Thermochemistry of the Decomposition Reactions of Solid Solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$

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Abstract

The dependence of the enthalpy of formation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ with low oxygen content on composition (x = 0.1–0.9) is investigated with the help of calorimetric methods. It is shown on the basis of experimental data that the indicated compounds within the range x = 0.1-0.7 are able to decompose into solid solutions with higher and lower neodymium content. In addition, the possibility of the decomposition of solid solutions at medium temperatures into the phases Nd_2CuO_4, $BaCuO_2$ is demonstrated. The obtained results are useful for understanding the reasons of peak effect in magnetic field. The discovery of this effect opens new possibilities to obtain high-temperature superconductors (HTSC) with improved technological parameters. Solution-free technological methods used to obtain HTSC allow synthesizing the samples of higher quality, in comparison with the phases prepared according to the technologies that involve solutions, because the consumption of pure natural water and the formation of waste water are eliminated.

INTRODUCTION

The discovery of peak effect [1] (an increase in critical current) for $NdBa_2Cu_3O_x$ caused intensive investigation of physicochemical properties of cuprates in magnetic field. Due to the complexity of the systems containing high-temperature superconductors (HTSC), and the lack of investigation methods for unambiguous interpretation of the obtained results, the nature of peak effect in cuprate systems remains unclear yet. Obtaining materials with large critical current opens new possibilities for improving technology and technological parameters of HTSC. One of important aspects of investigating the nature of peak effect is preparation of high-quality and well-characterized samples for investigation. From this viewpoint, methods of solution-free technology remain among the most promising methods of synthesis of high-temperature superconductors with required properties. Success of using these methods is determined by the extent of physicochemical, in particular thermodynamic advance for cuprate systems.

One of the possible reasons of the appearance of peak effect in the systems R–Ba–Cu–O (R = La, Nd, Sm, Gd, Eu) can be decomposition of solid solutions $R_{1+x}Ba_{2-x}Cu_3O_z$ into phases with lack and with excess of a rare earth element. In order to reveal the possibility of decomposition process, one should investigate thermodynamic properties of compounds in the system R–Ba–Cu–O. The goal of the present work is to investigate thermodynamic characteristics of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ phases with low oxygen content, and to calculate thermodynamics of decomposition reactions on this basis. The published investigations into thermodynamic properties of Nd–Ba–Cu–O compounds report on fragmentary data on solid solutions with high oxygen content [2–7]. The data for phases with low oxygen content are absent.

EXPERIMENTAL

We investigated the samples $Nd_{1+x}Ba_{2-x}Cu_3O_y$ (x = 0.1–0.9) with low oxygen content, synthe-

TABLE 1

Composition of investigated compounds

No.	Compound	No.	Compound
1	$Nd_{1.1}Ba_{1.9}Cu_3O_{6.03}$	5	$Nd_{1.6}Ba_{1.4}Cu_3O_{6.57}$
2	$Nd_{1.3}Ba_{1.7}Cu_3O_{6.19}$	6	$Nd_{1.7}Ba_{1.3}Cu_3O_{6.73}$
3	$Nd_{1.4}Ba_{1.6}Cu_3O_{6.44}$	7	$Nd_{1.8}Ba_{1.2}Cu_3O_{6.81}$
4	$Nd_{1.5}Ba_{1.5}Cu_3O_{6.51}$	8	$Nd_{1.9}Ba_{1.1}Cu_3O_{7.00}$

sized from barium nitrate, copper oxide, neodymium oxide. Before synthesis, barium content of barium nitrate was determined by means of gravimetry; copper content of the copper oxide was measured by iodometric titration; neodymium oxide was obtained from neodymium nitrate by heating to 1173 K. The initial compounds were mixed at the stoichiometric ratio, ground together, heated for 4 h to 1023 K and kept for 5 h at this temperature. After that, the mixture was again ground, heated from 1023 to 1123 K for 2 h, kept 5–10 h at this temperature, ground once more, then pulverized in acetone for 15 min; the powder was dried in air at 573–673 K, pressed in tablets 20 mm in diameter (mass: about 5 g), annealed at the temperature of 1273 K for 24 h, quenched, ground, pressed, annealed at 1273 K for 24 h, quenched in liquid nitrogen and in Wood's alloy from vertical furnace. Then the sample was placed into a box with nitrogen atmosphere and cooled to room temperature in exsiccator. The samples were characterized by means of X-ray phase and chemical analysis [8, 9]. According to the results of analysis, the samples were individual phases; their composition is shown in Table 1.

