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Thermochemistry of $Nd_{4-2x}Ba_{2+2x}Cu_2O_z$ ($x = 0, 0.1$)

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Abstract

Two various techniques of solution calorimetry were applied to determine thermochemical properties of $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ solid solutions ($x = 0$, 0.1). A satisfactory agreement between results of different experiments is observed. The heat capacity of $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ has been measured by using a differential scanning calorimeter (DSC) in the temperature range of 173–573 K. The results were consistent with the values calculated by Neumann–Kopp's law.

Keywords: Ceramics; Thermochemistry; Enthalpy; Heat capacity

1. Introduction

The presence of the "brown phase" $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ (Nd-422) in materials with melt-textured growth has a strong effect on the superconductivity of Nd-123. Some information about thermodynamic properties of Nd-422 is available only for the limiting composition $x = 0$ [1]. The purpose of this work was to determine the thermochemical properties of $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ solid solutions by various experimental methods.

2. Experimental

2.1. Sample preparation and characterization

The existence of the solid solution $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ ($x = 0$–0.2) with a certain range of homogeneity was reported in [2,3]. In order to investigate the cation nonstoichiometry we prepared a series of solid solutions in steps of $x = 0.05$. The starting substances for the ceramic technology were $BaCO_3$ (pure for analysis), Ln_2O_3 (99.99%) and CuO (99.99%). In the case of solid-phase synthesis preliminarily calcined reagents were thoroughly mixed, ground, pressed into pellets and annealed at 1300 K up to the decomposition of barium carbonate. Then the samples were fired in air at 1173 K for 120 h. The grinding, pressing and annealing procedures were repeated three times. During the final stage of synthesis the samples were kept in oxygen atmosphere at 973 K for 10 h.

The phase composition of the samples was determined by X-ray powder diffraction using a STADI-P diffractometer (Cu $K\alpha_1$-radiation). According to X-ray analysis the samples with $x = 0$, 0.05 and 0.1 were single phase.

2.2. Calorimetric measurements in aqueous solution of HCl at 298.15 K

The enthalpy of dissolution of $Nd_{4-2x}Ba_{2+2x}Cu_2O_z$ (two samples) in an aqueous solution of HCl (1.07 mol dm^{-3}) was determined experimentally. The measurements were performed in a sealed swinging calorimeter with an isothermal ($T = 298.15$ K) jacket, similar to that described in [4,5]. The calorimeter consisted of a thin-walled titanium reaction vessel fitted with a copper resistance thermometer, a calibration heater and a holder for spherical glass bulbs. The calorimeter was contained within a chromium-plated brass case. The resistance thermometer formed one arm of a Wheatstone bridge with a thermometric detection limit of 3×10^{-5} K. The chromium-plated brass case was submerged in a thermostatically controlled water bath with a thermal stability better than 10^{-3} K. The energy equivalent of the calorimeter was determined by electrical heating. The potentiometric circuit used for this purpose provides an accuracy of a few hundredths of a percent.

The investigated substance was dissolved in 55.000(3) g 1.07 mol dm^{-3} HCl and the heat evolved in each experiment was measured. Each attempt was repeated three to four times. The average values of the enthalpy of dissolution of $Nd_{4-2x}Ba_{2+2x}Cu_2O_z$ are:

$$\Delta_{\text{solv}} \bar{H}^\circ_{\text{m}} = -1412 \pm 9\,\text{kJ mol}^{-1} \quad \text{for } x = 0,$$

$$\Delta_{\text{solv}} \bar{H}^\circ_{\text{m}} = -1409 \pm 12\,\text{kJ mol}^{-1} \quad \text{for } x = 0.1.$$

Errors are related to a 95% confidence interval. The overall errors of the enthalpies of formation in all thermochemical cycles were calculated by the

