Thermochimica Acta 519 (2011) 12–15

Contents lists available at ScienceDirect

Thermochimica Acta

journal homepage: www.elsevier.com/locate/tca

Thermodynamics of formation of double perovskites $GdBaCo_{2-x}M_xO_{6-\delta}$ ($M = Fe$, Mn; $x = 0$, 0.2)

D.S. Tsvetkov*, I.L. Ivanov, I.V. Urusov, A.Yu. Zuev

Department of Chemistry, Ural State University, Lenin av.51, 620083 Ekaterinburg, Russia

ARTICLE INFO

Article history:
Received 14 October 2010
Received in revised form 8 February 2011
Accepted 14 February 2011
Available online 2 March 2011

Keywords:
Dissolution enthalpy
Standard enthalpy of formation
Calorimetry
Double perovskite
$RBaCo_2O_{5.5}$

ABSTRACT

Standard enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ ($M = Fe$, Mn; $x = 0$, 0.2) from constituent oxides, $\Delta_{ox}H_i^\circ$, and elements, $\Delta_f H_i^\circ$, at 298 K were calculated using dissolution enthalpies of corresponding double perovskites. Both $\Delta_{ox}H_i^\circ$ and $\Delta_f H_i^\circ$ were found to decrease in the sequence of $GdBaCo_2O_{5.5}$, $GdBaCo_{1.8}Fe_{0.2}O_{5.5}$ and $GdBaCo_{1.8}Mn_{0.2}O_{5.5}$ indicating growth of relative thermodynamic stability of $GdBaCo_2O_{5.5}$ caused by the substitution of Fe or Mn for Co.

1. Introduction

Mixed ionic and electronic conducting oxides $AA'Co_2O_5$, where A is a rare earth element (RE), A′–Ba, with double perovskite structure have been extensively investigated in past decade. The crystal structure of $GdBaCo_2O_{6-\delta}$ was studied using X-ray, neutron and electron diffraction methods [1–5]. Ba and RE cations were shown [1–5] to be ordered in the layers along *c* axis and hence the unit cell parameter *c* is doubled as compared to that of simple (nonlayered) cubic perovskite. Moreover oxygen vacancies can be ordered along *b* axis and, as a consequence, doubling of the unit cell parameter *b* is observed [1–6]. The crystal structure of $GdBaCo_2O_{6-\delta}$ was shown to depend strongly on its oxygen content [1,2]. The oxygen vacancies are believed to be ordered along *b* axis at $\delta = 0.5$ in Gd-contained layers thus that half of oxygen positions are vacant and another are occupied. Aforementioned layers do not contain oxygen entirely at $\delta = 1$ whereas all oxygen positions available in these layers are fully occupied at $\delta = 0$ [1,2].

$GdBaCo_2O_{6-\delta}$ was shown to have sufficiently high oxygen ionic conductivity and oxygen chemical diffusion coefficient even at temperatures as low as 673 K [3]. Relatively fast oxygen transport in $GdBaCo_2O_{6-\delta}$ was explained by the presence of extended channels in its structure due to oxygen vacancies ordering mentioned above. The double perovskite $GdBaCo_2O_{6-\delta}$ was also found to possess giant magnetoresistance [2,7] and large Seebek coefficient at low temperatures [2]. Double perovskite $GdBaCo_2O_{6-\delta}$ has been recently shown to exhibit good performance as a cathode material for SOFC [8–10] and oxygen permeable dense ceramic membrane [9] as well.

Despite that knowledge of the thermodynamic properties such as formation enthalpy of materials is the fundamental basis for understanding their thermodynamic stability, chemical reactivity etc., there are no these data for $GdBaCo_2O_{6-\delta}$ and its derivatives so far. The main goals of the present paper were, therefore, (i) to measure dissolution enthalpy of the double perovskites $GdBaCo_{2-x}M_xO_{5.5}$ ($M = Fe$, Mn; $x = 0$, 0.2) in 4 N HCl and (ii) to calculate standard enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ ($M = Fe$, Mn; $x = 0$, 0.2) from constituent oxides ($\Delta_{ox}H_i^\circ$) and elements ($\Delta_f H_i^\circ$) at 298 K.

