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Thermochemical characteristics of $La_{n+1}Ni_nO_{3n+1}$ oxides

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Abstract

Lanthanum nickelates: $La_2NiO_{4+\delta}$, $La_3Ni_2O_{7-\delta}$, $La_4Ni_3O_{10-\delta}$ and $LaNiO_{3-\delta}$ the members of Ruddlesden–Popper series $La_{n+1}Ni_nO_{3n+1}$ were prepared using citrate route. Dissolution enthalpies of complex oxides as well as a number of subsidiary substances were measured by means of Calvet calorimeter in 1 M solution of hydrochloric acid at 25 °C. The dissolution scheme of complex oxides in hydrochloric acid was proposed and enthalpies of formation of the complex oxides from binary oxides were calculated considering oxygen nonstoichiometry of these substances. Enthalpies of step-by-step oxidation were evaluated. Partial enthalpy contribution of LaO layers was calculated endothermic equals to 30.9 J/mol while partial enthalpy contribution of perovskite $LaNiO_3$ layers was negative equals to −97.0 J/mol. Enthalpy of formation of any complex oxide of Ruddlesden–Popper series fits very well to the linear regression based on these values.

Keywords: Lanthanum nickelates; Oxygen nonstoichiometry; Solution calorimetry; Enthalpies of dissolution; Enthalpies of formation

1. Introduction

Four complex oxides La_2NiO_4 ($n = 1$), $La_3Ni_2O_7$ ($n = 2$), $La_4Ni_3O_{10}$ ($n = 3$), $LaNiO_3$ ($n = \infty$) belonging to the Ruddlesden–Popper homologous series with general formula $La_{n+1}Ni_nO_{3n+1}$, where n consecutive perovskite layers $(LaNiO_3)_n$ alternate with rock salt layers (LaO), exist in the La–Ni–O system. Rare earth nickelates are perspective materials for practical use as electrodes for solid oxide fuel cells and other electrochemical devices, catalysts of reduction and oxidation. Since physical properties such as electrical conductivity and others were studied earlier their thermochemical characteristics are still unstudied [1–17].

$La_2NiO_{4+\delta}$ possesses overstoichiometry with respect to the oxygen content. It was shown that oxygen nonstoichiometry in this phase could widely varied and reached values up to $\delta = 0.25$ depending on the synthesis conditions [1–3]. The value of δ estimated on the basis of the data reported by Schartman and Honig [4] was found to be ∼0.075 at 1100 °C in air ($PO_2 = 0.21$ atm).

Oxygen nonstoichiometry of $La_3Ni_2O_{7-\delta}$ and $La_4Ni_3O_{10-\delta}$ were studied earlier. $La_3Ni_2O_{7-\delta}$ synthesized in air at 1100 °C was reported to have slight oxygen deficiency $\delta \approx 0.08$ [5], while in [6] Rietveld refinement resulted to the formula $La_3Ni_2O_{7.02}$ and chemical analysis made in [7] led to the formula $La_3Ni_2O_{6.72}$. Oxygen content in the phase with $n = 3$ was reported either close to stoichiometric $La_4Ni_3O_{10}$ [8] or $La_4Ni_3O_{10.03}$ [6], or as oxygen deficient $La_4Ni_3O_{9.66}$ [7]. In our previous work we studied oxygen nonstoichiometry of $La_3Ni_2O_{7-\delta}$ and $La_4Ni_3O_{10-\delta}$ as a function of oxygen partial pressure and temperature [9]. Oxygen content at 1100 °C in air expressed by the following formulas $La_3Ni_2O_{6.932}$ and $La_4Ni_3O_{9.835}$ have been taken for further calculations in this work.

It was reported that $LaNiO_{3-\delta}$ has oxygen deficiency [10,11]. Rakshit and Gopalakrishnan observed small loss of oxygen about 0.05% by weight after keeping the stoichiometric sample at 800 °C in air [11]. Such weight loss yields the value of δ equal to ∼0.008.

The literature survey shows that available experimental information about thermochemical characteristics of the La–Ni–O system is very few and contradictory. Matskevich et al. [12] gives analysis of thermodynamic data for the La–Sr–Ni–O system although it is not sufficient to adopt it completely for La–Ni–O system. Thus the present work is aimed to study the standard enthalpy of formation of mentioned above complex oxides as well as enthalpies of their synthesis from binary oxides and enthalpies of the consequent oxidation of these phases. Therefore enthalpies of dissolution of these complex oxides were

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studied taking into account oxygen nonstoichiometry of lanthanum nickelates.

2. Experimental

Lanthanum oxide La_2O_3 of “LaO–D” purity grade and nickel oxide NiO of “special purity” grade used as starting materials were preliminary annealed in air: La_2O_3 at 1100 °C for 12 h and NiO at 800 °C for 4 h. Complex oxides $La_2NiO_{4+\delta}$, $La_3Ni_2O_{7-\delta}$, $La_4Ni_3O_{10-\delta}$ and $LaNiO_{3-\delta}$ were synthesized using the citrate route [9]. The samples were characterized by X-ray powder diffraction.

In order to remove absorbed water and gases and equilibrate the oxygen content all samples were preliminary dried: $La_2NiO_{4+\delta}$, $La_3Ni_2O_{7-\delta}$, $La_4Ni_3O_{10-\delta}$, La_2O_3 at 1100 °C, $LaNiO_{3-\delta}$, NiO at 800 °C and $NiCl_2$ at 300 °C for 24 h and then quenched to room temperature. Compositions with following values of oxygen nonstoichiometry: $La_2NiO_{4.075}$ [4], $La_3Ni_2O_{6.932}$ [9], $La_4Ni_3O_{9.835}$ [9] and $LaNiO_{2.992}$ [11] were taken for the further calculations.

