DOI: 10.1002/ejic.200800745

Thermodynamic Properties of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ Compounds and Their Application for Optimizing the Synthesis of Superconducting Materials

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Keywords: Calorimetry / Thermodynamics / Heats of formation / Superconductors

The standard enthalpies of formation from oxides of $Nd_{1+x}Ba_{2-x}Cu_3O_y$, where x = 0–0.8 and y = 6.65–7.24, were determined by using dissolution enthalpies of these compounds measured by solution calorimetry. The temperature dependence of the heat capacity of $NdBa_2Cu_3O_{6.87}$ was measured over the range 5–320 K by adiabatic calorimetry. The absolute entropy, $S°(T)$, the enthalpy of heating, $H°(T\,K) - H°(0\,K)$, and the reduced Gibbs energy, $\Phi°(T) = S°(T) - [H°(T) - H°(0)]/T$, were calculated by using the temperature dependence of C_p in the interval 0–320 K. The heat capacity and absolute entropy of $NdBa_2Cu_3O_{6.87}$ over the temperature range 320–1380 K were estimated by methods of quantum chemistry with use of the temperature dependence of C_p at low temperatures. A thermodynamic simulation was performed on the basis of the obtained data, and the conditions for synthesis of the $NdBa_2Cu_3O_{6.9}$ phase were determined.

Introduction

The practical employment of new superconducting materials based on compounds of Ln–Ba–Cu–O (Ln: lanthanoid) systems has been steadily increasing.[1–4] Among such compounds, $NdBa_2Cu_3O_y$ (Nd-123) is the most promising because of its high superconducting transition temperature and enhanced critical current density.[5–7] Contrary to $YBa_2Cu_3O_y$ (Y-123), the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ phase reveals a region of homogeneity, and the superconducting properties of the material deteriorate sharply when barium is replaced by neodymium.[8] The region of homogeneity stretches from $x = 0$ to $x = 1$ in the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solution.[9] Unfortunately, the thermodynamic parameters of the compounds in this region of homogeneity, which are necessary for optimizing the synthesis of superconducting materials, are lacking.

The aim of this study is to obtain these parameters and to outline regions of experimental conditions suitable for the synthesis of the pure $NdBa_2Cu_3O_{6.9}$ phase by using thermodynamic simulation.

Results and Discussion

The results of experiments on the determination of the calorimetric reaction enthalpies [reactions (1)–(5)] are shown in Tables 1 and 2, where the values of enthalpies are the average of five measurements. The uncertainties quoted in this work refer to a 95% confidence limit. The mean cooling constant in the experiments was $25 \times 10^{-4}\,s^{-1}$. The correction for heat exchange, calculated according to the Renyo–Pfaundler method, was in general not more than 7% of the total increase in temperature.

As shown in Table 2, the enthalpy of dissolution of the mixture [$\Delta_{sol}H_5 = (-423.9 \pm 5.0)\,kJ\,mol^{-1}$] agrees well with the corresponding value calculated from the data on the dissolution of individual compounds [$(-425.9 \pm 1.2)\,kJ\,mol^{-1}$]. This circumstance provides evidence for the identity of the final states of solution 4 obtained as a result of reaction (6) and after reactions (7)–(9) (see Experimental Section). Another indirect confirmation is the fact that the heats of dissolution are not dependent on the order in which reactions (7)–(9) are carried out, that is, the order in which the oxides are dissolved.

The enthalpies of formation of the compounds under investigation are shown in Table 3. Within the range of the compositions studied, we observed for a fixed value of x a monotonous increase in the absolute values of formation enthalpies for the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions with increasing oxygen content.

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Table 1. Enthalpies of calorimetric reactions (1): $Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+0.5x+\delta}$ + solution 1 = solution 4 + $[(0.5x + \delta)/2]O_2 + \Delta H_1$.