2. Experimental

Powder samples of $GdBaCo_{2-x}M_xO_{5.5}$ ($M = Fe$, Mn; $x = 0$, 0.2) were synthesized by means of standard ceramic technique using Gd_2O_3, $BaCO_3$, Co_3O_4, Fe_2O_3 and MnO_2 as starting materials. All materials used had a purity of 99.99% and were preliminary calcined to remove absorbed H_2O and CO_2. Stoichiometric mixture of starting materials was calcined at temperatures between 1073 and 1373 K in air with 100 K step for 10 h at each stage followed by mixture regrinding. The phase composition of the powder samples prepared accordingly was studied by means of X-ray diffraction (XRD) with a DRON-6 diffractometer using Cu K_α radiation. XRD showed no indication for the presence of a second phase.

---

* Corresponding author. Tel.: +7 343 251 7927; fax: +7 343 261 7411.
E-mail address: Dmitrii.Tsvetkov@usu.ru (D.S. Tsvetkov).

0040-6031/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.tca.2011.02.022

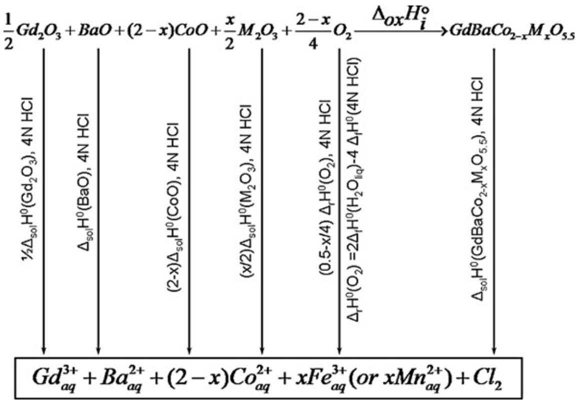

Fig. 1. Thermochemical cycle used for calculation of formation enthalpies of double perovskites from binary oxides.

It is well known that thermodynamic properties of oxides depend on their oxygen nonstoichiometry [11,12]. Therefore it is necessary to compare thermochemical properties of different double perovskites $GdBaCo_{2-x}M_xO_{6-\delta}$ (M = Fe, Mn; x = 0, 0.2) with the same oxygen content. The oxide samples with oxygen content of 5.5 were prepared in this work. In order to reach this content the preliminary obtained single phase sample of $GdBaCo_2O_{6-\delta}$ was slowly cooled from 1100 °C to room temperature in air and those of $GdBaCo_{1.8}Fe_{0.2}O_{6-\delta}$ and $GdBaCo_{1.8}Mn_{0.2}O_{6-\delta}$ were quenched from 773 K to 973 K to room temperature in air, respectively. Oxygen content in the samples of $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) prepared in this way was determined using iodometric titration technique described elsewhere [12] with accuracy ±0.02.

Enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) from constituent oxides ($\Delta_{ox}H_i^\circ$) and elements ($\Delta_fH_i^\circ$) at 298 K were determined using an isothermal solution calorimeter. The calorimetric setup and technique are described in detail elsewhere [13]. The volume of the calorimetric vessel used in this study was 200 ml. 4 N solution of HCl was employed as a solvent. Temperature of the calorimeter was measured by means of thermistor ($R_{298\,K} = 150\ k\Omega$). All measurements were carried out at temperature 298 ± 0.15 K. Calibration was carried out after each calorimetric experiment using electrical heater mounted inside the calorimeter vessel. The thermometric sensitivity of the calorimeter was 5×10^{-5} K and calorimetric sensitivity was 0.05 J. The energy equivalent was found to be 973.5 ± 2 J/K with 4 N HCl as solvent. Uncertainty of the experimental results was checked by dissolving KCl as a standard substance. Measured enthalpy of solution of KCl comes to value 17.52 ± 0.05 kJ/mol at solution molality 0.11 mol/kg and seems to be in good agreement with the value 17.584 ± 0.017 kJ/mol recommended in literature [14,15]. The chemical composition of all substances used for measurements was preliminary determined using ICP spectrometer ICAP 6500 DUO and atomic absorption spectrometer Solaar M6, Thermo Scientific, USA. All substances used for calorimetric measurements were shown to have the stoichiometric composition within the accuracy of 2%.

