The Formation Enthalpies of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ Solid Solutions

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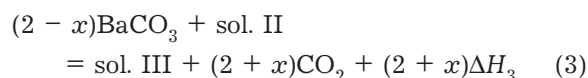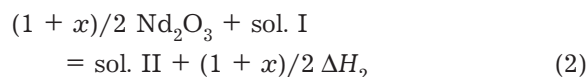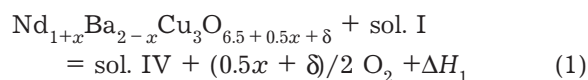Pr. Akademika Lavrentyeva 3, Novosibirsk 630090 (Russia)*

Abstract

The solid phase of the composition $NdBa_2Cu_3O_y$ is at present one of promising superconductor materials. However, the preparation of high-quality superconducting samples in the $Nd - Ba - Cu - O$ system is complicated due to the possibility of the formation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions; superconducting characteristics of these solutions sharply decrease when neodymium content of the compound increases. We report experimental determination of the enthalpies of formation of these compounds, which is one of the basic thermodynamic characteristics.

INTRODUCTION

At present, the solid phase $NdBa_2Cu_3O_y$ is one of promising superconducting materials exhibiting rather high temperature of the transition into superconducting state and conserving superconducting properties in stronger magnetic fields than other 1,2,3-compounds do [1]. However, the preparation of high-quality superconducting samples in the system $Nd - Ba - Cu - O$ is complicated by the possibility of the formation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions whose superconducting properties deteriorate sharply when the neodymium content increases in the compound. According to literature data, the homogeneity region stretches from $x = 0$ to $x = 1.0$ [2]. Unfortunately, thermodynamic properties of these compounds are studied only poorly [2]. Because of this, we determined experimentally one of the most important thermodynamic characteristics of these compounds, *i. e.* the enthalpy of their formation.

The standard enthalpy of the formation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ where $0 \leq x \leq 0.8$, and $6.65 \leq y \leq 7.24$ was determined on the basis of the measurements of heat effects of the calorimetric reactions:

$$Nd_{1+x}Ba_{2-x}Cu_3O_{6.5+0.5x+\delta} + \text{sol. I}$$
$$= \text{sol. IV} + (0.5x + \delta)/2 \ O_2 + \Delta H_1 \qquad (1)$$

$$(1 + x)/2 \ Nd_2O_3 + \text{sol. I}$$
$$= \text{sol. II} + (1 + x)/2 \ \Delta H_2 \qquad (2)$$

$$(2 - x)BaCO_3 + \text{sol. II}$$
$$= \text{sol. III} + (2 + x)CO_2 + (2 + x)\Delta H_3 \qquad (3)$$

We also measured the heat of dissolution of a mixture of oxides taken in the ratio corresponding to the stoichiometry of $NdBa_2Cu_3O_{6.5}$:

$$1/2Nd_2O_3 + 2BaCO_3 + 3CuO + \text{sol. I}$$
$$= \text{sol. IV} + 2CO_2 + \Delta H_5 \qquad (5)$$
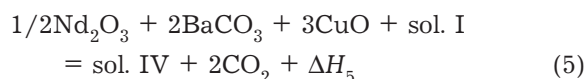
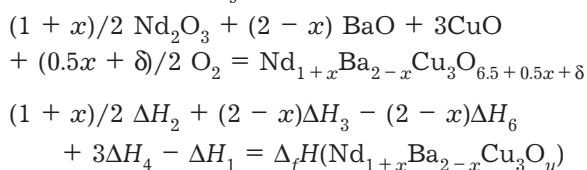where solution I is $0.35Nd_{123} + 6 \cdot 10^3 \ HCl + 27 \cdot 10^3 \ H_2O$.

The selected concentrations of calorimetric solutions provided, on the one hand, a sufficient reaction rate at 298.15 K (CuO and BaO were dissolved within $20-30$ min, Nd_2O_3 and $Nd_{1+x}Ba_{2-x}Cu_3O_y$ within $10-15$ min), on the other hand, independence of reaction heat, for

the reactions (1)−(4), on the changes in the concentrations of the corresponding cations in solution.

Using the enthalpy of the reaction

$$BaCO_3 = BaO + CO_2 + \Delta H_6$$
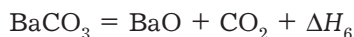
where $\Delta H_6 = (272.50 \pm 2.5)$ kJ/mol [3], we obtain the enthalpy of the formation of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from oxides:

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

$$(1 + x)/2 \ \Delta H_2 + (2 - x)\Delta H_3 - (2 - x)\Delta H_6$$
$$+ 3\Delta H_4 - \Delta H_1 = \Delta_f H(Nd_{1+x}Ba_{2-x}Cu_3O_y)$$

where $y = = 6.5 + 0.5x + \delta$.

