

Thermochemistry of 1 : 2 : 4 phases in the $\text{Ho}_2\text{O}_3\text{--CuO--BaO}$, $\text{Dy}_2\text{O}_3\text{--CuO--BaO}$ systems

N.I. Matskevich^{a,*}, T.L. Popova^a, L.-J. Johansson^b, P. Berastegui^b

^a *Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russia*

^b *Chalmers University of Technology and Gothenburg University, S-412 96 Gothenburg, Sweden*

Received 14 May 1997; received in revised form 9 December 1997; accepted 17 December 1997

Abstract

Thermochemical investigations of 1 : 2 : 4 phases in the Ho(Dy)--Ba--Cu--O systems were performed by solution calorimetry in 6 N HCl at 323 K. On the basis of direct dissolution enthalpies of Ho_2O_3 , Dy_2O_3 , BaCO_3 , $\text{HoBa}_2\text{Cu}_4\text{O}_8$, $\text{DyBa}_2\text{Cu}_4\text{O}_8$ and CuO thermodynamic data were obtained for the formation of 1 : 2 : 4 phases: 1 – from the oxides; 2 – from the mixture including BaCuO_2 ; and 3 – from the mixture including BaCO_3 . The data obtained showed that the abovementioned phases were thermodynamically stable with respect to the mixture with BaCuO_2 , namely, with respect to the reaction: $1/2\text{Ln}_2\text{O}_3 + 2\text{CuO} + 2\text{BaCuO}_2 + 1/4\text{O}_2 = \text{LnBa}_2\text{Cu}_4\text{O}_8$. © 1998 Elsevier Science B.V.

Keywords: Calorimetry; Quaternary system; Stability; Thermodynamics

1. Introduction

For the successful development of any field of material science, a knowledge of the thermodynamic stability of the compounds involved is necessary. The existence of the superconducting cuprates thus raises the question of their thermodynamic stability. The thermodynamic stability of the 1 : 2 : 3 and 1 : 2 : 4 compounds in the Y--Ba--Cu--O system has been examined by these authors as well as other researchers [1–7]. It has been shown that the stability of Y-1 : 2 : 4 was greater than that of Y-1 : 2 : 3 . As a continuation of this work, it was considered that to investigate the stability of the 124 compounds with different lanthanoids was of interest. This paper is devoted to the

investigation of the thermodynamic stability of 1 : 2 : 4 phases in the Ho(Dy)--Ba--Cu--O system. Two aspects of the stability problem have been studied:

1. the stability with respect to the mixture of oxides with the same nominal composition; and
2. the stability with respect to external reagent, namely, CO_2 .

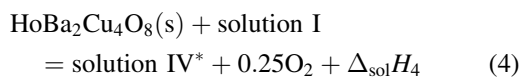
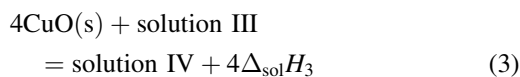
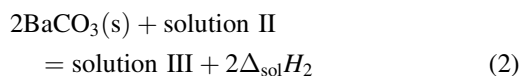
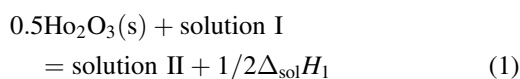
2. Experimental

2.1. Method of investigation

Solution calorimetry in 6 N HCl was used to obtain thermochemical data in the Ho(Dy)--Ba--Cu--O system. The experiments were performed in an automatic

*Corresponding author. Fax: 007 3832 35 59 60; e-mail: nata@casper.che.nsk.su

dissolution calorimeter with an isothermal shield which has been described elsewhere [8,9]. The temperature of measurements was 323 K. The thermodynamic cycles were constructed as described in a previous paper [3]. The set of thermochemical reactions chosen allows one to obtain an internally consistent set of thermochemical data without making use of reference literature data. The calorimetric reactions were designed in such a way that it was possible to compare the dissolution enthalpy, H , of the mixture, namely, $1/2\text{Ln}_2\text{O}_3 + 2\text{BaCO}_3 + 4\text{CuO}$ with the dissolution enthalpy of $\text{LnBa}_2\text{Cu}_4\text{O}_8$. The example of dissolution processes to get the formation enthalpy of the Ho124 phase from Ho_2O_3 , BaCO_3 , CuO is given below:

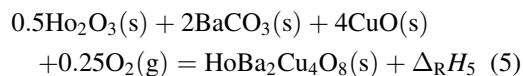


Here, solution I is a solution of HCl with concentration of 6 N.

