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Thermochimica Acta 342 (1999) 41–46
thermochimica
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The 1 : 2 : 3 phases in the Y(Ho, Gd, Nd)–Ba–Cu–O: calorimetric investigations, correlations between thermodynamic and structural properties

N.I. Matskevich[a,*], R.W. McCallum[b]

[a]*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Science, Novosibirsk 630090, Russia*
[b]*Ames Laboratory, Iowa State University, Ames, IA 50011, USA*

Received 7 April 1999; received in revised form 17 August 1999; accepted 23 August 1999

Abstract

On the basis of dissolution enthalpies of Y_2O_3, Gd_2O_3, Nd_2O_3, Ho_2O_3, CuO, $BaCO_3$, $YBa_2Cu_3O_{6.9}$, $HoBa_2Cu_3O_{6.9}$, $GdBa_2Cu_3O_{6.9}$, $NdBa_2Cu_3O_{6.98}$ measured by solution calorimetry in 6 N HCl at 323.15 K the following values were determined. (1) enthalpies of formation of Re1 2 3 phases from binary oxides: $\Delta_{ox}H^0(\mathrm{Y123},\ 323.15\,\mathrm{K}) = -127.5 \pm 4.6\,\mathrm{kJ\,mol^{-1}}$; $\Delta_{ox}H^0(\mathrm{Ho123},\ 323.15\,\mathrm{K}) = -131.4 \pm 8.6\,\mathrm{kJ\,mol^{-1}}$; $\Delta_{ox}H^0(\mathrm{Gd123},\ 323.15\,\mathrm{K}) = -180.0 \pm 7.3\,\mathrm{kJ\,mol^{-1}}$; $\Delta_{ox}H^0(\mathrm{Nd123},\ 323.15\,\mathrm{K}) = -165.0 \pm 8.8\,\mathrm{kJ\,mol^{-1}}$; (2) enthalpies of formation of Re1 2 3 phases from mixtures of Re_2O_3, $BaCO_3$, CuO; (3)enthalpies of formation of Re1 2 3 phases from mixtures of Re_2O_3, $BaCuO_2$, CuO; (4) standard formation enthalpies of Re1 2 3 phases$\Delta_fH^0(\mathrm{Y123},\ 323.15\mathrm{K}) = -2643.5 \pm 9.6\,\mathrm{kJ\,mol^{-1}}$; $\Delta_fH^0(\mathrm{Ho123},\ 323.15\,\mathrm{K}) = -2635.3 \pm 12.2\,\mathrm{kJ\,mol^{-1}}$; $\Delta_fH^0(\mathrm{Gd123},\ 323.15\,\mathrm{K}) = -2663.4 \pm 11.0\,\mathrm{kJ\,mol^{-1}}$; $\Delta_fH^0(\mathrm{Y123},\ 323.15\,\mathrm{K}) = -2632.6 \pm 12.0\,\mathrm{kJ\,mol^{-1}}$.

The correlations between thermodynamic data and structural parameters of Re1 2 3 phases were established. It had been noted that the stability increase was correlated with the relative difference decrease of lattice parameters of Re_2O_3 and BaO layers from 4.65% for BaO–Ho_2O_3 to 4.37% for BaO–Y_2O_3, 3.86% for BaO–Nd_2O_3, 2.42% for BaO–Gd_2O_3.

Keywords: Calorimetry; Re–Ba–Cu–O system; Stability; Thermodynamics

1. Introduction

The discovery of superconductors with high T_c such as $YBa_2Cu_3O_x$, $HoBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, $NdBa_2Cu_3O_x$ in Y_2O_3(Ho_2O_3, Gd_2O_3, Nd_2O_3)–BaO–Cu–O systems leads to the necessity of the thorough physicochemical investigation of these compounds. At present the most perspective compounds for the application are 1 : 2 : 3 phases. For example, one of the most technologically promising superconducting compounds is $Nd_{1+y}Ba_{2-y}Cu_3O_x$ solid solution with T_c up to 95 K with potentially good flux pinning when processed under preparation conditions. A good understanding of thermodynamic stability of high T_c oxide superconductors is essential to optimize synthesis as well. It is necessary to have thermodynamic data of compounds to study the thermodynamic stability.