INITIAL SUBSTANCES

The samples of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ were prepared from Nd_2O_3 (99.99 %), $BaCO_3$ (99.999 %) and CuO (99.99 %) at 920 °C in the air according to a method that proved to be good [2]. According to the data of X-ray diffraction studies, DTA (Setaram HT 1500), scanning electron microscopy (SEM Philips XL 30), and X-ray spectroscopy (EDX Philips CH 20 EFG), all the samples were monophase. Mass spectral analysis revealed the presence of impurities (~0.16 at. % Sr and Al). The samples of the composition $x = 0$ used for the preparation of textured materials exhibited a sharp transition ($\Delta T_c < 1$ K) at $T_c \geq 95$ K and $J_c \geq 30$ kA/cm^2 (1.5 T, 77 K) [4]. Directly before being packed in calorimetric ampoules, the initial substances were annealed at the corresponding temperature and oxygen partial pressure.

Weighed portions of the substances were determined from the difference between the mass of empty ampoule and the ampoule with the substance at an accuracy of 10^{-5} g. Hydrochloric acid of a specially pure grade and distilled water were used to prepare the solutions.

INSTRUMENTATION AND TECHNIQUE

The heats of dissolution were measured in a liquid calorimeter with an isothermal shell at 298K (Fig. 1). The temperature of the shell was
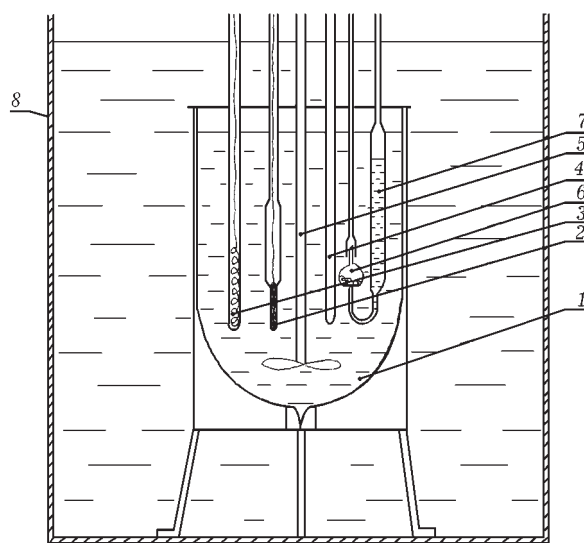

Fig. 1. Liquid calorimeter with an isothermal shell: *1* − calorimetric vessel, *2* − temperature sensor, *3* − calibration heater, *4* − quartz tube (cooler), *5* − glass mixer, *6* − ampoule with the substance under investigation, *7* − striker with the reservoir, *8* − thermostat.

maintained at an accuracy of 0.002 K. Temperature in the calorimeter was measured with a MMT-4 thermistor ($R_{25} = 8906$ Ω). The sensitivity of the thermometric scheme was $10^{-4} - 10^{-5}$ K. Heat value of the calorimeter was determined by calibration with respect to electric current within the same temperature interval as in the corresponding experiment.

The heat of KCl dissolution in water measured with our calorimeter coincided with the reference value [5] at an accuracy of 0.1 % which is the evidence of the absence of substantial systematic errors in the calorimetric scheme used.

In order to avoid the transport of vapour on the cup of the calorimeter, all the experiments on the measurement of dissolution heat were carried out at temperatures below the convergence point.

RESULTS AND DISCUSSION

The results of experiments on the determination of reaction enthalpies (1)−(5) are shown in Tables 1−15. The designations are: m − a weighed portion of the substance; Δt − the corrected temperature increase; Q − an amount of heat corresponding to Δt; ΔH − the enthalpy of dissolution. All the errors given here and below are shown for a 95 % confidence interval.

TABLE 1
The enthalpy of the reaction
$(1 + x)/2Nd_2O_3 + sol. I = sol. II + (1 + x)/2\Delta H_2$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.06373	30.38	82.72	1308.42
0.06149	29.20	80.79	1313.90
0.06310	29.99	82.63	1309.51
0.06319	29.94	82.72	1309.30
0.06327	29.90	82.59	1305.78

$\Delta H_{av} = (-1309.38 \pm 2.93)$ J/g = (-440.6 ± 1.0) kJ/mol.

TABLE 2
The enthalpy of the reaction $(2 - x)BaCO_3 + sol. II$
$= sol. III + (2 + x)CO_2 + (2 + x)\Delta H_3$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.15147	6.12	17.11	112.97
0.14806	6.10	16.82	113.76
0.14895	5.37	14.98	119.66
0.15057	6.29	17.11	115.23
0.14809	6.02	16.74	112.93

$\Delta H_{av} = (-114.93 \pm 2.80)$ J/g = (-22.7 ± 0.6) kJ/mol.