Table 1
Measured standard enthalpies of dissolution of different substances in 4 N HCl at 298 K.

Substance	Sample no.	Sample mass, mg	ΔT, K	Q, J/g	$\bar{Q}$, J/g	$\Delta_{sol}\bar{H}_i^\circ$, kJ/mol
Gd_2O_3	1	187.5	0.26401	−1370.71	−1352.7 ± 17	−491.0 ± 6.3
	2	137.0	0.18944	−1346.09		
	3	335.8	0.47012	−1362.86		
	4	339.5	0.47264	−1355.22		
	5	149.5	0.20404	−1335.31		
$GdBaCo_2O_{5.5}$	1	245.2	0.32515	−1290.85	−1288.1 ± 18	−644.6 ± 9.2
	2	223.0	0.29457	−1285.88		
	3	398.7	0.51919	−1267.65		
	4	141.0	0.18643	−1287.10		
	5	139.4	0.18745	−1309.01		
$GdBaCo_{1.8}Fe_{0.2}O_{5.5}$	1	135.4	0.16564	−1190.86	−1213.2 ± 16	−606.4 ± 8.2
	2	308.7	0.38539	−1215.29		
	3	267.0	0.33434	−1218.99		
	4	336.0	0.41946	−1215.27		
	5	244.3	0.30761	−1225.72		
$GdBaCo_{1.8}Mn_{0.2}O_{5.5}$	1	231.3	0.25199	−1060.53	−1074.6 ± 13	−536.9 ± 6.5
	2	250.2	0.27613	−1074.34		
	3	69.1	0.07736	−1089.77		
	4	158.9	0.17562	−1075.90		
	5	288.3	0.31763	−1072.50		
$BaCO_3$	1	1147.9	0.11637	−98.69	−92.4 ± 8	−18.2 ± 1.6
	2	1512.9	0.14376	−92.50		
	3	1659.1	0.14659	−86.01		
	4	1100.9	0.09727	−86.01		
	5	1288.3	0.13063	−98.71		
Co	1	55.0	0.06559	−1160.94	−1162.5 ± 1.4	−68.5 ± 0.1
	2	62.7	0.07496	−1163.84		
	3	47.9	0.05721	−1162.67		
	4	88.4	0.10550	−1161.78		
	5	70.5	0.08422	−1163.02		
Fe	1	45.0	0.08286	−1792.37	−1788.8 ± 3	−99.9 ± 0.2
	2	65.7	0.12060	−1786.84		
	3	48.9	0.08988	−1789.17		
	4	38.4	0.07056	−1788.78		
	5	55.8	0.10243	−1787.02		
Mn	1	10.5	0.05106	−4734.35	−4742.9 ± 9	−260.6 ± 0.5
	2	22.7	0.11056	−4741.25		
	3	17.9	0.08741	−4753.98		
	4	28.4	0.13844	−4745.25		
	5	10.5	0.05112	−4739.50		

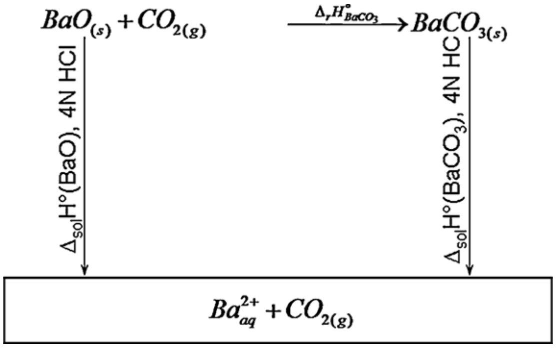

Fig. 2. Thermochemical cycle used for calculation of dissolution enthalpy of $BaCO_3$.