In this study we determined solution enthalpies for $YBa_2Cu_3O_x$, $HoBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, $NdBa_2$-

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[*] Corresponding author. Tel.:+7-3832-341449; fax: +7-3832-344489
E-mail address: nata@casper.che.nsk.su (N.I. Matskevich)

0040-6031/99/$ – see front matter
PII: S0040-6031(99)00314-7

Cu_3O_x, $BaCuO_2$, $BaCO_3$, as well as for binary oxides Y_2O_3, Ho_2O_3, Gd_2O_3, Nd_2O_3, CuO. We then used data to discuss the phase stability and to relate thermodynamic characteristics with crystal structure.

2. Sample preparation

The following samples were employed in thermochemical measurements: Y_2O_3, Ho_2O_3, Gd_2O_3, Nd_2O_3, CuO, $BaCO_3$, $BaCuO_2$, $YBa_2Cu_3O_x$, $HoBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, $NdBa_2Cu_3O_x$.

Samples of Y_2O_3, Ho_2O_3, Gd_2O_3 (high purity) used for calorimetric measurements and for preparation of 1 : 2 : 3 phases in the Y(Gd,Ho)–Ba–Cu–O systems were held in air at 1023 K for 10 h before using as it was described in papers [1–3]. Nd_2O_3 used to make the $NdBa_2Cu_3O_{6.9}$ phase was manufactured by Ames Lab. It was dried in air at 1173 K for 24 h and placed warm in drybox, where it cooled to room temperature in an atmosphere of N_2.

CuO (high purity) used for the preparation of $BaCuO_2$, $ReBa_2Cu_3O_x$ (where Re is a rare-earth element such as Y, Ho, Gd) was heated in O_2 for 15 h ($T = 900$ K). CuO used to make $NdBa_2Cu_3O_x$ was manufactured by Johnson Mathey. It was dried in air at 823 K for 24 h and placed warm in drybox, where it cooled to room temperature in an atmosphere of N_2.

$BaCO_3$ (high purity) used to prepare the $ReBa_2Cu_3O_x$ phases (Re = Y, Ho, Gd) was held in air at 650 K for 4 h. $BaCO_3$ used to make the $NdBa_2Cu_3O_x$ sample was manufactured by Johnson Mathey. It was dried in air at 973 K for 24 h and placed warm in drybox, where it cooled to room temperature in an atmosphere of N_2.

Samples of $YBa_2Cu_3O_x$, $HoBa_2Cu_3O_x$, $GdBa_2Cu_3O_x$, $NdBa_2Cu_3O_x$ were prepared by solid state reactions from Re_2O_3 (Re = Y, Ho, Gd, Nd), $BaCO_3$, and CuO powder at appropriate stoichiometry. Samples of 1 : 2 : 3 phases in the Y(Ho, Gd)–Ba–Cu–O systems were prepared at the Institute of Inorganic Chemistry, SB RAS (Russia). The Nd 1 2 3 phase was prepared in Ames Lab. (USA). The preparation of the 1 : 2 : 3 samples in the Y(Ho, Gd)–Ba–Cu–O systems were described in papers [1–3]. $NdBa_2Cu_3O_x$ was calcined three times in air at 1153 K for about 48–72 h each time. It was then annealed in 100% oxygen using the following profile: held at 1223 K for 1 h, ramped slowly to 1323 K and held there for 48 h, cooled to 723 K and held there for 48 h, and then furnace cooled. This sample was then annealed a second time in 1% oxygen at 1253 K for 24 h followed by a 100% oxygen soak for 48 h and then furnace cooled.

The samples were characterised by X-ray powder diffraction and chemical analysis. The content of all the metallic components was determined by atomic absorption spectroscopy [3]. The oxygen content was analysed by iodometric titration [3]. According to the analysis results the compounds employed were found to be single phases. The chemical analysis allows one to write the following formulas for the samples: $BaCu_{0.98\pm0.04}O_{2.01\pm0.03}$, $YBa_{2.01\pm0.03}Cu_{2.98\pm0.05}O_{6.91\pm0.02}$, $GdBa_{1.98\pm0.03}Cu_{2.98\pm0.05}O_{6.92\pm0.03}$, $HoBa_{1.97\pm0.04}Cu_{3.04\pm0.05}O_{6.89\pm0.04}$, $NdBa_{2.00\pm0.03}Cu_{2.96\pm0.05}O_{6.87\pm0.03}$. The content of impurities were determined by spectral methods [3]. The analyses performed indicated that impurities of Dy, Eu, Yb, La, Lu, Tm, Er, Pr, Sm, Ce, Te, Ca, Mg, Mn, Pb, Ag metals were present at the level 10^{-3}–10^{-4} at.%.