It is also possible to construct an analogous cycle for the Dy–Ba–Cu–O system phases to determine the formation enthalpy of Dy124 phase.

It is useful to add some comments to the above-mentioned cycle. As is well known, copper in superconducting cuprate can have different valence states (Cu^{+1} , Cu^{+2} , Cu^{+3}). Hence, solutions obtained in different ways, i.e. solution IV obtained after dissolution of the mixture and solution IV* obtained after dissolution of $\text{LnBa}_2\text{Cu}_4\text{O}_8$ (Ln=Ho, Dy) phase may be different. This method makes it necessary to solve the most difficult problem of solution calorimetry, namely, the establishment of the identity of solutions obtained in different ways. The identity of two solutions, namely, solution IV and solution IV* was proved by measuring the spectra of these solutions in the 10^4 – $3 \times 10^4 \text{ cm}^{-1}$ range. It was shown that, in experiments conducted in air, the spectra of the solutions became identical within 1–2 min after dissolution is com-

pleted. Another problem connected with identity of solutions obtained in different ways, which the authors would like to describe in this paper, is the problem connected with the possibility of Cu^{+3} to react with HCl forming Cl_2 and then with that of Cu^{+1} to react with Cl_2 forming HCl. To prove that there is no chlorine here, the authors performed the following experiment. Ho124 phase was dissolved in a special vessel (with HCl) which has the tube placed in water. When Ho124 reacted with HCl, there were no vials of gas going through water. Then the authors tried to detect chlorine in water by adding KI. There was no reaction with KI. In addition, the paper with the solution of KI was placed under solution of HCl where Ho124 phase was dissolved. There was no reaction with KI. Taking into account the above-mentioned facts, it was possible to conclude that there was no chlorine here. So, the solutions obtained in different ways were identical. On the basis of obtained facts, it is possible to write the following summing reaction (5) as reaction (1)+reaction (2)+reaction (3)–reaction (4):



Here, $\Delta_{\text{R}}H_5 = 0.5\Delta_{\text{sol}}H_1 + 2\Delta_{\text{sol}}H_2 + 4\Delta_{\text{sol}}H_3 - \Delta_{\text{sol}}H_4$.

2.2. Preparation of samples

The following materials were used in the experiments:

- Ho_2O_3 (high purity), Dy_2O_3 (high purity) which before use were kept at 1023 in air for 10 h;
- CuO (high purity) which was heated in O_2 for 15 h ($T=900 \text{ K}$); and
- BaCO_3 (high purity) which was kept at 650 K in air for 4 h.

The samples of $\text{HoBa}_2\text{Cu}_4\text{O}_8$, $\text{DyBa}_2\text{Cu}_4\text{O}_8$ were prepared from $\text{Ho}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ or $\text{Dy}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$, $\text{Ba}(\text{NO}_3)_2$ and $\text{Cu}(\text{NO}_3)_2 \cdot n\text{H}_2\text{O}$ at Chalmers University of Technology and University of Gothenburg, Gothenburg, Sweden [10]. Synthesis procedure included two simple steps:

1. the formation of metal citrate chelates in a mixed solvent of ethylenglycol and water without ageing and pH adjustment; and

2. the subsequent heat-decomposition of the gel to obtain a power precursor.

The required amount of nitrate salts was dissolved in H₂O. Citric acid and ethylenglycol were added in the ratio of one and 30 mol to each mole of metal, respectively. The solution was condensed at 393 K, and then heated at 463 K until a brownish black gel was obtained. The gel was decomposed to a powder at 573 K. The powder precursor was calcined at 1073 K for 24 h under an atmosphere of flowing oxygen. The resulting black product was then pressed into pellets, sintered at 1093 K for 60 h with one intermediate grinding and cooled down to room temperature at a rate of 150 K/h; all heating and cooling procedures were performed in oxygen at 1 atm pressure. Further sintering at 1093 K for 4 days was necessary to obtain a single phase.

All compounds were characterized by X-ray powder diffraction and chemical analyses. According to the results of the analyses, the involved compounds were found to be of single phases. The phase analysis performed by a differential solution method indicated the purity of the compounds to be ca. 1–2%. The only impurity phase was CuO. No 1 : 2 : 3 phase or BaCuO₂ was detected.