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formula $\sigma = \left(\sum_i \sigma_i^2\right)^{1/2}$, where σ is the standard error of the value used in the calculations. The standard enthalpy of formation of Nd-422 from the elements ($\Delta_f H^\circ_{298}$) can be obtained from an adequate summation of the enthalpies of the following reactions [6–10]:

$$\begin{aligned}&\mathrm{Nd}_{4-2x}\mathrm{Ba}_{2+2x}\mathrm{Cu}_2\mathrm{O}_{10-x(\mathrm{cr})} + 2(10-x)\,\mathrm{HCl}_{(\mathrm{sol})}\\ &\quad = (4-2x)\,\mathrm{NdCl}_{3(\mathrm{sol})} + (2\,+\,2x)\mathrm{BaCl}_{2(\mathrm{sol})}\\ &\qquad + 2\mathrm{CuCl}_{2(\mathrm{sol})} + (10-x)\,\mathrm{H_2O}, \quad \Delta_r H_1 \end{aligned} \tag{1}$$

$$\mathrm{Nd}_{(\mathrm{cr})} + 3\mathrm{HCl}_{(\mathrm{sol})} = \mathrm{NdCl}_{3(\mathrm{sol})} + 3/2\mathrm{H}_{2(\mathrm{g})}, \quad \Delta_r H_2 = -689.6 \pm 2.0\,\mathrm{kJ\,mol^{-1}} \tag{2}$$

$$\mathrm{Ba}_{(\mathrm{cr})} + \mathrm{Cl}_{2(\mathrm{g})} + [\mathrm{HCl}_{(\mathrm{sol})}] = \mathrm{BaCl}_{2(\mathrm{sol})}, \quad \Delta_r H_3 = -863.7 \pm 1.3\,\mathrm{kJ\,mol^{-1}} \tag{3}$$

$$\mathrm{Cu}_{(\mathrm{cr})} + \mathrm{Cl}_{2(\mathrm{g})} + [\mathrm{HCl}_{(\mathrm{sol})}] = \mathrm{CuCl}_{2(\mathrm{sol})}, \quad \Delta_r H_4 = -256.6 \pm 1.6\,\mathrm{kJ\,mol^{-1}} \tag{4}$$

$$\begin{aligned}&1/2\mathrm{H}_{2(\mathrm{g})} + 1/2\mathrm{Cl}_{2(\mathrm{g})} + [\mathrm{H_2O}_{(\mathrm{sol})}] = \mathrm{HCl}_{(\mathrm{sol})},\\ &\Delta_r H_5 = -164.4 \pm 0.2\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{5}$$

$$\begin{aligned}&\mathrm{H}_{2(\mathrm{g})} + 1/2\mathrm{O}_{2(\mathrm{g})} + [\mathrm{HCl}_{(\mathrm{sol})}] = \mathrm{H_2O}_{(\mathrm{sol})},\\ &\Delta_r H_6 = -285.85 \pm 0.04\,\mathrm{kJ\,mol^{-1}}\end{aligned} \tag{6}$$

The standard enthalpy of formation of the solid solution according to

$$\begin{aligned}&(4-2x)\mathrm{Nd}_{(\mathrm{cr})} + (2\,+\,2x)\mathrm{Ba}_{(\mathrm{cr})} + 2\mathrm{Cu}_{(\mathrm{cr})} + (10-x)/2\mathrm{O}_{2(\mathrm{g})}\\ &\quad = \mathrm{Nd}_{4-2x}\mathrm{Ba}_{2+2x}\mathrm{Cu}_2\mathrm{O}_{10-x(\mathrm{cr})}\end{aligned} \tag{7}$$

is given as

$$\begin{aligned}\Delta_r H_7 &= \Delta_f H^\circ_{298} = -\Delta_r H_1 + 2\cdot(2-x)\Delta_r H_2\\ &\quad + 2\cdot(1+x)\Delta_r H_3 + 2\times\Delta_r H_4 - (8+4x)\Delta_r H_5 + (10-x)\Delta_r H_6.\end{aligned}$$