3. Experimental

The calorimetric measurements were performed in a solution calorimeter with isothermal shields which was described in detail elsewhere [1–3]. The procedure of experiments was described elsewhere as well [1–3]. The calorimetric cycles were designed in such a way that it was possible to determine the formation enthalpies of 1 : 2 : 3 phases in the Y(Ho, Gd, Nd)–Ba–Cu–O systems from mixtures of initial products for synthesis, namely, from $0.5Re_2O_3 + 2BaCO_3 + 3CuO$ mixtures. The scheme of the process is given below:

$$0.5Re_2O_3(s) + \text{solution 1} = \text{solution 2} + 0.5\Delta_{sol}H_1^0 \quad (1)$$

$$3CuO(s) + \text{solution 2} = \text{solution 3} + 3\Delta_{sol}H_2^0 \quad (2)$$

$$2BaCO_3(s) + \text{solution 3} = \text{solution 4} + 2CO_2 + 2\Delta_{sol}H_3^0 \quad (3)$$

$$ReBa_2Cu_3O_{6.9} + \text{solution 1} = \text{solution 4}' + 0.2O_2 + \Delta_{sol}H_4^0 \quad (4)$$

Here,

$$\begin{aligned}
\text{solution 1} &= \text{6N HCl}\\
\text{solution 2} &= \text{solution 1} + \mathrm{ReCl}_{3(\mathrm{sol})} - 3\mathrm{HCl}_{(\mathrm{sol})} + 1.5\mathrm{H_2O}_{(\mathrm{sol})}\\
\text{solution 3} &= \text{solution 1} + \mathrm{ReCl}_{3(\mathrm{sol})} + 2\mathrm{BaCl}_{2(\mathrm{sol})} - 7\mathrm{HCl}_{(\mathrm{sol})} + 3.5\mathrm{H_2O}_{(\mathrm{sol})}\\
\text{solution 4} &= \text{solution 1} + \mathrm{ReCl}_{3(\mathrm{sol})} + 2\mathrm{BaCl}_{2(\mathrm{sol})} + 3\mathrm{CuCl}_{2(\mathrm{sol})} - 13\mathrm{HCl}_{(\mathrm{sol})} + 6.5\mathrm{H_2O}_{(\mathrm{sol})}
\end{aligned}$$

If solution 4, obtained after the dissolution of $0.5\mathrm{Re_2O_3} + 2\mathrm{BaCO_3} + 3\mathrm{CuO}$ mixtures, and solution 4′, obtained after the dissolution of $\mathrm{ReBa_2Cu_3O_{6.9}}$ phases are assumed to be identical, the following equation can be written:

$$0.5\mathrm{Re_2O_3(s)} + 3\mathrm{CuO(s)} + 2\mathrm{BaCO_3(s)} + 0.2\mathrm{O_2(g)} = \mathrm{LnBa_2Cu_3O_{6.9}(s)} + \Delta_\mathrm{r}H_5^0 \quad (5)$$

Here,

$$\Delta_\mathrm{r}H_5^0 = 0.5\Delta_\mathrm{sol}H_1^0 + 3\Delta_\mathrm{sol}H_2^0 + 2\Delta_\mathrm{sol}H_3^0 - \Delta_\mathrm{sol}H_4^0.$$

The identical state of solution 4 and solution 4′ was proved by measuring electronic spectra of these solutions in the range of 10^4 to $3 \times 10^4\ \mathrm{cm^{-1}}$. It was shown that in experiments conducted in air, the spectra of the solutions became identical in 10 min after dissolution was finished.

The mass of $\mathrm{ReBa_2Cu_3O_{6.9}}$ samples employed in calorimetric measurements was about 0.15 g. The volume of calorimeter vessel was 200 ml. According to these data the ratio of employed samples ($\mathrm{ReBa_2Cu_3O_{6.9}}$) to HCl and $\mathrm{H_2O}$ was the following: 1 mol of $\mathrm{ReBa_2Cu_3O_{6.9}}$: 4 425 mol of HCl : 43 274 mol of $\mathrm{H_2O}$.

All the experiments were performed at 323.15 K. At lower temperature the rate of $\mathrm{Y_2O_3}$ dissolution is small, which results in a low precision of the measurements.

4. Results and discussion

The values for dissolution enthalpies of $\mathrm{Re_2O_3}$ (Re = Y, Gd, Ho, Nd), CuO, $\mathrm{BaCO_3}$ and 1 : 2 : 3 phases obtained in our calorimetric experiments were used to calculate enthalpies of some reactions with superconducting phases.