We chose dissolution calorimetry as the main method to obtain thermochemical characteristics. Enthalpy of dissolution of the phases under investigation was determined in automated calorimeter with isothermal shell at 323.15 K in 2 M HCl. The procedure of calorimetric measurements, design of the calorimeter, choice of experimental conditions (weighed portions, temperature, time of the main period, *etc.*), and test for the reliability of calorimetric setup have been described in detail in [2–7]. The determined enthalpy of the samples under investigation was compared with the enthalpy of dissolution of stoichiometric mixture of Nd_2O_3, $BaCO_3$, CuO, which allowed us to calculate enthalpies of the formation of solid solutions $R_{1+x}Ba_{2-x}Cu_3O_z$ from neodymium oxide, copper oxide, and barium carbonate, *i. e.* the enthalpy of reaction of the following general type:

$$(1 + x)/2\ Nd_2O_3(s) + (2 - x)BaCO_3(s) + 3CuO(s) + zO_2(g) = Nd_{1+x}Ba_{2-x}Cu_3O_y + (2 - x)CO_2 + \Delta_{car}H^\circ \qquad (1)$$

The averaged $\Delta_{car}H^\circ$ values calculated using the data of five parallel experiments are shown in Table 2.

RESULTS AND DISCUSSION

The determined enthalpies of formation according to reactions (1) allowed us to calculate the enthalpy of the formation of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from binary oxides (Nd_2O_3, BaO, CuO) using the following scheme:

TABLE 2

Enthalpy of formation of $Nd_{1+x}Ba_{2-x}Cu_3O_y$ from neodymium oxide, copper oxide, barium carbonate

Compound	$\Delta_{car}H^\circ$, kJ/mol	Compound	$\Delta_{car}H^\circ$, kJ/mol
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.03}$	+411.86±4.98	$Nd_{1.6}Ba_{1.4}Cu_3O_{6.57}$	+267.90±5.44
$Nd_{1.3}Ba_{1.7}Cu_3O_{6.19}$	+367.59±5.75	$Nd_{1.7}Ba_{1.3}Cu_3O_{6.73}$	+219.45±6.65
$Nd_{1.4}Ba_{1.6}Cu_3O_{6.44}$	+326.77±5.48	$Nd_{1.8}Ba_{1.2}Cu_3O_{6.81}$	+230.29±6.23
$Nd_{1.5}Ba_{1.5}Cu_3O_{6.51}$	+290.42±5.87	$Nd_{1.9}Ba_{1.1}Cu_3O_{7.00}$	+198.27±5.82

$$\begin{aligned}
&\Delta_{ox}H^\circ(Nd_{1+x}Ba_{2-x}Cu_3O_y,\ \text{solid},\ 323.15\ \text{K})\\
&\quad = \Delta_{car}H^\circ\ (323.15\ \text{K})\\
&\quad + (2-x)\Delta_f H^\circ(BaCO_3,\ \text{solid},\ 323.15\ \text{K})\\
&\quad - (2-x)\Delta_f H^\circ(BaO,\ \text{solid},\ 323.15\ \text{K})\\
&\quad - (2-x)\Delta_f H^\circ(CO_2,\ \text{gas},\ 323.15\ \text{K})
\end{aligned}$$

These data are listed in Table 3. Reference parameters which are necessary for calculations have been taken from the Database on the properties of materials for electronics [10]. Errors are given for a 95 % confidence interval using Student's coefficient. Possible systematic error calculated as described in monograph [11] does not bring any contribution into the reaction enthalpies.

On the basis of the obtained experimental data on enthalpy of formation of solid solutions $Nb_{1+x}Ba_{2-x}Cu_3O_y$ from oxides, we calculated its dependence on neodymium content within the range $x = 0.1-0.9$ for $y = 6$ and 7. Enthalpy of formation of the composition with $y > 6$ was recalculated for the enthalpy of formation of compositions with $y = 6$ and 7 using enthalpy of oxidation in neodymium system, which is 96 kJ per one oxygen atom. Enthalpy of oxidation was calculated as mean value over the data of [2–4, 12]. The enthalpy of the formation of phases $Nd_{1+x}Ba_{2-x}Cu_3O_6$ and $Nd_{1+x}Ba_{2-x}Cu_3O_7$ from binary oxides is shown in Table 4 and in Fig. 1. The results shown in Fig. 1 indicate that there are three different regions of the curve exhibiting the dependence of enthalpy of formation of solid solutions Nd123 on neodymium content: the 1st, $x = 0-0.3$; the 2nd, $x = 0.3-0.7$, the 3rd, $x = 0.7-0.9$. This is cjnsistency with the structural data [9].