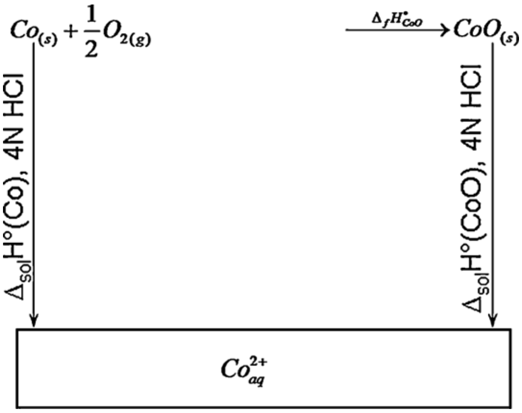

Fig. 3. Thermochemical cycle used for calculation of dissolution enthalpy of CoO.

3. Results and discussion

Standard enthalpies of formation of double perovskites $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; $x = 0$, 0.2) from constituent oxides were determined using thermochemical cycle shown in Fig. 1 according to the following equation:

$$\Delta_{ox}H^\circ_{GdBaCo_{2-x}M_xO_{5.5}} = \frac{1}{2}\Delta_{sol}H^\circ_{Gd_2O_3} + \Delta_{sol}H^\circ_{BaO} + (2-x)\Delta_{sol}H^\circ_{CoO} + \frac{x}{2}\Delta_{sol}H^\circ_{M_2O_3} + \frac{2-x}{2}\Delta_f H^\circ_{H_2O} - (2-x)\Delta_f H^\circ_{HCl,4\,N} - \Delta_{sol}H^\circ_{GdBaCo_{2-x}M_xO_{5.5}} \quad (1)$$

where $\Delta_{sol}H^\circ_{Gd_2O_3}$, $\Delta_{sol}H^\circ_{BaO}$, $\Delta_{sol}H^\circ_{CoO}$, $\Delta_{sol}H^\circ_{M_2O_3}$ and $\Delta_{sol}H^\circ_{GdBaCo_{2-x}M_xO_{5.5}}$ are standard dissolution enthalpies at 298 K of Gd_2O_3, BaO, CoO, M_2O_3 (M = Fe, Mn) and $GdBaCo_{2-x}M_xO_{5.5}$, respectively. Such calculations require rapid and complete dissolution of corresponding substances in 4 N HCl whereas Fe_2O_3 and Mn_2O_3 slowly react with HCl solution at 298 K. On the contrary BaO quickly reacts with HCl but it is too hygroscopic and sensitive to the presence of CO_2 in the atmosphere. Therefore only enthalpies of dissolution ($\Delta_{sol}H_i^\circ$) of Gd_2O_3, $BaCO_3$ and $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; $x = 0$, 0.2) were measured directly whereas that of BaO, CoO, Fe_2O_3 and Mn_2O_3 were calculated according to Eqs. (2)–(5) from measured $\Delta_{sol}H_i^\circ$ of $BaCO_3$, Co, Fe and Mn, respectively. Corresponding experimental values of $\Delta_{sol}H_i^\circ$ are given in Table 1. Thermochemical cycles used to calculate $\Delta_{sol}H^\circ_{BaO}$, $\Delta_{sol}H^\circ_{CoO}$, $\Delta_{sol}H^\circ_{Fe_2O_3}$ and $\Delta_{sol}H^\circ_{Mn_2O_3}$ are shown in Figs. 2–5.

$$\Delta_{sol}H^\circ_{BaO} = \Delta_{sol}H^\circ_{BaCO_3} + \Delta_r H^\circ_{BaCO_3} \quad (2)$$

$$\Delta_{sol}H^\circ_{CoO} = \Delta_{sol}H^\circ_{Co} + \Delta_f H^\circ_{H_2O(liq)} - \Delta_f H^\circ_{CoO} \quad (3)$$

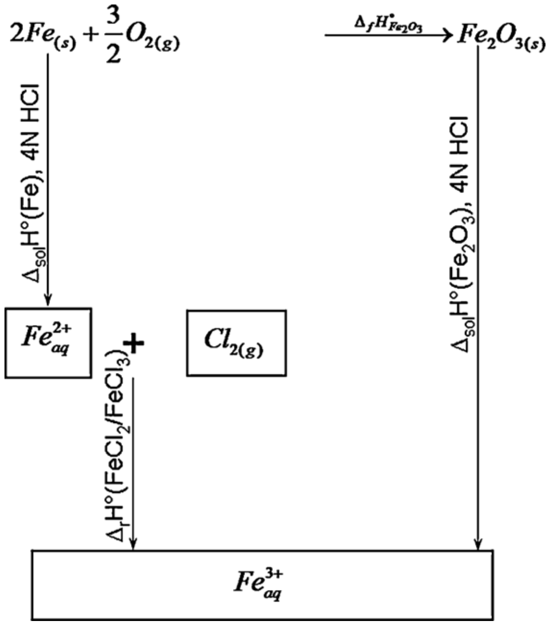

Fig. 4. Thermochemical cycle used for calculation of dissolution enthalpy of Fe_2O_3.