The standard enthalpies of formation of the solid solutions from the oxides ($\Delta_{f,ox} H^\circ_{298}$) were calculated using the obtained values $\Delta_f H^\circ_{298}$ for both solutions and reliable reference data on the standard enthalpies of formation of neodymium oxide (-1806.9 ± 3.0 [11]), barium oxide (-548.02 ± 1.97 [12]) and copper oxide (-157.07 ± 0.84 [13]); all values in kJ mol^{-1}:

$$\Delta_{f,ox} H^\circ_{298} = \Delta_f H^\circ_{298} - \sum_i \nu_i \Delta_f H^\circ_{298,i},$$

where ν_i is an index for the corresponding oxide in the formula $(\mathrm{Nd_2O_3})_{2-x}(\mathrm{BaO})_{2+2x}(\mathrm{CuO})_2$. The results of the calculations of the thermodynamic functions are summarized in Table 1.

Table 1
Thermochemical properties of $\mathrm{Nd}_{4-2x}\mathrm{Ba}_{2+x}\mathrm{Cu_2O}_z$ (in kJ mol^{-1})

Phase	$\Delta_f H^\circ_{298}$	$\Delta_{f,ox} H^\circ_{298}$	$\Delta_{f,ox} H^\circ_{974}$	$H^\circ_{974} - H^\circ_{298}$
$x=0$, $z=10$	-5131 ± 12	-107 ± 15	-92 ± 24	324.4 ± 6.0
$x=0.1$, $z=9.9$	-5074 ± 15	-121 ± 17	–	323.2 ± 6.0

2.3. Calorimetry measurements in a lead–borate melt at 974 K

The heat content and enthalpy of solution of $\mathrm{Nd_4Ba_2Cu_2O_{10}}$ were determined in a Tian–Calvet high-temperature heat-conducting microcalorimeter; the experimental procedure was described in [14]. In a first step of the experiment we tried to reproduce the result of the analogous investigation of $\mathrm{Y_2BaCuO_5}$ [15]. The results of our experiments are in excellent agreement with the literature data (Table 2).

To determine the enthalpy of formation from the oxides ($\Delta_f H^\circ_{ox}$), weighed samples of $\mathrm{Nd_4Ba_2Cu_2O_{10}}$ (10–30 mg) were dissolved in a lead–borate melt $2\mathrm{PbO}\cdot\mathrm{B_2O_3}$ (~30 g); the ratio between the solute and the solvent virtually corresponded to infinite dilution. The samples were preliminarily held at a constant temperature 974 K at air and then dropped into the calorimeter cell filled with the melt heated to the same temperature. The following formula was used for the calculation of the enthalpy of formation from the oxides at 974 K:

$$\Delta_{f,ox} H^\circ_{974} = \sum_i \nu_i \Delta_{solv} H^\circ_{974,i} - \Delta_{solv} H^\circ_{974,\text{Nd-422}},$$

where the terms on the right hand denote the respective enthalpies of solution. The heat content of $\mathrm{Nd_4Ba_2Cu_2O_{10}}$ was determined by dropping a sample held at 298 K into an empty calorimeter cell heated to 974 K. Unfortunately, the results of drop solution were unsatisfactory due to kinetic restrictions so we used only $\Delta_{solv} H^\circ_{974,i}$ and $[H_T - H_{298}]_i$ for the subsequent calculations. The heat contents and enthalpies of solution of $\mathrm{Nd_2O_3}$, BaO and CuO for the calculations are listed in Table 2.

2.4. DSC-calorimetry measurements

The temperature dependences of the heat capacities of $\mathrm{Nd}_{4-2x}\mathrm{Ba}_{2+x}\mathrm{Cu_2O}_z$ ($x=0$, 0.1) were studied in air ($P_{\mathrm{O_2}} = 0.21$ atm) by differential scanning calorimetry (DSC-30 unit, Mettler TA-3000 thermal analyzer) in the range 173–573 K. The heat capacity of each sample was measured three times within successive temperature intervals of 150 K which overlapped in the range of at least 30 K. The relative error of the heat capacity measurements was 3–5%. The accuracy of the calorimetric measurements was periodically checked with certified samples of sapphire, corundum and aluminum.