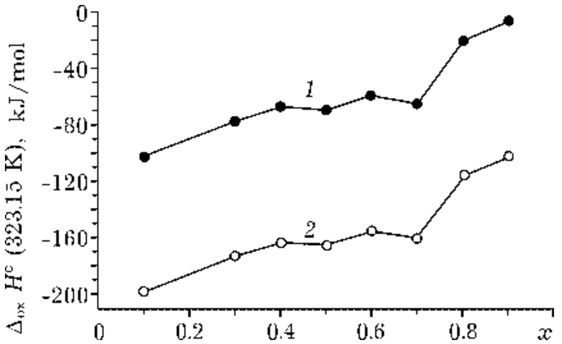

Fig. 1. Dependence of enthalpy of formation of phases $Nd_{1+x}Ba_{2-x}Cu_3O_6$ (*1*) and $Nd_{1+x}Ba_{2-x}Cu_3O_7$ (*2*) from oxides on composition.

Let us turn to the analysis of the dependence of enthalpy of formation of solid solutions on neodymium content within the range $x = 0.1-0.9$, where angularities occur at $x =$

TABLE 3

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

Compound	$\Delta_{ox}H^\circ$(323.15 K)	Compound	$\Delta_{ox}H^\circ$(323.15 K)
$Nd_{1.1}Ba_{1.9}Cu_3O_{6.03}$	−105.71±4.98	$Nd_{1.6}Ba_{1.4}Cu_3O_{6.57}$	−113.46±5.44
$Nd_{1.3}Ba_{1.7}Cu_3O_{6.19}$	−95.49±5.75	$Nd_{1.7}Ba_{1.3}Cu_3O_{6.73}$	−134.68±6.65
$Nd_{1.4}Ba_{1.6}Cu_3O_{6.44}$	−109.08±5.48	$Nd_{1.8}Ba_{1.2}Cu_3O_{6.81}$	−96.60±6.23
$Nd_{1.5}Ba_{1.5}Cu_3O_{6.51}$	−118.19±5.87	$Nd_{1.9}Ba_{1.1}Cu_3O_{7.00}$	−101.37±5.82

TABLE 4

Enthalpy of formation of $Nd_{1+x}Ba_{2-x}Cu_3O_6$ and $Nd_{1+x}Ba_{2-x}Cu_3O_7$ phases from binary oxides, kJ/mol

Compound	$\Delta_{ox}H^\circ$(323.15 K)	Compound	$\Delta_{ox}H^\circ$(323.15 K)
$Nd_{1.1}Ba_{1.9}Cu_3O_6$	−102.83±4.98	$Nd_{1.1}Ba_{1.9}Cu_3O_7$	−198.83±4.98
$Nd_{1.3}Ba_{1.7}Cu_3O_6$	−77.25±5.75	$Nd_{1.3}Ba_{1.7}Cu_3O_7$	−173.25±5.75
$Nd_{1.4}Ba_{1.6}Cu_3O_6$	−67.22±5.48	$Nd_{1.4}Ba_{1.6}Cu_3O_7$	−163.22±5.48
$Nd_{1.5}Ba_{1.5}Cu_3O_6$	−69.13±5.87	$Nd_{1.5}Ba_{1.5}Cu_3O_7$	−165.13±5.87
$Nd_{1.6}Ba_{1.4}Cu_3O_6$	−58.84±5.44	$Nd_{1.6}Ba_{1.4}Cu_3O_7$	−154.84±5.44
$Nd_{1.7}Ba_{1.3}Cu_3O_6$	−64.31±6.65	$Nd_{1.7}Ba_{1.3}Cu_3O_7$	−160.31±6.65
$Nd_{1.8}Ba_{1.2}Cu_3O_6$	−19.13±6.23	$Nd_{1.8}Ba_{1.2}Cu_3O_7$	−115.13±6.23
$Nd_{1.9}Ba_{1.1}Cu_3O_6$	−5.57±5.82	$Nd_{1.9}Ba_{1.1}Cu_3O_7$	−101.56±5.82

0.3 and $x = 0.7$. If we admit that the entropy factor does not have any substantial effect on this dependence, then, according to Fig. 1, solid solutions of the composition $0.1 < x < 0.7$ will decompose to form a mixture of solid solutions with $x = 0.1$ and 0.7, while the phases of the composition $0.7 < x < 0.9$ do not decompose. If we link this result with pinning changes, the reason of which is decomposition, the following can be admitted. There is an interval of compositions $0.1 < x < 0.7$ in which the change of the critical current density is observed, and an interval $0.7 < x < 0.9$ in which no changes in pinning should be observed. To reveal the real situation, it is necessary to know the dependence of critical current on the applied magnetic field for all the compositions of solid solutions Nd123. These data are absent from literature.

Let us consider the effect of temperature on the boundary of decomposition of solid solutions. To do this, one should calculate free Gibbs' energy of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_6$ at a temperature close to the synthesis temperature (about 1000 K). As a first approximation, the calculation was performed assuming the independence of enthalpy of formation and entropy on temperature, and the absence of phase transitions within temperature range under consideration. Entropy was estimated using the additive scheme and entropies of binary oxides. Results of estimations are shown in Fig. 2. One can see that an increase in temperature did not bring substantial changes into the decomposition limits. However, it should be noted that calculations at high temperature were performed in the approximation estimating heat capacity and entropy of phases under investigation using the additive scheme with binary oxides. In reality, such an approximation is not always true, which can lead to changes in decomposition limits.