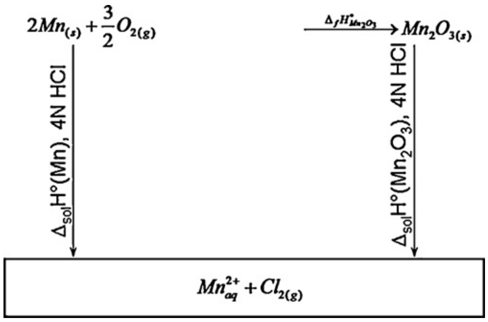

Fig. 5. Thermochemical cycle used for calculation of dissolution enthalpy of Mn_2O_3.

$$\Delta_{sol}H^\circ_{Fe_2O_3} = 2\Delta_{sol}H^\circ_{Fe} + 3\Delta_f H^\circ_{H_2O(liq)} - \Delta_f H^\circ_{Fe_2O_3} + 2\Delta_r H^\circ_{FeCl_2/FeCl_3} - 2\Delta_f H^\circ_{HCl,4\,N} \quad (4)$$

$$\Delta_{sol}H^\circ_{Mn_2O_3} = 2\Delta_{sol}H^\circ_{Mn} + 3\Delta_f H^\circ_{H_2O(liq)} - 2\Delta_f H^\circ_{HCl,4\,N} - \Delta_f H^\circ_{Mn_2O_3} \quad (5)$$

Values of $\Delta_{sol}H_i^\circ$ given in Table 1 are related to the following chemical reactions:

$$Gd_2O_{3(s)} + 6HCl_{(aq)} = 2GdCl_{3(aq)} + 3H_2O_{(liq)} \quad (6)$$

$$BaCO_{3(s)} + 2HCl_{(aq)} = BaCl_{2(aq)} + H_2O_{(liq)} + CO_{2(g)} \quad (7)$$

$$Co_{(s)}(Mn, Fe) + 2HCl_{(aq)} = Co(Mn, Fe)Cl_{2(aq)} + H_{2(g)} \quad (8)$$

$$GdBaCo_{2-x}Mn_xO_{5.5(s)} + 11HCl_{(aq)} = GdCl_{3(aq)} + BaCl_{2(aq)} + (2-x)CoCl_{2(aq)} + xMnCl_{2(aq)} + 5.5H_2O_{(liq)} + Cl_{2(q)} \quad (9)$$

$$GdBaCo_{1.8}Fe_{0.2}O_{5.5(s)} + 11HCl_{(aq)} = GdCl_{3(aq)} + BaCl_{2(aq)} + 1.8CoCl_{2(aq)} + 0.2FeCl_{3(aq)} + 5.5H_2O_{(liq)} + 0.9Cl_{2(g)} \quad (10)$$

One can see that formal oxidation state of a 3d-metal in double perovskites $GdBaCo_{2-x}M_xO_{5.5}$ studied is equal to +3 whereas that stable in aqueous solution is +2 for M = Co, Mn and +3 for Fe. Hence Red-Ox reaction must proceed during dissolution of

Table 2
Calculated standard enthalpies of dissolution of different substances in 4 N HCl at 298 K.

Substance	$\Delta_{sol}H_i^\circ$(calc), kJ/mol
BaO	−289.7 ± 1.3
CoO	−116.4 ± 1.0
Fe_2O_3	−161.9 ± 2.0
Mn_2O_3	−95.2 ± 1.0

Table 3
Standard enthalpies of formation of different substances from elements at 298 K [16].