Compound	$-\Delta_{sol}H_1$ [kJ mol^{-1}]
$NdBa_2Cu_3O_{6.65}$	830.9 ± 4.4
$NdBa_2Cu_3O_{6.82}$	813.6 ± 3.2
$NdBa_2Cu_3O_{6.87}$	806.9 ± 6.5
$NdBa_2Cu_3O_{6.90}$	805.9 ± 8.7
$NdBa_2Cu_3O_{6.92}$	808.7 ± 1.5
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.68}$	844.7 ± 7.9
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.94}$	819.9 ± 4.1
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.98}$	811.2 ± 5.8
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.89}$	821.5 ± 2.6
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.99}$	811.6 ± 1.7
$Nd_{1.5}Ba_{1.5}Cu_3O_{7.18}$	842.0 ± 7.3
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.07}$	805.9 ± 3.9
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.19}$	796.4 ± 2.7
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.21}$	793.7 ± 3.0
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.24}$	789.3 ± 1.4

Table 2. Enthalpies of calorimetric reactions (2)–(5).

N_i	$-\Delta H_i$ [kJ mol^{-1}]
2	440.6 ± 1.0
3	22.7 ± 0.6
4	53.4 ± 0.3
5	423.9 ± 5.0

Table 3. Standard enthalpies of formation of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from oxides.

Compound	$-\Delta_f H^\circ_{298}$ [kJ mol^{-1}]
$NdBa_2Cu_3O_{6.65}$	140.0 ± 5.3
$NdBa_2Cu_3O_{6.82}$	157.3 ± 4.3
$NdBa_2Cu_3O_{6.87}$	164.0 ± 7.0
$NdBa_2Cu_3O_{6.90}$	165.0 ± 9.1
$NdBa_2Cu_3O_{6.92}$	162.2 ± 3.3
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.68}$	118.7 ± 8.4
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.94}$	143.6 ± 5.0
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.98}$	159.7 ± 6.3
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.89}$	130.7 ± 3.9
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.99}$	140.6 ± 3.4
$Nd_{1.5}Ba_{1.5}Cu_3O_{7.18}$	128.9 ± 7.7
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.07}$	121.4 ± 4.9
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.19}$	129.6 ± 4.0
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.21}$	117.6 ± 3.5
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.24}$	121.7 ± 3.2

The temperature dependence of the heat capacity of $NdBa_2Cu_3O_{6.87}$ was measured at 130 experimental points over the temperature range 5–320 K by adiabatic calorimetry. The results are presented in Figure 1. The mean-square deviations of the experimental values from the smoothed $C_p(T)$ curve were 1, 0.2, and 0.1% over the temperature ranges 5–20, 20–80, and 80–320 K, respectively. The accuracy of the calculated values was estimated by taking into account errors in calorimeter calibration against benzoic acid and the spread of experimental heat capacity values over the whole temperature interval. There is an anomaly in the $C_p(T)$ dependence curve connected with the transition of the $NdBa_2Cu_3O_{6.87}$ sample into the superconducting state. The temperature of this transition ($T_c = 95.5 \pm 0.3$ K) was detected as the temperature of minimum $dC_p(T)/dT$ in the interval 70–110 K. The differentiation was performed by numerical computing[10] at the experimental points (Figure 2). The heat capacity jump, ΔC_p, was 3.3 J mol^{-1} K^{-1} at T_c.

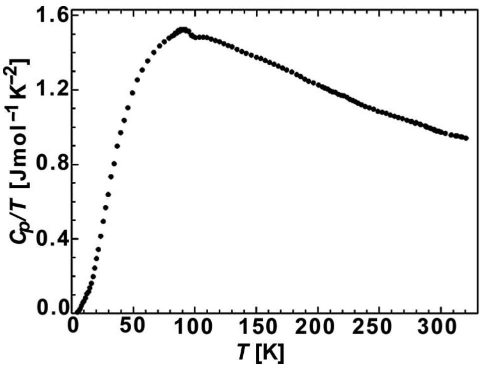

Figure 1. Experimental heat capacity of the $NdBa_2Cu_3O_{6.87}$ sample plotted as C_p/T vs. T in the temperature interval 5–320 K.

