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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^-.

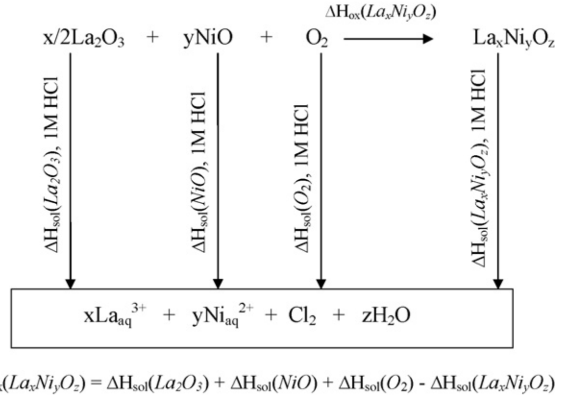


Fig. 1. Thermochemical cycle used for calculations enthalpies of formation of complex oxides from binary oxides.

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:

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

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

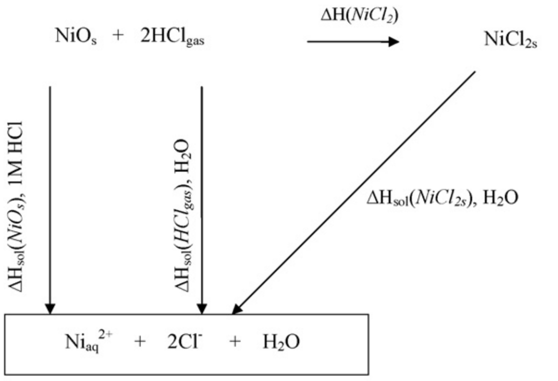
$$La_2NiO_{4+\delta} + (8 + 2\delta)H_{aq}{}^{+} + 2\delta Cl_{aq}{}^{-} \rightarrow 2La_{aq}{}^{3+} + Ni_{aq}{}^{2+} + (4+\delta)H_2O + \delta Cl_2 \quad (\Delta H_3) \tag{3}$$

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

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

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)



$$\Delta H_{sol}(NiO_s),\ 1\,M\ HCl = \Delta H(NiCl_2) + \Delta H_{sol}(NiCl_{2s}),\ H_2O - 2\Delta H_{sol}(HCl_{gas}),\ H_2O$$

Fig. 2. Thermochemical cycle used for calculation enthalpy of dissolution NiO in 1 M HCl at 25 °C.

$$\begin{aligned}&\mathrm{LaNiO_{3-\delta}} + (6-2\delta)\mathrm{H_{aq}}^{+} + (1-2\delta)\mathrm{Cl_{aq}}^{-}\\ &\quad\rightarrow\ \mathrm{La_{aq}}^{3+} + \mathrm{Ni_{aq}}^{2+} + (3-\delta)\mathrm{H_2O}\\ &\quad + (1-2\delta)/2\mathrm{Cl_2}\quad (\Delta H_6)\end{aligned}\tag{6}$$

One can see that the value for enthalpy of NiO dissolution in 1 M HCl is not presented in Table 1. The reason is that NiO very slowly dissolves in 1 M hydrochloric acid at ambient temperature and this process could not be accomplished inside the calorimetric cell. In order to estimate enthalpy of NiO dissolution the additional thermodynamic cycle was used (Fig. 2).

Enthalpies of reactions presented in Fig. 2 were taken from the literature [13] and were listed in Table 2.

Thus the dissolution reaction of NiO can be presented as

$$\mathrm{NiO_s} + 2\mathrm{H_{aq}}^{+} \rightarrow\ \mathrm{Ni_{aq}}^{2+} + \mathrm{H_2O}\quad (\Delta H_{11})\tag{7}$$

According to the cycle presented in Fig. 2 the following combination resulted in the enthalpy of reaction (7):

$$\Delta H_{11} =\ \Delta H_7 + \Delta H_1 - 2\Delta H_8 =\ -107.4\,\mathrm{kJ/mol}$$

Since enthalpies of all reactions in Fig. 1 were obtained either in calorimetric experiment or by calculation it became possible to use the cycle for the calculation of the enthalpies of formation of four complex oxides from binary oxides. The related reactions and their thermochemical equations were the following:

$$\begin{aligned}&\mathrm{La_2O_3} + \mathrm{NiO} + \delta/2\mathrm{O_2} \rightarrow \mathrm{La_2NiO_{4+\delta}},\\ &\Delta H_{12} = -\Delta H_3 + \Delta H_2 + \Delta H_{11} + 2\delta\Delta H_9 + 2\delta\Delta H_{10}\\ &\qquad = -70.8\,\mathrm{kJ/mol}\quad (\Delta H_{12})\end{aligned}\tag{8}$$