Experimental values used for the calculation of above reactions are presented below:

$$\begin{aligned}
&\Delta_\mathrm{sol}H^0(\mathrm{Ho_2O_3},\ 323.15\ \mathrm{K}) = -364.07 \pm 4.28\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{Y_2O_3},\ 323.15\ \mathrm{K}) = -382.71 \pm 1.84\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{Gd_2O_3},\ 323.15\ \mathrm{K}) = -411.41 \pm 3.24\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{Nd_2O_3},\ 323.15\ \mathrm{K}) = -430.21 \pm 4.74\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{CuO},\ 323.15\ \mathrm{K}) = -51.13 \pm 2.13\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{BaCO_3},\ 323.15\ \mathrm{K}) = -15.27 \pm 2.57\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{HoBa_2Cu_3O_{6.9}},\ 323.15\ \mathrm{K}) = -779.34 \pm 6.19\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{GdBa_2Cu_3O_{6.9}},\ 323.15\ \mathrm{K}) = -754.46 \pm 5.09\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{YBa_2Cu_3O_{6.9}},\ 323.15\ \mathrm{K}) = -792.59 \pm 3.89\ \mathrm{kJ\ mol^{-1}},\\
&\Delta_\mathrm{sol}H^0(\mathrm{NdBa_2Cu_3O_{6.9}},\ 323.15\ \mathrm{K}) = -778.86 \pm 6.33\ \mathrm{kJ\ mol^{-1}}.
\end{aligned}$$

All the dissolution enthalpies used for the calculation of reaction enthalpies (5) were calculated as average values of six experiments. The errors were calculated for the 95% confidence interval using the Students coefficient.

The first reaction which we consider in the paper is the interaction between $\mathrm{Re_2O_3}$, CuO, $\mathrm{BaCO_3}$ with the formation of Re1 2 3 phases. The reaction can be written as follows:

$$0.5\mathrm{Re_2O_3} + 3\mathrm{CuO} + 2\mathrm{BaCO_3} + 0.2\mathrm{O_2} = \mathrm{ReBa_2Cu_3O_{6.9}} + \Delta_\mathrm{r}H_6^0 \quad (6)$$

The following values for reactions (6) with Re = Y, Ho, Gd, Nd were determined on the basis of measured calorimetric data in the paper:

$$0.5Y_2O_3 + 2BaCO_3 + 3CuO + 0.2O_2 = YBa_2Cu_3O_{6.9} + 2CO_2 + \Delta_r H_7^0 \qquad (7)$$

$$\Delta_r H_7^0(323.15\,\mathrm{K}) = +417.3 \pm 4.6\,\mathrm{kJ\,mol^{-1}},$$

$$0.5Ho_2O_3 + 2BaCO_3 + 3CuO + 0.2O_2 = HoBa_2Cu_3O_{6.9} + 2CO_2 + \Delta_r H_8^0 \qquad (8)$$

$$\Delta_r H_8^0(323.15\,\mathrm{K}) = +413.4 \pm 8.6\,\mathrm{kJ\,mol^{-1}},$$

$$Gd_2O_3 + 2BaCO_3 + 3CuO + 0.2O_2 = GdBa_2Cu_3O_{6.9} + 2CO_2 + \Delta_r H_9^0 \qquad (9)$$

$$\Delta_r H_9^0(323.15\,\mathrm{K}) = +364.8 \pm 7.3\,\mathrm{kJ\,mol^{-1}},$$

$$Nd_2O_3 + 2BaCO_3 + 3CuO + 0.2O_2 = NdBa_2Cu_3O_{6.98} + 2CO_2 + \Delta_r H_{10}^0 \qquad (10)$$

$$\Delta_r H_{10}^0(323.15\,\mathrm{K}) = +379.8 \pm 8.8\,\mathrm{kJ\,mol^{-1}}.$$

Literature data for the reaction heat $BaO + CO_2 = BaCO_3$ [4] were used to calculate the formation enthalpies of the $ReBa_2Cu_3O_{6.9}$ phases from binary oxides on the basis of enthalpies of reactions (7)–(10). The formation enthalpies of the 1 : 2 : 3 phases from binary oxides ($\Delta_{ox}H^0$) are presented below:

$$\Delta_{ox}H^0(YBa_2Cu_3O_{6.9},\ 323.15\,\mathrm{K}) = -127.5 \pm 4.6\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_{ox}H^0(HoBa_2Cu_3O_{6.9},\ 323.15\,\mathrm{K}) = -131.4 \pm 8.6\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_{ox}H^0(GdBa_2Cu_3O_{6.9},\ 323.15\,\mathrm{K}) = -180.0 \pm 7.3\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_{ox}H^0(NdBa_2Cu_3O_{6.9},\ 323.15\,\mathrm{K}) = -165.0 \pm 8.8\,\mathrm{kJ\,mol^{-1}}.$$