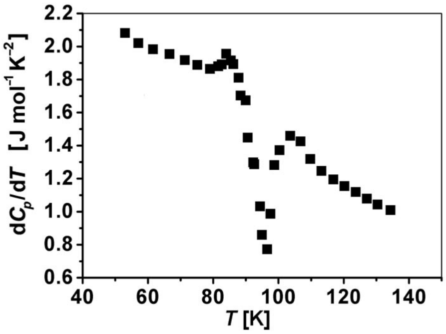

Figure 2. The derivative $dC_p(T)/dT$ vs. T in the superconducting transition region of $NdBa_2Cu_3O_{6.87}$.

The smoothed $C_p(T)$ dependence was used to calculate the thermodynamic functions – the absolute entropy $S^\circ(T)$, the enthalpy of heating $H^\circ(T) - H^\circ(0\ K)$, and the reduced Gibbs energy, $\Phi^\circ(T) = S^\circ(T) - [H^\circ(T) - H^\circ(0)]/T$ – in the temperature interval 0–320 K. The values at selected temperatures are listed in Table 4. We assumed that the heat capacity of samples below 5 K did not contain anomalous components and obeyed the Debye law ($C \approx T^3$).

The following values of thermodynamic functions at 298.15 K were obtained [Equations (1), (2), (3), and (4)].

$$C^\circ_p(298.15\ K) = 291.27 \pm 0.31\ J mol^{-1} K^{-1} \tag{1}$$

$$S^\circ(298.15\ K) = 341.27 \pm 0.55\ J mol^{-1} K^{-1} \tag{2}$$

$$H^\circ(298.15\ K) - H^\circ(0\ K) = 53231 \pm 34\ J mol^{-1} \tag{3}$$

$$\Phi^\circ(298.15\ K) = 162.77 \pm 0.27\ J mol^{-1} K^{-1} \tag{4}$$

The heat capacity of the $NdBa_2Cu_3O_{6.87}$ phase in the temperature range from 298.15 K to 1380 K was calculated. This calculation is based on the application of the special technique[11–13] of low-temperature (5–320 K) heat capacity

Table 4. Smoothed values of the thermodynamic functions of $NdBa_2Cu_3O_{6.87}$.

T [K]	$C°_p(T)$ [J mol^{-1} K^{-1}]	$S°(T)$ [J mol^{-1} K^{-1}]	$H°(T) – H°(0)$ [J mol^{-1}]	$\Phi°(T)$ [J mol^{-1} K^{-1}]
4	0.0129	0.0043	0.012	0.0011
6	0.0900	0.0215	0.104	0.0040
8	0.344	0.0769	0.506	0.0136
10	0.668	0.189	1.53	0.0363
12	1.16	0.351	3.32	0.0740
14	1.72	0.571	6.20	0.128
16	2.60	0.856	10.5	0.200
18	3.92	1.23	16.9	0.293
20	5.71	1.74	26.5	0.410
22	7.79	2.38	40.0	0.558
24	10.4	3.16	58.1	0.741
26	13.2	4.10	81.6	0.962
28	16.4	5.20	111	1.22
30	19.6	6.44	147	1.53
35	29.10	10.2	269	2.49
40	39.0	14.7	439	3.72
45	49.0	19.9	659	5.22
50	59.7	25.6	930	6.97
55	70.1	31.8	1255	8.94
60	80.1	38.3	1630	11.11
65	90.0	45.1	2060	13.46
70	99.7	52.1	2530	15.97
75	109.2	59.3	3050	18.62
80	118.5	66.7	3620	21.40
85	127.9	74.1	4240	24.27
90	136.8	81.7	4900	27.25
95	143.2	89.3	5600	30.32
100	148.5	96.8	6330	33.45
110	162.6	111.6	7890	39.88
120	174.9	126.3	9580	46.47
130	186.0	140.70	11380	53.16
140	196.1	154.9	13290	59.92
150	206.3	168.7	15300	66.72
160	215.9	182.4	17400	73.52
170	224.5	195.7	19620	80.32
180	232.3	208.8	21900	87.10
190	238.6	221.5	24260	93.84
200	245.4	233.9	26680	100.5
210	251.2	246.0	29160	107.2
220	257.1	257.9	31700	113.8
230	261.6	269.4	34300	120.3
240	265.9	280.6	36930	126.7
250	270.9	291.6	39620	133.1
260	276.3	302.3	42360	139.4
270	281.4	312.8	45150	145.6
280	286.1	323.2	47980	151.8
290	289.2	333.3	50860	157.9
298.15	**291.3**	**341.3**	**53230**	**162.8**
300	291.8	343.1	53770	163.9
310	296.3	352.7	56700	169.8
320	301.2	362.2	59700	175.7