TABLE 3
The enthalpy of the reaction
$3CuO + sol. III = sol. IV + 3\Delta H_4$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.08921	21.83	60.25	675.59
0.08958	21.94	60.50	675.30
0.08902	21.40	59.20	664.84
0.08930	21.63	59.91	670.82
0.08922	21.81	59.91	671.45

$\Delta H_{av} = (-671.66 \pm 4.22)$ J/g = (-53.4 ± 0.3) kJ/mol.

TABLE 4
The enthalpy of the reaction
$1/2\ Nd_2O_3 + 2\ BaCO_3 + 3CuO + sol. I = sol. IV + 2CO_2$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.30134	57.78	159.33	527.31
0.30275	58.91	160.16	529.48
0.30249	57.77	159.45	527.18
0.30305	58.43	161.92	535.38
0.30256	58.15	158.70	524.71

$\Delta H_{av} = (-528.81 \pm 5.02)$ J/g = $-(423.9 \pm 5.0)$ kJ/mol.

TABLE 5
The enthalpy of the reaction
$NdBa_2Cu_3O_{6.65} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27033	113.10	312.67	1156.58
0.27108	113.62	313.17	1155.33
0.27098	114.40	313.84	1165.75
0.27023	113.97	315.05	1165.91
0.27057	113.34	313.63	1159.18

$\Delta H_{av} = (-1160.56 \pm 6.28)$ J/g = (-830.9 ± 4.4) kJ/mol.

TABLE 6
The enthalpy of the reaction
$NdBa_2Cu_3O_{6.82} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.25008	101.23	281.83	1126.96
0.19985	81.04	225.98	1130.77
0.10793	44.25	122.26	1132.94
0.10632	43.42	120.50	1133.28
0.07002	28.85	79.58	1136.71

$\Delta H_{av} = (-1132.15 \pm 4.45)$ J/g = (-813.6 ± 3.2) kJ/mol.

TABLE 7
The enthalpy of the reaction
$NdBa_2Cu_3O_{6.92} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27151	110.73	305.56	1122.82
0.27120	110.04	303.80	1121.02
0.27002	110.06	303.51	1124.07
0.27025	109.61	303.63	1123.61
0.27030	109.83	303.34	1122.23

$\Delta H_{av} = (-1122.73 \pm 1.50)$ J/g = (-808.7 ± 1.5) kJ/mol.

TABLE 8
The enthalpy of the reaction
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.68} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27013	114.87	317.23	1174.41
0.27084	117.63	323.21	1193.40
0.27010	113.66	313.38	1167.67
0.27099	115.75	318.86	1176.71
0.27022	114.34	318.11	1177.38

$\Delta H_{av} = (-1177.83 \pm 11.04)$ J/g = (-844.7 ± 7.9) kJ/mol.

TABLE 9
The enthalpy of the reaction
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.94} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27001	110.48	305.01	1140.39
0.27025	111.09	308.15	1140.26
0.27008	109.74	304.34	1126.83
0.27010	111.21	306.81	1135.92
0.27022	111.68	308.03	1139.85

$\Delta H_{av} = (-1136.67 \pm 5.69)$ J/g = (-819.9 ± 4.1) kJ/mol.

TABLE 10
The enthalpy of the reaction
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.89} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27014	111.68	308.49	1142.02
0.27038	111.64	307.61	1137.75
0.27047	112.07	308.36	1140.06
0.27026	111.64	307.77	1138.76
0.27002	110.73	304.72	1134.11

$\Delta H_{av} = (-1138.55 \pm 3.64)$ J/g = (-821.5 ± 2.6) kJ/mol.

TABLE 11

The enthalpy of the reaction
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.99} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, Дж	$-\Delta H$, J/g
0.27008	109.32	301.67	1119.22
0.26997	109.73	303.46	1124.16
0.27014	110.04	303.21	1122.48
0.27019	110.04	303.59	1123.65
0.27045	110.17	303.51	1122.19

$\Delta H_{av} = (-1122.36 \pm 5.40)$ J/g = (-811.6 ± 1.7) kJ/mol.

TABLE 12

The enthalpy of the reaction
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.07} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, Дж	$-\Delta H$, J/g
0.27025	107.84	298.07	1105.12
0.27027	108.10	299.62	1108.34
0.27020	108.41	299.16	1106.43
0.27044	108.43	299.70	1108.17
0.27009	108.61	301.50	1116.29

$\Delta H_{av} = (-1108.84 \pm 5.39)$ J/g = -805.9 kJ/mol.