Substance	$\Delta_f H_i^\circ$, kJ/mol
Gd_2O_3	−1819.6 ± 0.1
BaO	−548.0 ± 0.1
CoO	−237.9 ± 0.1
Fe_2O_3	−824.2 ± 0.1
Mn_2O_3	−959 ± 1
$BaCO_3$	−1213.0 ± 0.1
H_2O	−285.8 ± 0.1
HCl 4 N	−162.17 ± 0.01
CO_2	−393.5 ± 0.1
$Fe^{2+}{}_{aq}$	−89.1 ± 0.1
$Fe^{3+}{}_{aq}$	−48.5 ± 0.1
$Cl^-{}_{aq}$	−167.2 ± 0.1

Table 4
Standard enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) from constituent oxides at 298 K.

Substance	$\Delta_{ox}H_i^\circ$, kJ/mol
$GdBaCo_2O_{5.5}$	−84.9 ± 10
$GdBaCo_{1.8}Fe_{0.2}O_{5.5}$	−119.8 ± 10
$GdBaCo_{1.8}Mn_{0.2}O_{5.5}$	−182.7 ± 12

Table 5
Standard enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) from elements at 298 K.

Substance	$\Delta_f H_i^\circ$, kJ/mol
$GdBaCo_2O_{5.5}$	−2018.5 ± 10
$GdBaCo_{1.8}Fe_{0.2}O_{5.5}$	−2088.3 ± 10
$GdBaCo_{1.8}Mn_{0.2}O_{5.5}$	−2164.6 ± 12

$GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) in 4 N HCl. It follows from the comparison of standard electrode potentials for possible Red-Ox processes that chloride anion is the most oxidizable agent. As a result gaseous chlorine is formed during dissolution of double perovskites in 4 N HCl according to Eqs. (9) and (10).

Calculated enthalpies of dissolution for BaO, CoO, Fe_2O_3 and Mn_2O_3 are presented in Table 2. Table 3 contains additional thermodynamic data [16] used for calculations.

Standard enthalpies of formation of double perovskites $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) from constituent oxides at 298 K calculated accordingly are summarized in Table 4. $\Delta_f H_i^\circ$ of corresponding double perovskites at 298 K were calculated from the values of their $\Delta_{ox}H_i^\circ$ according to Eq. (11) and summarized in Table 5.

$$\Delta_f H^\circ_{GdBaCo_{2-x}M_xO_{5.5}} = \Delta_{ox}H^\circ_{GdBaCo_{2-x}M_xO_{5.5}} + \frac{1}{2}\Delta_f H^\circ_{Gd_2O_3} + \Delta_f H^\circ_{BaO} + (2-x)\Delta_f H^\circ_{CoO} + \frac{x}{2}\Delta_f H^\circ_{M_2O_3} \qquad (11)$$

As seen both $\Delta_{ox}H_i^\circ$ and $\Delta_f H_i^\circ$ decrease in the sequence of $GdBaCo_2O_{5.5}$, $GdBaCo_{1.8}Fe_{0.2}O_{5.5}$ and $GdBaCo_{1.8}Mn_{0.2}O_{5.5}$ indicating growth of relative thermodynamic stability of $GdBaCo_2O_{5.5}$ upon substitution of Fe or Mn for Co as well as increase of 3d-metal–oxygen average bond energy.

4. Conclusion

Dissolution enthalpies of double perovskites $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) in 4 N HCl were measured using isothermal solution calorimetry. Standard enthalpies of formation of $GdBaCo_{2-x}M_xO_{5.5}$ (M = Fe, Mn; x = 0, 0.2) from constituent oxides ($\Delta_{ox}H_i^\circ$) and elements ($\Delta_f H_i^\circ$) at 298 K were calculated on the basis of experimental data obtained. Both $\Delta_{ox}H_i^\circ$ and $\Delta_f H_i^\circ$ were found to decrease in the sequence of $GdBaCo_2O_{5.5}$, $GdBaCo_{1.8}Fe_{0.2}O_{5.5}$ and $GdBaCo_{1.8}Mn_{0.2}O_{5.5}$ indicating growth of relative thermodynamic stability of $GdBaCo_2O_{5.5}$ upon substitution of Fe or Mn for Co most likely due to increase of 3d-metal–oxygen binding energy.