Calorimetric measurements were performed using Calvet calorimeter at 25 °C with cell volume 10 cm^3 and sensitivity 10^{-6} J/s. The calibration of calorimeter was carried out using dissolution enthalpy of potassium chloride. Preliminary weighted powder samples were placed into the thin glass ampoules, which were vacuum sealed after that. Calorimetric cell was filled with 1 M HCl solution (~8 ml) and the ampoule was placed inside the cell in a special holder. After few hours when thermal equilibrium was established the ampoule was broken and oxide powder began to dissolve in HCl media. The dependence of thermo-EMF versus time was registered during the dissolution process, providing the heat evolution curve. Integration of heat evolution curves gave the value of enthalpy of dissolution. Typically complete dissolution of 2 mg sample took about 2 h.

Heat evolution curve for each sample was measured four times. The error did not exceed 2%.

3. Results and discussion

Since individual solid metal oxides cannot directly interact with each other unless temperature is raised above 800 °C one should use appropriate thermochemical cycles in order to calculate standard (298 K) enthalpies of formation of complex oxides from binary oxides. The thermochemical cycle used for the calculations is presented in Fig. 1.

The excess of oxygen with respect to the stoichiometric composition in $La_2NiO_{4.075}$ implies that Ni ions partly exist in the oxidation state 3+. Same coexistence of oxidation states for nickel ions Ni^{2+} and Ni^{3+} appears in all other complex oxides: $La_3Ni_2O_{6.932}$, $La_4Ni_3O_{9.835}$ and $LaNiO_{2.992}$. Taking into account that under mentioned conditions the stable form of Ni ions in water solutions is 2+, it was supposed that the Red-Ox reaction took place during the dissolution process. This effect is the basis of iodometric titration analysis widely used for the determination of oxygen nonstoichiometry in complex oxides. A comparison of electrode potentials for possible Red-Ox processes led to the conclusion that the most favorable reducer in this system was chloride ion Cl^-.

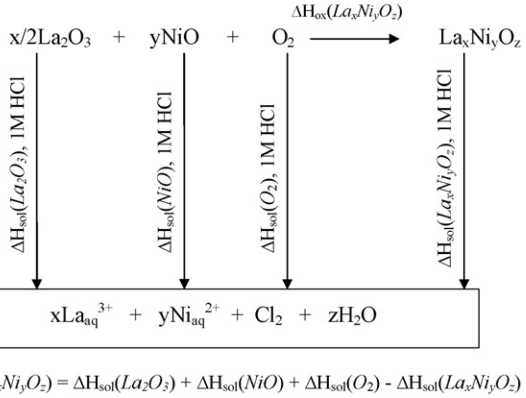

Fig. 1. Thermochemical cycle used for calculations enthalpies of formation of complex oxides from binary oxides.

Calculation of standard enthalpies of complex oxides formation by means of cycle in Fig. 1 requires quantitative and quick dissolution of all reagents and products of reactions in the selected solvent. Average values of specific and molar enthalpies of dissolution in 1N hydrochloric acid at 25 °C are given in Table 1.

The values presented in Table 1 correspond to the following reactions:

$$NiCl_{2s} + H_2O \rightarrow Ni_{aq}{}^{2+} + 2Cl_{aq}{}^{-} + H_2O \quad (\Delta H_1) \qquad (1)$$

$$La_2O_3 + 6H^+ \rightarrow 2La_{aq}{}^{3+} + 3H_2O \quad (\Delta H_2) \qquad (2)$$

$$La_2NiO_{4+\delta} + (8 + 2\delta)H_{aq}{}^{+} + 2\delta Cl_{aq}{}^{-} \rightarrow 2La_{aq}{}^{3+} + Ni_{aq}{}^{2+} + (4+\delta)H_2O + \delta Cl_2 \quad (\Delta H_3) \qquad (3)$$

$$La_3Ni_2O_{7-\delta} + (14 - 2\delta)H_{aq}{}^{+} + (1 - 2\delta)Cl_{aq}{}^{-} \rightarrow 3La_{aq}{}^{3+} + 2Ni_{aq}{}^{2+} + (7-\delta)H_2O + (1-2\delta)/2Cl_2 \quad (\Delta H_4) \qquad (4)$$

$$La_4Ni_3O_{10-\delta} + (20 - 2\delta)H_{aq}{}^{+} + 2(1 - \delta)Cl_{aq}{}^{-} \rightarrow 4La_{aq}{}^{3+} + 3Ni_{aq}{}^{2+} + (10-\delta)H_2O + (1-\delta)Cl_2 \quad (\Delta H_5) \qquad (5)$$

Table 1
Experimental values of specific and molar enthalpies of dissolution at 25 °C

Compound	Specific enthalpy of dissolution (J/g)	Molar enthalpy of dissolution (kJ/mol)
$NiCl_2$	−683 (±3)	$\Delta H_1 = -88.6$ (±0.4)
La_2O_3	−1667 (±10)	$\Delta H_2 = -543.1$ (±3.3)
$La_2NiO_{4.075}$	−1487 (±7)	$\Delta H_3 = -597.4$ (±2.8)
$La_3Ni_2O_{6.932}$	−1502 (±8)	$\Delta H_4 = -968.8$ (±5.2)
$La_4Ni_3O_{9.835}$	−1531 (±7)	$\Delta H_5 = -1361.1$ (±6.2)
$LaNiO_{2.992}$	−1614 (±9)	$\Delta H_6 = -396.2$ (±2.2)