Table 2
Enthalpies of reactions calculated from the data [13]

Reaction	Enthalpy (kJ)
$\mathrm{NiO_s} + 2\mathrm{HCl_{gas}} \rightarrow \mathrm{NiCl_{2s}} + \mathrm{H_2O}$	$\Delta H_7 = -165.7$
$\mathrm{HCl_{gas}} + \mathrm{H_2O} \rightarrow \mathrm{H_{aq}}^{+} + \mathrm{Cl_{aq}}^{-} + \mathrm{H_2O}$	$\Delta H_8 = -73.4$
$\mathrm{Cl_{aq}}^{-} - 1\mathrm{e} \rightarrow \frac{1}{2}\mathrm{Cl_2}$	$\Delta H_9 = 167.5$
$\frac{1}{4}\mathrm{O_2} + \mathrm{H_{aq}}^{+} + 1\mathrm{e} \rightarrow \frac{1}{2}\mathrm{H_2O}$	$\Delta H_{10} = -285.8$

Table 3
Results of calculations based on the calorimetric data

Reaction	Enthalpy (kJ/mol)
$\mathrm{La_2O_3} + \mathrm{NiO} + \delta/2\mathrm{O_2} \rightarrow \mathrm{La_2NiO_{4+\delta}}$	$\Delta H_{12} = -70.8$
$\frac{3}{2}\mathrm{La_2O_3} + 2\mathrm{NiO} + (1-2\delta)/4\mathrm{O_2} \rightarrow \mathrm{La_3Ni_2O_{7-\delta}}$	$\Delta H_{13} = -162.9$
$2\mathrm{La_2O_3} + 3\mathrm{NiO} + (1-\delta)/2\mathrm{O_2} \rightarrow \mathrm{La_4Ni_3O_{10-\delta}}$	$\Delta H_{14} = -244.9$
$\frac{1}{2}\mathrm{La2O_3} + \mathrm{NiO} + (1-2\delta)/4\mathrm{O_2} \rightarrow \mathrm{LaNiO_{3-\delta}}$	$\Delta H_{15} = -99.2$
$\frac{3}{2}\mathrm{La_2NiO_{4.075}} + \frac{1}{2}\mathrm{NiO} + 0.165\mathrm{O_2} \rightarrow \mathrm{La_3Ni_2O_{6.932}}$	$\Delta H_{16} = -56.7$
$4\mathrm{La_3Ni_2O_{6.932}} + \mathrm{NiO} + 0.3885\mathrm{O_2} \rightarrow 3\mathrm{La_4Ni_3O_{9.835}}$	$\Delta H_{17} = -83.1$
$\mathrm{La_4Ni_3O_{9.835}} + \mathrm{NiO} + 0.5665\mathrm{O_2} \rightarrow 4\mathrm{LaNiO_{2.992}}$	$\Delta H_{18} = -151.9$

$$\begin{aligned}&\frac{3}{2}\mathrm{La_2O_3} + 2\mathrm{NiO} + (1-2\delta)/4\mathrm{O_2} \rightarrow \mathrm{La_3Ni_2O_{7-\delta}},\\ &\Delta H_{13} = -\Delta H_4 + \frac{3}{2}\Delta H_2 + 2\Delta H_{11} + (1-2\delta)\Delta H_9\\ &\qquad + (1-2\delta)\Delta H_{10} = -162.9\,\mathrm{kJ/mol}\quad (\Delta H_{13})\end{aligned}\tag{9}$$

$$\begin{aligned}&2\mathrm{La_2O_3} + 3\mathrm{NiO} + (1-\delta)/2\mathrm{O_2} \rightarrow \mathrm{La_4Ni_3O_{10-\delta}},\\ &\Delta H_{14} = -\Delta H_5 + 2\Delta H_2 + 3\Delta H_{11} + 2(1-\delta)\Delta H_9\\ &\qquad + 2(1-\delta)\Delta H_{10} = -244.9\,\mathrm{kJ/mol}\quad (\Delta H_{14})\end{aligned}\tag{10}$$

$$\begin{aligned}&\frac{1}{2}\mathrm{La_2O_3} + \mathrm{NiO} + (1-2\delta)/4\mathrm{O_2} \rightarrow \mathrm{LaNiO_{3-\delta}},\\ &\Delta H_{15} = -\Delta H_6 + \frac{1}{2}\Delta H_2 + \Delta H_{11} + (1-2\delta)\Delta H_9\\ &\qquad + (1-2\delta)\Delta H_{10} = -99.2\,\mathrm{kJ/mol}\quad (\Delta H_{15})\end{aligned}\tag{11}$$