extrapolation to the high-temperature region (298.15–1380 K). This extrapolation was realized by using the electron heat capacity coefficient and the moments of the photon densities of states obtained from experimental heat capacities. In this way, the temperature dependence of the heat capacity of the $NdBa_2Cu_3O_{6.87}$ phase may be presented by the expression in Equation (5).

$$C°_p(T) = 304.91 + 5.8416 \times 10^{-2}\,T - 2.7206 \times 10^{6}\,T^{-2} - 1.5744 \times 10^{-5}\,T^{2} \quad (5)$$

The heat capacities and absolute entropies of the $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions from 300 K to their decomposition temperatures[8,18] were estimated by an additive scheme based on the heat capacities and absolute entropies of the phases $NdBa_2Cu_3O_{6.87}$, Nd_2O_3, and BaO.[14] According to the literature,[15,16] the difference between the experimental values and those estimated by the additive scheme does not exceed 3% for $LnBa_2Cu_3O_y$.

By using the data obtained, the Gibbs free energies of formation from oxides of the investigated compounds were calculated. Figure 3 shows the dependence of $\Delta_fG°$ on x at fixed oxygen content (y = 6.9). As shown in Figure 3, for the homogeneity region ($Nd_{1+x}Ba_{2-x}$), an increase in neodymium content leads to a decrease in the absolute value of $\Delta_fG°$.

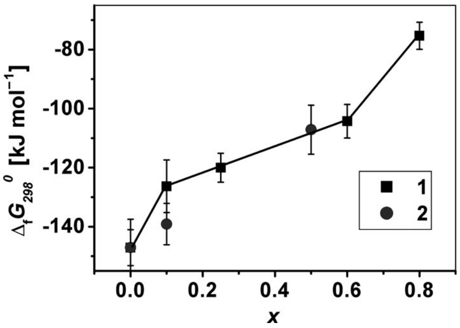

Figure 3. The dependence of the Gibbs free energy of formation ($\Delta_fG_{298}°$) of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from oxides on x at fixed oxygen content (y = 6.9) for two groups of investigated compounds.

It is known[9] that the structure of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ depends on x as follows: orthorhombic for $0 \le x \le 0.1–0.3$; tetragonal for $0.3 \le x \le 0.6$; orthorhombic for $0.6 \le x \le 0.8$. As Figure 3 shows, there are fractures in the curve near $x \approx 0.1$ and $x \approx 0.6$. This agrees with the structural transitions.

The information obtained was used for thermodynamic simulation in the systems Nd–Ba–Cu–O (1a), Nd–Ba–Cu–O–Ar (1b), Nd–Ba–Cu–O–C (2a), Nd–Ba–Cu–O–C–Ar (2b), Nd–Ba–Cu–O–N (3a), and Nd–Ba–Cu–O–N–Ar (3b). The aim of the simulation was to outline regions of experimental conditions suitable for the synthesis of the pure $NdBa_2Cu_3O_y$ phase without admixtures of initial compounds and $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions.