3. Results and discussion

The enthalpies of dissolution of Ho₂O₃, Dy₂O₃, BaCO₃, CuO were taken from previous papers of

the present authors [1–4]. The average values calculated from six experimental values are presented below.

$$\begin{aligned} \Delta_{\text{sol}}H(\text{Ho}_2\text{O}_3, 323.15 \text{ K}) \\ = -364.06 \pm 4.28 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{sol}}H(\text{Dy}_2\text{O}_3, 323.15 \text{ K}) \\ = -370.72 \pm 4.97 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{sol}}H(\text{CuO}, 323.15 \text{ K}) \\ = -51.13 \pm 2.13 \text{ kJ/mol} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{sol}}H(\text{BaCO}_3, 323.15 \text{ K}) \\ = -15.27 \pm 2.51 \text{ kJ/mol} \end{aligned}$$

The data of dissolution enthalpies of HoBa₂Cu₄O₈, DyBa₂Cu₄O₈ are given in Table 1.

The solution enthalpies were used to calculate enthalpies of reaction of 1 : 2 : 4 phases from binary oxides. The procedure of calculation was the following. As the first step, measured enthalpies of the dissolution of Ho₂O₃, BaCO₃, CuO, Dy₂O₃ were used to calculate reaction enthalpies of the 1 : 2 : 4 phase formation from the mixture including BaCO₃, CuO, Ho₂O₃ (or Dy₂O₃) according to the reaction (5). Then, using the reaction enthalpy of BaO+CO₂=BaCO₃ [11], it was possible to obtain reaction enthalpies from binary oxides. The value of $\Delta_{\text{R}}H$ for BaO+CO₂=BaCO₃, taken from [11], was the following: -269.49 kJ/mol. The results are given in Table 2.

It may be noted that the enthalpy of formation of the 1 : 2 : 4 phase from binary oxides has a great negative

Table 1

Samples	<i>m/g</i>	Heat/J	$\Delta_{\text{sol}}H$ for single experiments/(kJ/mol) (<i>T</i> =323.15 K)	The mean value with error margin/(kJ/mol)
HoBa ₂ Cu ₄ O ₈	0.150410	144.114	-787.37	
HoBa ₂ Cu ₄ O ₈	0.150095	140.835	-771.07	
HoBa ₂ Cu ₄ O ₈	0.147335	139.988	-780.79	
HoBa ₂ Cu ₄ O ₈	0.151055	142.881	-777.30	
HoBa ₂ Cu ₄ O ₈	0.150500	141.869	-774.64	
HoBa ₂ Cu ₄ O ₈	0.148500	141.634	-783.77	-779.16±6.38
DyBa ₂ Cu ₄ O ₈	0.149965	142.412	-778.07	
DyBa ₂ Cu ₄ O ₈	0.150060	141.418	-772.15	
DyBa ₂ Cu ₄ O ₈	0.150440	141.835	-772.47	
DyBa ₂ Cu ₄ O ₈	0.150380	143.441	-781.53	
DyBa ₂ Cu ₄ O ₈	0.150265	144.423	-787.48	-778.34±8.08

Table 2

Phase	$\Delta_{\text{ox}}H^{\text{a}}$ (323.15 K)/(kJ/mol)	$\Delta_{\text{R}}H_1^{\text{b}}$ (323.15 K)/(kJ/mol)	$\Delta_{\text{R}}H_2^{\text{c}}$ (323.15 K)/(kJ/mol)
HoBa ₂ Cu ₄ O ₈	-177.0±9.0	-42.0±9.3	-362.1±9.0
DyBa ₂ Cu ₄ O ₈	-181.0±10.4	-46.1±10.7	-357.9±10.4

^a Enthalpy of formation of 1 : 2 : 4 phases from binary oxides, namely, 0.5Ln₂O₃+2BaO+4CuO+0.25O₂=LnBa₂Cu₄O₈.

^b Enthalpy of formation of 1 : 2 : 4 phases from Ln₂O₃, CuO, BaCuO₂, namely: 0.5Ln₂O₃+2CuO+2BaCuO₂+0.25O₂=LnBa₂Cu₄O₈.

