a + bx$; (2) $\Delta_f H = a + b/x$; (3) $\Delta_f H = a + b/x + c/x^2$ (exact form: $\Delta_f H = -1624.0 + 4.5780 \times 10^4/x - 1.3716 \times 10^6/x^2$)

The analysis of these three relations allows us to conclude that the third relation describes the experimental data better than the other two relations.

Finally, our data can be used for selecting the optimal way of synthesis. In the literature two different ways for the preparation of $LaSrNiO_4$ are described: the first one from La_2O_3, NiO, $SrCO_3$ mixture; and the second one from La_2O_3, NiO, $Sr(NO_3)_2$ mixture. One of the criteria to select the way of synthesis is a lower temperature at the start of the reaction. To clarify the situation, we studied the reactions of formation of $LaSrNiO_4$ from different mixtures (reactions (5), (10)).

To calculate the temperature at which the reaction becomes thermodynamically possible, we used the expression $\Delta G = H - T\Delta S = O$, where $T = H/\Delta S$, data given in Tables 1 and 2 and data of reactions (5) and (10). To calculate temperature, and ΔS of $LaSrNiO_4$ from $1/2La_2O_3$, SrO, NiO was assumed to be zero (see, for example reference [13]). The temperature for the first way of synthesis (synthesis of $LaSrNiO_4$ from La_2O_3, NiO, $SrCO_3$) is $T = 1918$ K. The temperature for the second way of synthesis (synthesis of $LaSrNiO_4$ from La_2O_3, NiO, $Sr(NO_3)_2$) is $T = 1172$ K.

5. Conclusions

The formation enthalpy of $LaSrNiO_4$ was measured by solution calorimetry. It was established that formation of $LaSrNiO_4$ from simple oxides (La_2O_3, SrO, NiO) was thermodynamically favourable. It was found out that $LaSrNiO_4$ reacted with CO_2 and H_2O. The temperatures of reactions to form $LaSrNiO_4$ from La_2O_3, NiO, $SrCO_3$ and from La_2O_3, NiO, $Sr(NO_3)_2$ are 1918 K and 1172 K, respectively. Thus, we come to the conclusion that the synthesis of $LaSrNiO_4$ from La_2O_3, NiO, $Sr(NO_3)_2$ can be performed at lower temperatures than synthesis from La_2O_3, NiO, $SrCO_3$, i.e. La_2O_3, NiO, $Sr(NO_3)_2$ are preferable as starting reagents to synthesise $LaSrNiO_4$.

Acknowledgements

This work is supported by the Russian government in framework of Russian Scientific-Technical Program, section 'Basis of chemistry and technology of superconductors' (Grant No. 96055 'Prognoz').

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