The substances $\mathrm{La_2NiO_{4+\delta}}$, $\mathrm{La_3Ni_2O_{7-\delta}}$, $\mathrm{La_4Ni_3O_{10-\delta}}$ and $\mathrm{LaNiO_{3-\delta}}$ belong to the homologous series where mean oxidation state of Ni ions gradually increases from +2 to +3. Thus one could evaluate the enthalpies of consequent oxidation of these phases. The following combinations of reactions were suggested for calculations:

$$\begin{aligned}&\frac{3}{2}\mathrm{La_2NiO_{4.075}} + \frac{1}{2}\mathrm{NiO} + 0.165\mathrm{O_2} \rightarrow \mathrm{La_3Ni_2O_{6.932}},\\ &\Delta H_{16} = -\frac{3}{2}\Delta H_{12} + \Delta H_{13} = -56.7\,\mathrm{kJ}\quad (\Delta H_{16})\end{aligned}\tag{12}$$

$$\begin{aligned}&4\mathrm{La_3Ni_2O_{6.932}} + \mathrm{NiO} + 0.3885\mathrm{O_2} \rightarrow 3\mathrm{La_4Ni_3O_{9.835}},\\ &\Delta H_{17} = 3\Delta H_{14} - 4\Delta H_{13} = -83.1\,\mathrm{kJ}\quad (\Delta H_{17})\end{aligned}\tag{13}$$

$$\begin{aligned}&\mathrm{La_4Ni_3O_{9.835}} + \mathrm{NiO} + 0.5665\mathrm{O_2} \rightarrow 4\mathrm{LaNiO_{2.992}},\\ &\Delta H_{18} = -\Delta H_{14} + 4\Delta H_{15} = -151.9\,\mathrm{kJ}\quad (\Delta H_{18})\end{aligned}\tag{14}$$

Summarized results of all calculations are listed in Table 3.

In order to compare obtained results with available reference data for a first approximation let us here assume that enthalpies

Table 4
The values of standard enthalpies of formation $\Delta H^\circ_{f,298}$ for complex oxides

Formula	$\Delta H^\circ_{f,298}$ (kJ/mol)
$La_2NiO_{4.075}$	−2103.7
$La_3Ni_2O_{6.932}$	−3333.6
$La_4Ni_3O_{9.835}$	−4552.4, −4334.0 [15], −4478.6 [16], −4508 [17]
$LaNiO_{2.992}$	−1236.0

of formation of nonstoichiometric complex oxides are close to those of stoichiometric compounds. Using the values of standard enthalpies of formation for NiO $\Delta H^\circ_{f,298} = -239.7$ kJ/mol [13] and for La_2O_3 $\Delta H^\circ_{f,298} = -1794.2$ kJ/mol [14] and calculated values of enthalpies for the reactions (8)–(11) the values of $\Delta H^\circ_{f,298}$ for all complex oxides have been calculated. The results were compared with available reference data in Table 4.

It can be seen that the value of standard enthalpy of formation calculated for $La_4Ni_3O_{10}$ is in a good agreement with reference data [16,17] while it is smaller than given in [15]. This difference is about 5% could arise because the reference value −4334.0 kJ/mol [15] was estimated using thermodynamic modeling and had not been measured directly. It may imply that energetic changes caused by intercalation of oxygen excess or oxygen deficit to the structure are negligible in comparison with enthalpy changes resulted from layers recombination during solid-state synthesis.

In our previous work [9] using EMF technique standard Gibbs energy for the following equilibrium reaction:

$$La_4Ni_3O_{10-\delta} \rightarrow 2La_2NiO_{4+\delta'} + NiO + (1-\delta-2\delta')/2O_2 \quad (\Delta H_{19}) \tag{15}$$

was determined in the form of following equation:

$$\Delta G^\circ\,(J) = 99300 - 62.18T\ (\pm 200\,J),$$

$$1396 \le T, K \le 1427$$

First item in this equation equals to 99.3 kJ can be refers to the enthalpy of reaction (15).

The enthalpy of reaction (15) can be also easily calculated using calorimetric data by combining enthalpies of reactions (12) and (13) as follows:

$$\Delta H_{19} = -\frac{4}{3}\Delta H_{16} - \frac{1}{3}\Delta H_{17} = 103.3\,\text{kJ}$$

Taking into account that the value of enthalpy ΔH_{19} calculated from the thermochemical cycle refer to 298 K and evaluated from EMF measurements to the temperature range $1396 \le T, K \le 1427$ they are in a good agreement.