^c Enthalpy of reaction of the 1 : 2 : 4 phase with CO₂, namely: LnBa₂Cu₄O₈+CO₂=1/2La₂O₃+4CuO+2BaCO₃+0.25O₂.

value. This is an unusual fact if superconducting complex oxides are compared with nonsuperconducting complex oxides. Some examples of formation enthalpies of nonsuperconducting complex oxides from binary oxides taken from Ref. [11] are given below.

$$\Delta_{\text{ox}}H(298.15, \text{MnSiO}_3) = -24.68 \text{ kJ/mol}$$

$$\Delta_{\text{ox}}H(298.15, \text{CdSiO}_3) = -20.08 \text{ kJ/mol}$$

$$\Delta_{\text{ox}}H(298.15, \text{CaAl}_4\text{O}_7) = -6.28 \text{ kJ/mol}$$

It is clear that the formation enthalpies of MnSiO₃, CdSiO₃, CaAl₄O₇ from binary oxides are not very large values. The reason why enthalpies of formation of superconducting oxides from binary oxides are negative large values is a question under discussion. Some investigators consider superconducting oxides as anion deficient perovskites and assume that high enthalpies are likely due to increased coordination number of Ba and of its high Lewis acidity. We tried to explain the high value of formation enthalpies from the following viewpoint. We suggest that it is possible to assume that the formation enthalpy of reaction LnBa₂Cu₃O_{6.0}+CuO=LnBa₂Cu₄O₇ is nearly zero. In this case, the formation enthalpy of 1 : 2 : 3 phase from binary oxides is equal to the formation enthalpy of the 1 : 2 : 4 phase. We have taken this value from our unpublished work: $\Delta_{\text{ox}}H(323.15 \text{ K}, \text{YBa}_2\text{Cu}_3\text{O}_{6.0}) = -88 \text{ kJ/mol}$. Thus, assuming that the value of oxidation of 1 : 2 : 3 phase is the same as the value of oxidation of BaO up to BaO₂, it was possible to estimate the enthalpy of reaction LnBa₂Cu₄O₇+1/2O₂=LnBa₂Cu₄O₈. The latter value is -85 kJ/mol of O [12]. On the basis of these data, we could estimate the formation enthalpy of LnBa₂Cu₄O₈ from binary oxides as the following value $\Delta_{\text{ox}}H(\text{LnBa}_2\text{Cu}_4\text{O}_8) = -173 \text{ kJ/mol}$. Evidently, the obtained values are in a good agreement with experimental data.

The data on the formation enthalpy of LnBa₂Cu₄O₈ from binary oxides, namely, 1/2Ln₂O₃+4CuO+2BaO+1/4O₂=LnBa₂Cu₄O₈ (see Table 1) allow us to conclude that the formation reaction of complex oxides from binary ones is thermodynamically favourable. Of course, it is necessary to take into account the Gibbs free energy in order to obtain the direction of reaction. The Gibbs free energy is defined as $G=H-T\times S$. Below, we shall show that it is possible to assume that the entropy of formation of LnBa₂Cu₄O₈ from binary oxides is a small value. YBa₂Cu₄O₈ was chosen as an example because there are no data for entropies of DyBa₂Cu₄O₈ and HoBa₂Cu₄O₈. Entropies of binary oxides and YBa₂Cu₄O₈ taken from Refs. [13,14] are given below: $S^0(\text{Y}_2\text{O}_3) = 99.08 \pm 4.2 \text{ J/K mol}$, $S^0(\text{BaO}) = 72.07 \pm 0.38 \text{ J/K mol}$, $S^0(\text{CuO}) = 42.63 \pm 0.21 \text{ J/K mol}$ and $S^0(\text{YBa}_2\text{Cu}_4\text{O}_8) = 364.5 \text{ J/K mol}$. The entropy of the mixture of 1/2Y₂O₃+2BaO+4CuO (YBa₂Cu₄O_{7.5}) is 364.2 J/K mol. As it is possible to see, this value is practically the same as the measured entropy of YBa₂Cu₄O₈ phase. It is also necessary to mention that, according to our experiments, the entropies of complex oxides change slightly with the oxygen index for reliable calculations. Entropies measured using low-temperature calorimetry by the authors for two samples of 1 : 2 : 3 phases with different oxygen indices had no large difference: $S^0(\text{YBa}_2\text{Cu}_3\text{O}_{6.9}) = 321.7 \pm 1.3 \text{ J/K mol}$; and $S^0(\text{YBa}_2\text{Cu}_3\text{O}_{6.5}) = 319.5 \pm 1.2 \text{ J/K mol}$. In this connection, it is possible to assume that entropies of HoBa₂Cu₄O₈ or DyBa₂Cu₄O₈ are the same values as entropies of HoBa₂Cu₄O_{7.5} or DyBa₂Cu₄O_{7.5}. As is shown below, the last values were assumed to be those of the mixture of 1/2Ho₂O₃ (or Dy₂O₃)+2BaO+4CuO. The value of $T\times S$ connected with 1/4O₂ is not so large at room temperature. For $T=323.15 \text{ K}$, this value is 16.564 kJ/mol. So, it is possible to draw a conclusion about

thermodynamic stability on the basis of the enthalpy of formation.