TABLE 13

The enthalpy of the reaction
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.19} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27003	106.52	294.39	1090.18
0.27061	106.65	294.39	1089.97
0.27033	107.83	297.31	1095.91
0.27019	107.06	295.10	1092.15
0.27002	107.095	295.97	1096.04

$\Delta H_{av} = (-1092.86 \pm 3.68)$ J/g = (-796.4 ± 2.7) kJ/mol.

TABLE 14

The enthalpy of the reaction
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.21} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27030	106.71	293.12	1085.41
0.27044	106.38	293.63	1085.79
0.27000	106.27	292.38	1082.86
0.27030	106.92	294.68	1087.59
0.26994	106.98	294.68	1091.69

$\Delta H_{av} = (-1086.67 \pm 1.92)$ J/g = (-793.7 ± 3.0) kJ/mol.

TABLE 15

The enthalpy of the reaction
$Nd_{1.8}Ba_{1.2}Cu_3O_{7.24} + sol. I \rightarrow sol. IV$

m, g	Δt, Ω	Q, J	$-\Delta H$, J/g
0.27013	105.69	291.33	1078.63
0.27039	105.81	292.38	1081.27
0.27021	105.63	292.04	1081.14
0.27014	105.99	291.87	1080.52
0.27019	105.73	291.25	1077.96

$\Delta H_{av} = (-1079.89 \pm 1.92)$ J/g = (-789.3 ± 1.4) kJ/mol.

TABLE 16

Standard enthalpies of the formation of solid solutions
$Nd_{1+x}Ba_{2-x}Cu_3O_y$ from oxides, kJ/mol

Compound	$-\Delta$
$NdBa_2Cu_3O_{6.65}$	140.0 ± 5.3
$NdBa_2Cu_3O_{6.82}$	157.3 ± 4.3
$NdBa_2Cu_3O_{6.92}$	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
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.89}$	130.7 ± 3.9
$Nd_{1.25}Ba_{1.75}Cu_3O_{6.99}$	140.6 ± 3.4
$Nd_{1.6}Ba_{1.4}Cu_3O_{7.07}$	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
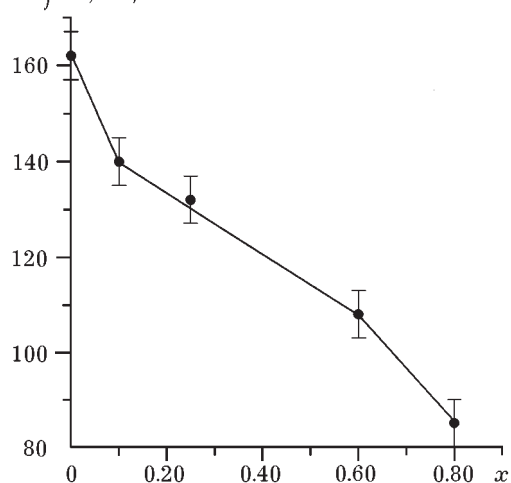
Fig. 2. The dependence of the formation enthalpy of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ on x.

Mean cooling constant in the experiments was $25 \cdot 10^{-4} \cdot s^{-1}$. The correction for heat exchange calculated according to the Renyo − Pfaundler method was in general not more than 7 % of total temperature increase.

As one can see from Tables 1−15, the enthalpy of the dissolution of the mixture ($\Delta H_5 = (-423.9 \pm 5.0)$ kJ/mol) agrees well with the corresponding value calculated from the data on the dissolution of individual oxides ((-425.7 ± 1.5) kJ/mol). This circumstance evidences in favour of the identity of the final states of solutions IV obtained as a result of reaction (1) and after reactions (2)−(4). Another indirect confirmation is the independence of dissolution heats on the order in which reactions (2)−(4) are carried out, *i. e.* in which the oxides are dissolved.

The enthalpies of the formation of compounds under investigation are shown in Table 16. Within the range of the compositions

studied, we observed a monotonous increase in the absolute values of formation enthalpies for the solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ with increasing oxygen content in them.

For the homogeneity region ($Nd_{1+x}Ba_{2-x}$), an increase in neodymium content leads to the decrease in absolute $\Delta_f H$. Figure 2 shows the dependence of $\Delta_f H$ on x at a fixed oxygen content ($y = 6.9$). It is known [2] that the structure of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ depends on x as follows: $0 \leq x \leq 0.1-0.3$ − orthorhombic; $0.3 \leq x \leq 0.6$ − tetragonal; $0.6 \leq x \leq 0.8$ − orthorhombic. As Fig. 2 shows, there are fractures in the curve near $x \approx 0.1$ and $x \approx 0.6$. This agrees with the structural transitions.

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