To elucidate the phase equilibria in these systems, the molecular compositions of gas phases in equilibrium with possible condensed phases have been calculated for a wide range of system parameters (T, p_{O_2}, ratios of atomic concentrations of elements). All condensed phases in the system were assumed to be phases of fixed composition. The calculation of the equilibrium is based on the minimization of the total Gibbs free energy of the investigated system.[17]

Standard thermodynamic parameters of individual substances $\Delta_fH°_{298}$, $S°_{298}$, $C°_p = f(T)$ were used as the initial thermodynamic information.

Sets of data used in our calculation are presented in this article and in the Data Bank on Properties of Electronic Materials.[14]

The calculations were performed for a total pressure of 1.013×10^5 Pa and the temperature interval 300–1380 K. The ratios of atomic concentrations of elements were varied

Table 5. The results of thermodynamic simulation.

System	Ratios of atomic concentrations of elements	Total pressure $p = 1.013 \times 10^5$ Pa			
		N	T [K]	Compositions of basic equilibrium phases	Number of moles of condensed phases and p_{O_2}
1a	Nd/Ba/Cu/O 1:2:3:7	1	300–1000	**$NdBa_2Cu_3O_{6.9}$**	**1**
				O_2	1×10^5 Pa
		2	1010–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	1×10^5 Pa
1b	Ar/Nd/Ba/Cu/O 5:1:2:3:7	3	300–950	**$NdBa_2Cu_3O_{6.9}$**	**1**
				O_2	0.24×10^5 Pa
		4	960–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.24×10^5 Pa
2a	Nd/Ba/Cu/O/C 1:2:3:11:2	5	300–1380	Nd_2O_3	0–0.5
				Nd_2CuO_4	0.5–0
				CuO	3–0
				$BaCO_3$	2–0
				$NdBa_2Cu_3O_{6.5}$	**0–0.96**
	Nd/Ba/Cu/O/C 1:2:3:17:2	6	300–1270	Nd_2O_3	0–0.5
				Nd_2CuO_4	0.5–0
				CuO	3–0
				$BaCO_3$	2–0
				$NdBa_2Cu_3O_{6.5}$	0–0.7
		7	1280–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.8×10^5 Pa
	Nd/Ba/Cu/O/C 1:2:3:22–33:2	8	1250–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.8×10^5 Pa
2b	Ar/Nd/Ba/Cu/O/C 1:1:2:3:11:2	9	400–1330	Nd_2O_3	0–0.5
				Cu_2O	0–0.01
				CuO	2.5–0
				$BaCO_3$	2–0.01
				$NdBa_2Cu_3O_{6.5}$	0–0.99
		10	1340–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.20×10^5 Pa
	Ar/Nd/Ba/Cu/O/C 20:1:2:3:22:2	11	400–1150	Nd_2O_3	0–0.55
				CuO	2.5–0.3
				$Nd_{1.8}Ba_{1.2}Cu_3O_{7.2}$	0–0.55
				$BaCO_3$	2–0.26
				$NdBa_2Cu_3O_{6.5}$	0–0.8
		12	1150–1380	**$NdBa_2Cu_3O_{6.65}$**	**1**
				O_2	0.22×10^5 Pa
	Ar/Nd/Ba/Cu/O/C 40:1:2:3:33:2	13	1120–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.22×10^5 Pa
3a	Nd/Ba/Cu/O/N 1:2:3:16.5–33:4	14	300–650	CuO	2.5–1.3
				Nd_2CuO_4	0.5–1.3
				$Ba(NO_3)_2$	2–0
				$Nd_{1.8}Ba_{1.2}Cu_3O_{7.24}$	0–0.5
		15	660–990	**$NdBa_2Cu_3O_{6.9}$**	**1**
				O_2	0.8 10^5 Pa
		16	1000–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.8 10^5 Pa
3b	Ar/Nd/Ba/Cu/O/N 15:1:2:3:25:4	17	300–600	CuO	2.5–0.9
				Nd_2CuO_4	0.5–0
				$Ba(NO_3)_2$	2.0–0.9
				$Ba_{1.2}Cu_3Nd_{1.8}O_{7.24}$	0–0.6
				$NdBa_2Cu_3O_{6.9}$	0–0.3
		18	610–960	**$NdBa_2Cu_3O_{6.9}$**	**1**
		19	970–1380	**$NdBa_2Cu_3O_{6.5}$**	**1**
				O_2	0.21×10^5 Pa