The experimental data were also used to study the thermodynamical phase stability. First of all, we will confine our attention to thermodynamic stability with respect to the phase mixture with the same nominal composition, i.e. $1/2\text{Ln}_2\text{O}_3+4\text{CuO}+2\text{BaCuO}_2$. Experimental results on synthesis showed that the main impurity phase was BaCuO_2 . So, it is necessary to study the thermodynamic stability with respect to mixtures involving this phase. Using experimental data for the reaction $1/2\text{Ln}_2\text{O}_3+4\text{CuO}+2\text{BaCO}_3+0.5\text{O}_2=\text{LnBa}_2\text{Cu}_4\text{O}_8+2\text{CO}_2$ ($\text{Ln}=\text{Ho}, \text{Dy}$) obtained in this paper, and the data for the reaction $\text{BaCO}_3+\text{CuO}=\text{BaCuO}_2+\text{CO}_2$ ($\Delta_{\text{R}}H=-202.01\pm 1.9$ kJ/mol [2]), it is possible to obtain thermodynamical data for the stability of 1 : 2 : 4 phases with respect to mixtures including BaCuO_2 . The results are given in Table 2. Here, $\Delta_{\text{ox}}H_1$ is the enthalpy of formation of 1 : 2 : 4 phases from Ln_2O_3 , CuO , BaCuO_2 , namely: $1/2\text{Ln}_2\text{O}_3+2\text{CuO}+2\text{BaCuO}_2+1/4\text{O}_2=\text{LnBa}_2\text{Cu}_4\text{O}_8$.

The results allow one to conclude the following: it was established that 1 : 2 : 4 phases were thermodynamically stable at room and lower temperatures. The result is different from that obtained for 1 : 2 : 3 phase in the Ho–Ba–Cu–O system. As it was shown in an earlier paper of the present authors [1], $\text{HoBa}_2\text{Cu}_3\text{O}_{6.9}$ was thermodynamically unstable at room and lower temperatures with respect to the mixture including Ho_2O_3 , CuO , BaCuO_2 . Some comments on our data and literature data for 124 phases are given below.

There were no data for Ho(Dy)124 phases in the literature. For this reason, we can compare our results on the stability of Ho(Dy)124 phases only with Y124 phase. According to available literature data, thermodynamic characteristics and thermodynamic stability of $\text{YBa}_2\text{Cu}_4\text{O}_8$ phase were studied in Refs. [5,7,15–17]. Navrotsky's research [7,15] performed by high-temperature reaction calorimetry using molten lead borate as a solvent showed that the 1 : 2 : 4 phase was thermodynamically less favourable than mixtures including BaCuO_2 mixtures. There is also a proof that $\text{YBa}_2\text{Cu}_3\text{O}_8$ is thermodynamically unstable with respect to mixtures including Y_2O_3 , $\text{Ba}_2\text{Cu}_3\text{O}_{5+d}$, CuO in the investigation [16] obtained by the solution calorimetry in 4 N HClO_4 . As a contradiction to these facts, Voronin [8] reported that 1 : 2 : 4 phase was

stable in exploitation regime. The stability of 1 : 2 : 4, 1 : 2 : 3, and 2 : 4 : 7 phases was studied by the present authors [17]. According to these data, the 1 : 2 : 4 phase is thermodynamically more stable than 1 : 2 : 3 compound.

The analysis of thermodynamic stability problem of 1 : 2 : 3, 1 : 2 : 4, 2 : 4 : 7 substances is given in Ref. [5]. The authors established thermodynamic instability of the 1 : 2 : 3 and thermodynamic stability of the 1 : 2 : 4 phases.