The first problem which we are going to discuss in the paper is an attempt to establish the correlations between thermodynamic values and structural parameters. We assume that the crystal network of $ReBa_2Cu_3O_x$ is an epitaxial structure built from Re_2O_3, BaO, CuO layers. It is possible to suppose, as done by Goodenough and Manthram [5], that if lattice parameters of two layers match, the structure is very favourable and stable. The structural–geometric aspects of epitaxial structures were considered in paper [6] as well. In paper [6] one of the criterion to estimate the crystal–structural compatibility of epitaxial layers is relative difference of lattice parameters of layers: $\delta = (a_1 - a_2)/\ a_1$, where a_1, a_2 are the lattice parameters of binary oxides.

For 1 : 2 : 3 phases we used the relative difference of Re_2O_3–BaO layers as a criterion to estimate the crystal-structural compatibility. The relative difference of lattice parameters is 2.42% for BaO–Gd_2O_3 layers, 3.86% for BaO–Nd_2O_3 layers, 4.65% for BaO–Ho_2O_3 layers, 4.37% for BaO–Y_2O_3 layers. It is worth noting that the increase in the formation enthalpy from simple oxides in absolute value correlates with the decrease in the relative difference of lattice parameters.

To get extrapolated data of $\Delta_{ox}H^0$ for other 1 : 2 : 3 phases in the Re–Ba–Cu–O systems we have constructed the dependence of $\Delta_{ox}H^0$ from δ as following: $\Delta_{ox}H^0 = -216.37 + 17.097\delta$. Here, $\Delta_{ox}H^0$ is the enthalpy of Re1 2 3 formation from binary oxides, δ the relative difference of lattice parameters. In Table 1 the experimental values of $\Delta_{ox}H^0$(Re1 2 3, 323.15 K) and calculated values from the above dependence are presented. It is possible to see that the obtained dependence describes the experimental data practically well.

Our data of reaction enthalpies (7)–(10) and literature data from [4,7] (Table 2) provide a possibility to calculate standard formation enthalpies for $YBa_2Cu_3O_{6.9}$, $HoBa_2Cu_3O_{6.9}$, $GdBa_2Cu_3O_{6.9}$, $NdBa_2Cu_3O_{6.9}$ as the following:

$$\Delta_f H^0(\mathrm{Y123},\ 323.15\,\mathrm{K}) = -2643.5 \pm 9.6\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_f H^0(\mathrm{Ho123},\ 323.15\,\mathrm{K}) = -2635.3 \pm 12.2\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_f H^0(\mathrm{Gd123},\ 323.15\,\mathrm{K}) = -2663.4 \pm 11.0\,\mathrm{kJ\,mol^{-1}},$$

$$\Delta_f H^0(\mathrm{Nd123},\ 323.15\,\mathrm{K}) = -2632.6 \pm 12.0\,\mathrm{kJ\,mol^{-1}}.$$

The last problem which we are going to discuss in the paper is stability of 1 : 2 : 3 phases in respect to mixtures with $BaCuO_2$. On the basis of values of reactions (7)–(10), data of $BaCuO_2 + CO_2 = BaCO_3$ taken from [3] and literature data of entropies and heat

Table 1
Experimental and calculated values of $\Delta_{ox}H^0$ for $ReBa_2Cu_3O_{6.9}$ phases

Compounds	δ^a (%)	$\Delta_{ox}H^0_{exp}(323.15\,K)$ $(kJ\,mol^{-1})$	$\Delta_{ox}H^0_{calc}(323.15\,K)$ $(kJ\,mol^{-1})$	$\Delta_{ox}H^0_{exp}-\Delta_{ox}H^0_{calc}(kJ\,mol^{-1})$
$HoBa_2Cu_3O_{6.9}$	4.65	−131.400	−136.870	5.470
$YBa_2Cu_3O_{6.9}$	4.37	−127.500	−141.657	14.157
$GdBa_2Cu_3O_{6.9}$	3.86	−165.000	−150.377	−14.623
$NdBa_2Cu_3O_{6.9}$	2.42	−180.000	−174.997	−5.003

[a] Relative difference of lattice parameters for Re_2O_3–BaO layers.