over a wide range. The following were taken into account: the condensed phases Nd_2O_3, BaO, α-$BaCO_3$, β-$BaCO_3$, γ-$BaCO_3$, Cu_2O, CuO, Nd_2CuO_4, $BaCuO_2$, $Ba(NO_3)_2$, and $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solution with x = 0–0.8 (see Table 1) and the gaseous species Ar, O, O_2, NdO, BaO, CuO, CO_2, CO, N_2, NO, NO_3, N_2O_5, N_2O_4, N_2O_3, N_2O, and NO_2. Argon was added to the system in order to simulate the composition of air (21% O_2 and 79% Ar). Thus, the variety of conditions used in our calculations approaches the real conditions of synthesis as much as possible.

The basic results of the calculations are presented in Table 5 for some fixed ratios of atomic concentrations of elements. The most interesting results were obtained in the simulation with systems 1a and 1b. In these systems, Nd-123 synthesis is proposed from oxides. $NdBa_2Cu_3O_y$ is the only condensed phase in all investigated temperature intervals at stoichiometric ratios of atomic concentrations of elements (Nd/Ba/Cu/O = 1:2:3:7). The $NdBa_2Cu_3O_{6.9}$ phase exists at low and medium temperatures: 300–1000 K (N 1), while the phase with lowered oxygen content ($NdBa_2Cu_3O_{6.65}$) exists at higher temperatures: 1010–1380 K (N 2). Upon addition of argon to the system in the quantity approximately corresponding to the composition of air (Ar/Nd/Ba/Cu/O = 5:1:2:3:7), the $NdBa_2Cu_3O_{6.9}$ phase disappears (see N 3, 4) at a lower temperature (960 K instead of 1010 K).

In systems 2a and 2b, Nd-123 synthesis is realized from neodymium and copper oxides and barium carbonate. The simulation with these systems revealed a strong dependence of condensed phase composition on oxygen content. In the absence of argon and at stoichiometric ratios of atomic concentrations of elements, the pure $NdBa_2Cu_3O_y$ phase (without other solid phases) does not form over the whole range of investigated temperatures (N 5). Upon increasing the oxygen concentration by 50% (Nd/Ba/Cu/O/C = 1:2:3:17:2), the pure $NdBa_2Cu_3O_{6.65}$ phase appears at 1280 K (N 6, 7). Increasing the oxygen concentration further has almost no influence on the result (N 8). Upon addition of argon to the system in the quantity simulating air composition (Ar/Nd/Ba/Cu/O/C = 1:1:2:3:11:2), the pure $NdBa_2Cu_3O_{6.65}$ phase appears at 1340 K (N 9, 10). When the oxygen concentration is increased from 11 to 33, the pure $NdBa_2Cu_3O_{6.65}$ phase appears already at 1120 K (N 13).

The simulation with systems 3a and 3b reproduces the conditions of Nd-123 synthesis from neodymium and copper oxides and barium nitrate. The result of this simulation is similar to that with systems 1a and 1b. In the system of composition Nd/Ba/Cu/O/N = 1:2:3:16.5 (stoichiometric), there is a mixture of oxides in the temperature interval 300–650 K (N 14), the $NdBa_2Cu_3O_{6.9}$ phase is present at 650–990 K (N 15), and the $NdBa_2Cu_3O_{6.65}$ phase is present at 990–1380 K (N 16). This result practically does not depend on oxygen content. Introduction of argon into the system reduces (by 30–40 K) the temperature at which the $NdBa_2Cu_3O_{6.9}$ phase still exists (N 18). Thus, there is a sufficiently broad region in which $NdBa_2Cu_3O_y$ exists without admixtures of initial compounds and the solid solution $Nd_{1+x}Ba_{2-x}Cu_3O_y$. However, by using barium carbonate (systems 2), the phase with low oxygen content (6.65) is mainly produced, which needs to be annealed in oxygen at temperatures of 300–950 K (Figure 4) to yield the superconducting $NdBa_2Cu_3O_{6.9}$ phase.