Our experimental data obtained are in a good agreement with the data of Refs. [5,8,17]. One of the reasons for the discrepancy with the results of other researchers is due to different qualities of the samples employed. Below, we give some special comments concerning discrepancies with Navrotsky's results. The authors had very good agreements with the data of Navrotsky on the 1 : 2 : 3 phase. $\Delta_{\text{ox}}H$ (298.15; $\text{YBa}_2\text{Cu}_3\text{O}_{6.88}$) obtained by Navrotsky is equal to 116.6 ± 5.8 kJ/mol [7]. $\Delta_{\text{ox}}H$ (323.15; $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$) obtained by the authors is equal to -122 ± 5 kJ/mol [3]. The difference between enthalpies of formation of the Y124 phases in the research of Navrotsky and ours is not so large:

$$\begin{aligned} \Delta_{\text{ox}}H(298.15; \text{YBa}_2\text{Cu}_4\text{O}_8) \\ = -155.8 \pm 6.7 \text{ kJ/mol [7]} \end{aligned}$$

$$\begin{aligned} \Delta_{\text{ox}}H(323.15; \text{YBa}_2\text{Cu}_4\text{O}_8) \\ = -174.6 \pm 6.4 \text{ kJ/mol [our work, in press]}. \end{aligned}$$

Navrotsky and our group essentially used different values of BaCuO_{2+x} for the calculation of the reaction enthalpy of formation of the 1 : 2 : 4 phase from the mixture, including Y_2O_3 , CuO and BaCuO_2 . We used $\Delta_{\text{ox}}H$ (323.15; BaCuO_2) = -66 ± 5 kJ/mol [3]. Navrotsky used $\Delta_{\text{ox}}H$ (298.15; BaCuO_2) = -85.2 ± 2.4 kJ/mol [7]. If our data for BaCuO_2 are used in Navrotsky experiments with the Y124 phase, the result would be that the Y124 phase is stable in respect to mixtures of Y_2O_3 , CuO , and BaCuO_2 , and the enthalpy of this reaction with our data for BaCuO_2 will be -23.8 instead of -39.6 , obtained in our study (Inorgan. Materials, 1997, in press).

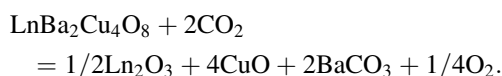
It is also useful to mention papers concerning the solution calorimetry of other superconducting phases in addition to 124 phases. There are about 10 works devoted to thermodynamic investigation of superconducting phases by solution calorimetry [18–25]. The

Table 3

Solvent	Phase	$\Delta_{\text{ox}}H/(\text{kJ/mol})$	Reference
HClO ₄	YBa ₂ Cu ₃ O _{6.93}	-124±17	[18]
HCl	YBa ₂ Cu ₃ O _{6.9}	-122±5	[3]
HCl	YBa ₂ Cu ₃ O _{6.96}	-114.6±9	[25]

two solvents were used for this purpose, namely, HCl and HClO₄. Investigations [18–20,23,25] were performed using HClO₄, whereas investigations [21,22,24,25] were performed using HCl. Most papers are devoted to the investigation of the Y–Ba–Cu–O system [18–25]. Using both, HCl and HClO₄ the calorimetric cycles were constructed in such a way that it was possible to compare solution enthalpies of mixtures including Y₂O₃ or Y, CuO, BaO or BaCO₃ and solution enthalpies of superconducting phases. As already mentioned, this was a disputable question even in case of superconducting phase investigations by solution calorimetry when the solutions obtained in different ways are identical. Nevertheless, the good agreement for data of YBa₂Cu₃O_x obtained in different solvents makes it possible to state that there are no essential systematic errors in both the cases. Some data for 123 phases obtained in different solvents are presented in Table 3, which confirm the above-mentioned facts.

Thus, the phase stability of HoBa₂Cu₄O₈ and DyBa₂Cu₄O₈ was studied with respect to the interaction with CO₂. Data are presented in Table 2. Here, $\Delta_{\text{R}}H$ is the enthalpy of formation of the reaction with CO₂, namely:



The data of Table 2 show that the reaction enthalpy is negative. It means that the reaction takes place at room temperature. It confirms the well-known fact that the superconducting phase reacts with CO₂. X-ray powder diffraction shows BaCO₃ impurity after 2–3 weeks.

4. Conclusion

The investigation of 1 : 2 : 4 phases in the Ho(Dy)–Ba–Cu–O system performed by solution calorimetry

has shown that HoBa₂Cu₄O₈ and DyBa₂Cu₄O₈ are stable at room temperature.