Table 2
Literature data used for calculation of formation enthalpies of $ReBa_2Cu_3O_{6.9}$ phases

Compounds	Δ_fH^0 (323.15 K) $(kJ\,mol^{-1})$
$BaCO_3$(s)	−1213.8 ± 5.0 [4]
CO_2(g)	−393.17 ± 0.05 [7]
CuO(s)	−155.7 ± 2.1 [7]
Y_2O_3(s)	−1904.8 ± 4.0 [4]
Ho_2O_3(s)	−1880.7 ± 5.0 [4]
Gd_2O_3(s)	−1839.7 ± 3.3 [4]
Nd_2O_3(s)	−1808.0 ± 2.5 [4]

capacities of compounds employed in reactions (11)–(14) [4,7–9] it is possible to get the following data for the interaction of 1 : 2 : 3 phases from mixtures of $0.5Re_2O_3 + CuO + 2BaCuO_2$:

$$0.5Y_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = YBa_2Cu_3O_{6.9}$$

$$\Delta_rH^0(298.15\,K) = +15.4 \pm 5.3\,kJ\,mol^{-1},$$

$$\Delta_rG^0(298.15\,K) = 29.3 \pm 5.4\,kJ\,mol^{-1},$$

$$0.5Ho_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = HoBa_2Cu_3O_{6.9}$$

$$\Delta_rH^0(298.15\,K) = +11.4 \pm 9.0\,kJ\,mol^{-1},$$

$$\Delta_rG^0(298.15) = 27.8 \pm 9.1\,kJ\,mol^{-1},$$

$$0.5Gd_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = GdBa_2Cu_3O_{6.9}$$

$$\Delta_rH^0(298.15\,K) = -37.2 \pm 7.8\,kJ\,mol^{-1},$$

$$\Delta_rG^0(298.15\,K) = -22.4 \pm 7.8\,kJ\,mol^{-1},$$

$$0.5Nd_2O_3 + CuO + 2BaCuO_2 + 0.24O_2 = NdBa_2Cu_3O_{6.98}$$

$$\Delta_rH^0(298.15\,K) = -22.3 \pm 9.2\,kJ\,mol^{-1},$$

$$\Delta_rG^0(298.15\,K) = -2.8 \pm 9.3\,kJ\,mol^{-1}.$$

The above data allow us to conclude that Y1 2 3 (Ho1 2 3) phase is thermodynamically less favourable than mixtures of barium cuprate, yttrium oxide (holmium oxide) and copper oxide at room and lower temperatures. The 1 : 2 : 3 superconducting phase in the Gd(Nd)–Ba–Cu–O system is thermodynamically more favourable than the 0.5 $Gd_2O_3(Nd_2O_3) + CuO + 2\ BaCuO_2$ mixture. The increase of the stability correlates with the decrease of the relative difference of lattice parameters of Re_2O_3 and BaO layers.

5. Conclusion

Solution calorimetry was used to measure dissolution enthalpies of Re_2O_3, CuO, $BaCO_3$, $ReBa_2Cu_3O_x$ (Re = Y, Ho, Gd, Nd), $BaCuO_2$ phases. Enthalpies of the following reactions with Re1 2 3 phases were calculated basing on the above data:

1. formation enthalpies of Re1 2 3 phases from simple oxides;
2. formation enthalpies of Re1 2 3 phases from elements;
3. formation enthalpies of Re1 2 3 phases from the mixture of $0.5Re_2O_3 + CuO + 2BaCuO_2$.

It was established that the formation of Re1 2 3 phases from simple oxides was thermodynamically preferable. Data obtained show the thermodynamical instability of Y1 2 3, Ho1 2 3 phases in respect to the mixture of $0.5Y_2O_3$ $(Ho_2O_3) + CuO + 2BaCuO_2$ but the thermodynamical stability of Gd1 2 3, Nd1 2 3 phases in respect to the mixture of $0.5Gd_2O_3$ $(Nd_2O_3) + CuO + 2BaCuO_2$.

The increase of formation enthalpies of 1 2 3 phases from simple oxides in the absolute value and the stability increase of 1 2 3 phases in respect to the mixture of 0.5 $Re_2O_3 + CuO + BaCuO_2$ correlates with the decrease of the relative difference of lattice parameters of Re_2O_3 and BaO layers.

Acknowledgements

The authors thank the Ministry of Science and Technology of the Russian Federation, subprogramme “Actual direction in physics of condenced state”, direction “Superconductivity”, section “Basis of chemistry of superconductors” for financial support of this work.

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