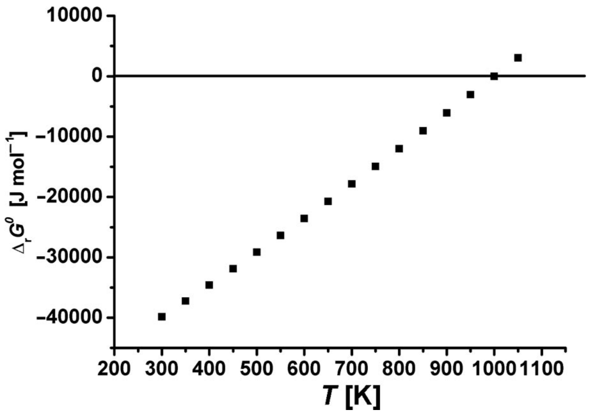

Figure 4. Temperature dependence of the Gibbs free energy ($\Delta_r G°$) of the reaction $2NdBa_2Cu_3O_{6.65}(s) + 0.25O_2(g) = 2NdBa_2Cu_3O_{6.9}(s)$.

Conclusion

By using solution calorimetry, adiabatic calorimetry, and estimation methods of thermodynamic properties, the set of thermodynamic parameters (standard enthalpies of formation, absolute entropies, and the temperature dependence of heat capacities in the interval 5–1380 K) for $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions (x = 0–0.8, y = 6.65–7.24) was obtained for the first time.

On the basis of the obtained data, a thermodynamic simulation was realized in the temperature interval 300–1380 K to reveal experimental conditions of synthesis of superconducting $NdBa_2Cu_3O_{6.9}$ phases.

The possibility of superconducting phase synthesis from (a) oxides; (b) neodymium oxide, copper oxide, and barium carbonate; (c) neodymium oxide, copper oxide, and barium nitrate was considered. The conditions of synthesis (T, p_{O_2}, ratios of atomic concentrations of elements) were obtained for all of these variants of synthesis.

Experimental Section

Materials

Two groups of compounds were investigated.

Group 1: 11 samples of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ (x = 0–0.8) were prepared by solid state reactions from stoichiometric amounts of Nd_2O_3 (mass fraction of neodymium oxide > 0.9999), $BaCO_3$ (mass fraction of barium carbonate > 0.99999) and finely ground CuO (mass fraction of copper oxide > 0.9999) at 1223–1323 K in dry and CO_2-free air. The details of the synthesis are described in a previously published article.[18]

Group 2: 4 samples ($NdBa_2Cu_3O_{6.9}$, $NdBa_2Cu_3O_{6.87}$, $Nd_{1.1}Ba_{1.9}Cu_3O_{6.98}$, $Nd_{1.5}Ba_{1.5}Cu_3O_{7.18}$) were obtained from Ames Lab (Iowa University, USA). The preparation of these samples is described in more detail in ref.[19]

The samples were characterized by X-ray powder diffraction and chemical analysis. The contents of all metallic components was determined by atomic absorption spectroscopy.[20] The oxygen content was analyzed by iodometric titration. According to the analysis results, all samples were homogeneous. The accuracy of determination amounted to ± 0.03 formula units for Nd, Ba, and O and ± 0.05 formula units and for Cu.

Sample weights were determined as the difference in the mass of an empty ampoule and the ampoule filled with the sample with an accuracy of 10^{-5} g. Hydrochloric acid grade HP 20–5 (the mass fraction of 20 checked impurities is not more than 10^{-7}) and distilled water were used for preparation of solutions.