Acknowledgements

This work was supported by Scientific Council of “Superconductivity” direction, Russian Scientific–Technical Programme, section “Basis of Chemistry and Technology of Superconductors” (Grant N 96055 “Prognoz”).

References

- [1] N.I. Matskevich, 49th Calorimetry Conference, New Mexico, USA, 1994, p. 102.
- [2] N.I. Matskevich, T.L. Popova, E.S. Zolotova, M.A. Starikov, *Thermochim. Acta* 254 (1995) 41.
- [3] N.I. Matskevich, T.L. Popova, F.A. Kuznetsov, V.A. Titov, O.G. Potapova, V.P. Shaburova, *Mendeleev Commun.* 1 (1993) 29.
- [4] N.I. Matskevich, T.L. Popova, L.-J. Johansson, P. Berastegui, The Third M.V. Mokhosoev Memorial International Seminar on New Materials, Irkutsk, Russia, 1996, p. 32.
- [5] I. Karpinski, H. Schwer, K. Conder, E. Jilek, E. Kaldis, C. Rossel, H.P. Lang, T. Baumann, *Appl. Supercond.* 1 (1993) 333.
- [6] G.F. Voronin, S.A. Degterov, *Physica C* 176 (1991) 387.
- [7] Z. Zhou, A. Navrotsky, *J. Mater. Res.* 7 (1992) 2920.
- [8] V.V. Repkov, N.I. Matskevich, G.Ye. Osipova, S.G. Yerofeev, Preprint, Inst. Inorg. Chem., Sib. Branch of the Russian Acad. of Sci., N 90-11, Novosibirsk, 1990.
- [9] V.V. Repkov, N.I. Matskevich, G.E. Osipova, International Symposium on Calorimetry and Chemical Thermodynamics, Moscow, Russia, 1991, p. 220.
- [10] M. Kakihana, M. Kall, L. Borjesson, H. Mazaki, H. Yasuaka, P. Berastegui, S. Eriksson, L.-G. Johansson, *Physica C* 173 (1991) 377.
- [11] L.V. Gurvich, *Thermodynamical Properties of Individual Substances*, vol. 1–4, Nauka, Moscow, 1982–1987.
- [12] A. Menta, J. Dicarolo, A. Navrotsky, *J. Sol. State Chem.* 101 (1992) 173.
- [13] A. Junod, D. Eckert, T. Graf, E. Kaldis, J. Karpinski, S. Rusiecki, D. Sanchez, G. Triscone, J. Muller, *Physica C* 168 (1990) 47.
- [14] R.A. Robie, B.S. Hemingway, J.R. Fisher, *U.S. Geol. Survey Bull.* 1452 (1979).
- [15] Z. Zhou, A. Navrotsky, *J. Mater. Res.* 8 (1993) 3023.
- [16] E.L. Brosha, P.K. Davies, F.H. Garson, I.D. Raistrick, *Science* 260 (1993) 196.
- [17] D.E. Morris, N.G. Asmar, I.H. Nickel, R.L. Sid, I.Y.T. Wei, *I.E. Post, Physica C* 159 (1989) 287.
- [18] L.R. Morss, D.C. Sonnenberger, R.J. Thorn, *Inorg. Chem.* 27 (1988) 21606.

- [19] F.H. Garson, I.D. Raistrick, D.S. Ginley, J.W. Halloran, *J. Mater. Res.* 6 (1991) 885.
- [20] Y. Idemoto, J. Takahashi, K. Fueki, *Physica C* 194 (1992) 177.
- [21] T.S. Konkova, Yu.N. Matyushin, J.H. Grinberg, V.B. Lazarev, Abstracts of the 11th IUPAC Conference on Chemical Thermodynamics, Como, Italy, August 26–31, 1990, p. 378.
- [22] V.S. Grunin, M.M. Pivovarov, I.B. Patrina, M.V. Razumeenko, M.M. Shults, Report of Russian Academy of Science 307 (1989) 143.
- [23] L.R. Morss, S.E. Dorris, T.B. Lindemer, N. Naito, *Eur. J. Solid State Inorg. Chem.* 27 (1993) 327.
- [24] T.S. Konkova, Yu.N. Matyushin, J.H. Greenberg, V.B. Lazarev, *J. Chem. Thermodyn.* 24 (1992) 225.
- [25] A.S. Monaenkova, A.A. Popova, N.V. Zaitheva, *Zh. Fiz. Chim.*, 65 (1995) 1543 (in Russian).