Acknowledgements

This work was financially supported by the Ministry of Education and Science of the Russian Federation within the framework of Federal Program "The scientific and scientific-education personnel of Innovative Russia" for 2009–2013.

References

[1] A. Maignan, C. Martin, D. Pelloquin, N. Nguyen, B. Raveau, Structural and magnetic studies of ordered oxygen-deficient perovskites $LnBaCo_2O_{5+\delta}$, closely related to the "112", J. Solid State Chem. 142 (1999) 247–260.
[2] A.A. Taskin, A.N. Lavrov, Y. Ando, Transport and magnetic properties of $GdBaCo_2O_{5+x}$ single crystals: a cobalt oxide with square-lattice CoO_2 planes over a wide range of electron and hole doping, Phys. Rev. B 71 (2005), 134414-1–134414-28.
[3] A.A. Taskin, A.N. Lavrov, Y. Ando, Achieving fast oxygen diffusion in perovskites by cation ordering, Appl. Phys. Lett. 86 (2005), 091910-1–091910-3.
[4] J.C. Burley, J.F. Mitchell, S. Short, D. Miller, Y. Tang, Structural and magnetic chemistry of $NdBaCo_2O_{5+\delta}$, J. Solid State Chem. 170 (2003) 339–350.
[5] L. Malavasi, Y. Diaz-Fernandez, M. Cristina Mozzati, C. Ritter, Structure and magnetism of $HoBaCo_2O_{5+\delta}$ layered cobaltites with $0.02 \le \delta \le 0.22$, Solid State Commun. 148 (2008) 87–90.
[6] A. Tarancón, D. Marrero-López, J. Peña-Martínez, J.C. Ruiz-Morales, P. Núñez, Effect of phase transition on high-temperature electrical properties of $GdBaCo_2O_{5+x}$ layered perovskite, Solid State Ionics 179 (2008) 611–618.
[7] C. Martin, A. Maignan, D. Pelloquin, N. Nguyen, B. Raveau, Magnetoresistance in the oxygen deficient $LnBaCo_2O_{5.4}$ (Ln = Eu, Gd) phases, Appl. Phys. Lett. 71 (1997) 1421–1423.
[8] J.-H. Kim, A. Manthiram, $LnBaCo_2O_{5+\delta}$ oxides as cathodes for intermediate-temperature solid oxide fuel cells, J. Electrochem. Soc. 155 (2008) B385–B390.
[9] K. Zhang, L. Ge, R. Ran, Z. Shao, S. Liu, Synthesis, characterization and evaluation of cation-ordered $LnBaCo_2O_{5+\delta}$ as materials of oxygen permeation membranes and cathodes of SOFCs, Acta Mater. 56 (2008) 4876–4889.
[10] J.-H. Kim, F. Prado, A. Manthirama, Characterization of $GdBa_{1-x}Sr_xCo_2O_{5+\delta}$ ($0 \le x \le 1.0$) double perovskites as cathodes for solid oxide fuel cells, J. Electrochem. Soc. 155 (2008) B1023–B1028.
[11] J. Cheng, A. Navrotsky, Energetics of magnesium, strontium, and barium doped lanthanum gallate perovskites, J. Solid State Chem. 177 (2004) 126–133.
[12] D.S. Tsvetkov, V.V. Sereda, A.Yu. Zuev, Oxygen nonstoichiometry and defect structure of the double perovskite $GdBaCo_2O_{6-\delta}$, Solid State Ionics 180 (2010) 1620–1625.
[13] N.I. Matskevich, T.L. Popova, E.S. Zolotova, M.A. Starikov, The thermodynamics of some reactions in the Gd–Ba–Cu–O system, Thermochim. Acta 254 (1995) 41–45.
[14] M.V. Kilday, Enthalpy of solution of SRM 1655 (KCl) in H_2O, J. Res. Nat. Bur. Stand. 85 (1980) 467–481.
[15] I. Wadso, R.N. Goldberg, Standards in isothermal microcalorimetry, Pure Appl. Chem. 73 (2001) 1625–1639.
[16] M.W. Chase Jr., NIST-JANAF thermochemical tables, fourth edition, J. Phys. Chem. Ref. Data Monograph 9 (1998) 1–1951.