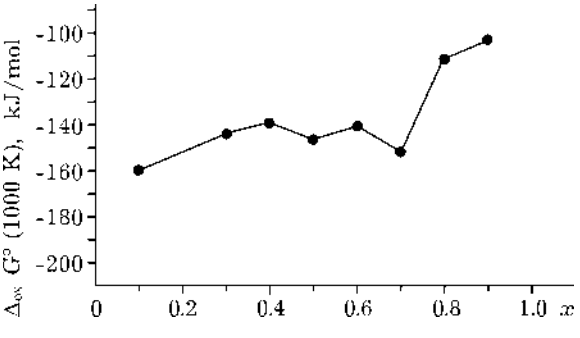

Fig. 2. Dependence of free Gibbs' energy of $Nd_{1+x}Ba_{2-x}Cu_3O_6$ at $T = 1000$ K on composition.

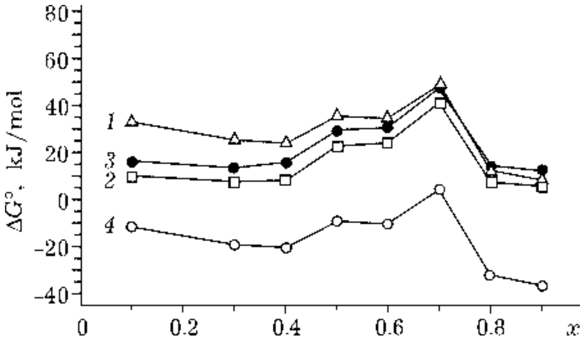

Fig. 3. Dependence of free Gibbs' energy on composition for $Nd_{1+x}Ba_{2-x}Cu_3O_7$ (*1, 2*) and $Nd_{1+x}Ba_{2-x}Cu_3O_6$ (*3, 4*). Temperature, K: 500 (*2, 4*) and 1000 (*1, 3*).

As regards the reasons of the change in the density of critical current, in order to understand whether the decomposition is the reason of peak effect or no, it is useful to examine the dependence of critical current in magnetic fields on time. In the case if the effect of time on the behaviour of critical current exists, then, in consistency with the theory described in [13], decomposition is one of the reasons of the change of critical current. No investigations of this kind had ever been performed.

Further on, let us consider the decomposition not inside the region of homogeneity with respect to neodymium but in the region of reactions resulting in the formation of other phases, for example decomposition into Nd_2CuO_4 and $BaCuO_2$ phases. Enthalpy values needed for calculations were taken from [2–5, 14]: $\Delta_{ox}H° = (-13.4 \pm 4.1)$ kJ/mol for Nd_2CuO_4 and $\Delta_{ox}H° = (-71.4 \pm 1.9)$ kJ/mol for $BaCuO_2$. Figure 3 shows the dependence of free Gibbs' energy for $Nd_{1+x}Ba_{2-x}Cu_3O_7$ and $Nd_{1+x}Ba_{2-x}Cu_3O_6$ at 100 and 500 K for reactions of the general type:

$$Nd_{1+x}Ba_{2-x}Cu_3O_y = (1 + x)/2Nd_2CuO_4 + (2 - x)BaCuO_2 + (0.5 + 0.5x)CuO + zO_2$$

One can see that the decomposition into Nd_2CuO_4 and $BaCuO_2$ phases is impossible at high temperature (1000 K) but it is possible at medium temperature (500 K) for solid solutions with low oxygen content.

It should be noted that investigations at high temperature are necessary for more reliable thermodynamic description of these systems, because the presence of phase transitions and temperature dependence of enthalpy and entropy can change the system's behaviour.

CONCLUSIONS

An experimental dependence of the enthalpy of formation of solid solutions $Nd_{1+x}Ba_{2-x}Cu_3O_y$ (x = 0.1–0.9) from oxides is obtained with the help of dissolution calorimetry procedures. It is demonstrated on the basis of this dependence that inside the homogeneity region ($0.1 < x < 0.7$) solid solutions can decompose into a mixture of phases $Nd_{1.2}Ba_{1.8}Cu_3O_y$ and $Nd_{1.7}Ba_{1.3}Cu_3O_y$. It is established that the decomposition of solid solutions with low oxygen content into a mixture of Nd_2CuO_4 and $BaCuO_2$ phases is possible. The observed decomposition of solid solutions can be a reason of the appearance of superconductor peak effect in Nd–Ba–Cu–O system in magnetic field. The data on the existence of decomposition limits for solid solutions are useful for the understanding of the nature of peak effect and for obtaining superconductors with improved technological parameters.

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