Solution Calorimetry

The heats of dissolution of the investigated compounds were measured in a solution calorimeter with an isothermal shell, which is described in detail elsewhere.[21] The dissolution enthalpy of potassium chloride in water measured in our calorimeter agreed with recommended data[22] to within 0.1%.

The calorimetric cycles were designed in such a way that it was possible to determine the formation enthalpies of Nd-123 phases from those of the initial reagents, namely, $0.5Nd_2O_3 + 2BaCO_3 + 3CuO$. The scheme of the process is given in Equations (6), (7), (8), and (9).

$$Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+0.5x+\delta} + \text{solution 1} = \text{solution 4} + [(0.5x + \delta)/2]O_2 + \Delta H_1 \quad (6)$$

$$[(1 + x)/2]Nd_2O_3 + \text{solution 1} = \text{solution 2} + [(1 + x)/2]\Delta H_2 \quad (7)$$

$$(2 - x)BaCO_3 + \text{solution 2} = \text{solution 3} + (2 + x)CO_2 + (2 + x)\Delta H_3 \quad (8)$$

$$3\ CuO + \text{solution 3} = \text{solution 4} + 3\ \Delta H_4 \quad (9)$$

The heat of dissolution of the initial mixture of compounds taken in the ratio corresponding to the stoichiometry of $NdBa_2Cu_3O_{6.5}$ was also measured [Equation (10)].

$$(1/2)Nd_2O_3 + 2BaCO_3 + 3CuO + \text{solution 1} = \text{solution 4} + 2CO_2 + \Delta H_5 \quad (10)$$

where solution 1 is $0.35\text{Nd-123} + 6 \times 10^3\,HCl + 48.9 \times 10^3\,H_2O$.

The selected concentrations of calorimetric solutions guaranteed, on the one hand a sufficiently fast reaction rate (CuO and $BaCO_3$ were dissolved within 20–30 min, Nd_2O_3 and $Nd_{1+x}Ba_{2-x}Cu_3O_y$ within 10–20 min) and on the other hand, the independence of the heats of reactions (1)–(4) on the changes in the concentrations of the corresponding cations in solution.

Using the enthalpy of the reaction in Equation (11),

$$BaCO_3 = BaO + CO_2 + \Delta H_6, \quad (11)$$

where $\Delta H_6 = (272.50 \pm 2.5)\ \text{kJ mol}^{-1}$ was taken from ref.[23], we obtain the enthalpy of formation of the solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from oxides [Equation (12)].

$$(1 + x)/2\ Nd_2O_3 + (2 - x)\ BaO + 3\ CuO + \delta/2\ O_2 = Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+0.5x+\delta} + \Delta H_7 \quad (12)$$

where $\Delta H_7 = (1 + x)/2\ \Delta_{sol}H_2 + (2 - x)\ \Delta_{sol}H_3 - (2 - x)\ \Delta H_6 + 3\ \Delta_{sol}H_4 - \Delta_{sol}H_1$, $y = 6.5 + 0.5x + \delta$.

The mass of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ samples employed in calorimetric experiments was about 0.27 g. The volume of calorimeter vessel was 200 mL. All the experiments were performed at 298.15 K.

Adiabatic Calorimetry

The measurement of the isobaric heat capacity was performed by the adiabatic method in the temperature interval 5–320 K with the equipment characterized in ref.[24] The investigated compound was located during the experiment in a demountable nickel calorimetric ampoule.[25] The results of the heat capacity measurement of benzoic acid (C_6H_5COOH) agreed well with standard data recommended at the Calorimetry Conference (NBS–49)[26]: the error in heat capacity measurements was 1% at 5–50 K and 0.2% at 50–320 K. The mass of the $NdBa_2Cu_3O_{6.87}$ sample employed in the calorimetric measurement was 4.025 g.

Acknowledgments

This work was financially supported by the "Program in Support of Leading Scientific Schools", project RF NSh no. 1042 2003.3.

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Received: July 28, 2008