The computation was carried out by using a reduced form of Bermann–Brown approximation [18]. The results are represented as

$$C_p\,(\mathrm{J\,mol^{-1}\,K^{-1}}) = 521.5 - 892.5T^{-0.5} - 1373586T^{-2} \quad (x=0),$$

$$C_p\,(\mathrm{J\,mol^{-1}}\,K^{-1}) = 497.7 - 266.3T^{-0.5} - 2477573T^{-2} \quad (x=0.1).$$

Table 2
Enthalpy of dissolution in a lead–borate melt ($\Delta_{solv}H$), enthalpy of drop solution from 298 K to T, K ($\Delta_{ds}H$) and heat contents ($H^\circ_T - H^\circ_{298}$) of $\mathrm{Ln_2BaCuO_5}$ (Ln = Y, Nd) and constituent oxides (in kJ mol^{-1})

Compound	T (K)	$\Delta_{solv}H$	$-\Delta_{ds}H$	$H^\circ_T - H^\circ_{298}$
$\mathrm{Y_2BaCuO_5}$	977	-96.9 ± 1.5 [15]	48.9 ± 2.0	145.8 ± 1.3 [15]
$\mathrm{Y_2BaCuO_5}$	974	–	48.0 ± 9.4	144.2 ± 2.8
$1/2\mathrm{Nd_4Ba_2Cu_2O_{10}}$	974	-133.4 ± 11.3	–	157.7 ± 2.7
$\mathrm{Nd_2O_3}$	977	-85.1 ± 3.7 [16]	–	88.37 [19]
BaO	975	-127.7 ± 1.9 [15]	-90.8 ± 2.2 [17]	36.15 [15]
CuO	977	33.5 ± 0.4 [16]	67.9 ± 0.6	33.9 ± 0.4 [15]

3. Results and discussion

The thermochemical properties of the investigated substances at 298.15 and 974 K were calculated by using Hess's law. The recommended values of thermodynamic functions are presented in Table 1, where it is evident that the enthalpies of formation of $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ ($x = 0$, 0.1) from oxides are close. It should be noted that the agreement between result of drop experiment and heat deduced from the measured values of C_p for $Nd_4Ba_2Cu_2O_{10}$ is satisfactory. They are 315.4 ± 5.7 and $324.4 \pm 6.0\,kJ\,mol^{-1}$, respectively. The sum of the heat contents of constituent oxides at 974 K is $315.5\,kJ\,mol^{-1}$ [19], therefore the heat capacities of $Nd_{4-2x}Ba_{2+x}Cu_2O_z$ are consistent with the values calculated by Neumann–Kopp's law.

Unfortunately, we cannot propose a reasonable explanation of essential difference in the values $\Delta_{f,ox}H^\circ$, which were obtained by calorimetry in this work and EMF-measurements reported in [1] ($\Delta_{f,ox}H^\circ_{298} = -137.8\,kJ\,mol^{-1}\,Nd_2BaCuO_5$). One of the possible reasons is an error in potential-forming reaction in [1]. We tried to reproduce analogous experiment with the same electrochemical cell, but the result was unsatisfactory: the value of $\Delta_f H^\circ_{ox}$ was smaller than that obtained in [1], but more than the result of calorimetry investigation. The same situation is observed in the case of Sm-422 which has cation nonstoichiometry too. On the other hand, the experiments with cation-stoichiometric phase Ln-211 (Ln = Y, Gd, Dy) demonstrate a better agreement between EMF and calorimetric methods. Apparently, it is necessary to solve two tasks to reveal the reasons of this discrepancy. The first task is to test the reproducibility of the EMF measurement with various ratios of components in the electrode mixture. And another task is to investigate additionally the high-temperature phase equilibria in the barium-rich part of Nd_2O_3–CuO–BaO–BaF_2 phase diagram.

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