3.1. An assessment of enthalpies of rock salt- and perovskite-layers formation contributions

Since in the complex oxides with general formula $La_{n+1}Ni_nO_{3n+1}$, where n consecutive perovskite layers $(LaNiO_3)_n$ alternate with rock salt layers (LaO), their structures can be represent as a combination of these layers. Formally the process of complex oxides formation (from such "structural point of view") can be written as

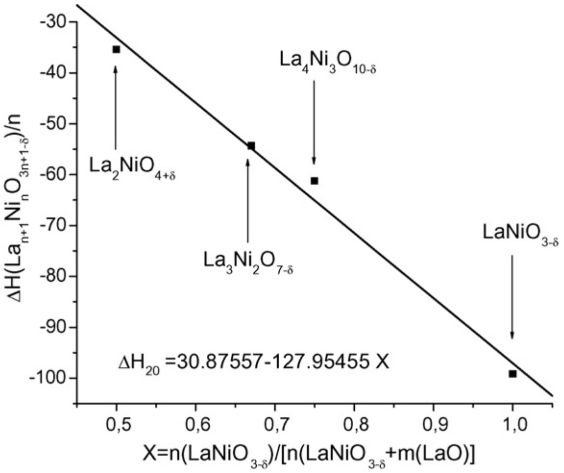


Fig. 3. Enthalpies of formation of complex oxides normalized to the mole of La vs. the mole fraction of perovskite layers in these substances.

$$LaO + nLaNiO_{3-\delta} = La_{n+1}Ni_nO_{3n+1-\delta}$$

Fig. 3 represents the enthalpies of formation of complex oxides from binary oxides (Table 3) normalized to the mole of La versus the mole fraction of perovskite layers in these substances.

Normalized enthalpy values were fitted by a linear regression giving rise to the following equation:

$$\Delta H_{20} = 30.9 - 127.95X\ (\pm 11.3\,\text{kJ})$$

In terms of the suggested type of presentation the extrapolation of equation (ΔH_{20}) to $X=0$ implies the contribution of LaO layer ($\Delta H(LaO) = 30.9$ kJ/mol La). The substitution of $X=1$ resulted in the value of $\Delta H_{20} = -97.1$ that corresponds to the contribution of perovskite layer ($\Delta H(LaNiO_{3-\delta}) = -97.1$ kJ/mol La).

Therefore enthalpies of formation of layered oxides $La_{n+1}Ni_nO_{3n+1-\delta}$ can be evaluated in terms of the partial contributions of enthalpies of formation LaO and $LaNiO_{3-\delta}$ layers:

$$\Delta H_{21} = 30.9 - 97.1n\ (\text{kJ/mol La})$$

It looks remarkable that while rock salt layer formation is energetically unfavorable ($\Delta H(LaO) = 30.9$ kJ/mol La), perovskite layer is more favorable in terms of enthalpy ($\Delta H(LaNiO_{3-\delta}) = -97.1$ kJ/mol La).

We do of course understand that even the structure of perovskite layers remains unchangeable in general, while n is changing in the formula of complex oxide, mean oxidation state of the ions inside the octahedrons gradually changes and bring in some contribution to the bonding energy. Nevertheless such "structural approach" gave satisfactory linearization and can be used as first approximation for evaluation of thermodynamic properties of complex oxides belonging to the homologous series $La_{n+1}Ni_nO_{3n+1}$.

4. Conclusion

Four complex oxides belonging to homologous series $La_{n+1}Ni_nO_{3n+1}$ ($La_2NiO_{4+\delta}$, $La_3Ni_2O_{7-\delta}$, $La_4Ni_3O_{10-\delta}$ and $LaNiO_{3-\delta}$) have been prepared by citrate technique. Dissolution enthalpies of these oxides as well as a number of concomitant substances in 1 M solution of hydrochloric acid at 25 °C have been measured by calorimetric technique. On the basis of the proposed dissolution mechanism enthalpies of formation of complex oxides from binary oxides have been calculated taking into account oxygen nonstoichiometry of these substances. Enthalpies of consequent oxidation have been evaluated. While partial contribution of enthalpies of formation LaO was found positive and equals to 30.9 kJ/mol La, the formation of perovskite layer $LaNiO_{3-\delta}$ was energetically favorable ($\Delta H = -97.1$ kJ/mol La). The enthalpy of formation of any complex oxide in Ruddlesden–Popper series was found to fit very well to the linear regression based on these values as follows:

$$\Delta H = 30.9 - 97.1n \ (\mathrm{kJ/mol\ La})$$

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