Synthesis and thermochemical study of 1 : 2 : 4 phases in the (Y,Gd)–Ba–Cu–O system

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Abstract

Synthesis of the $Y_xGd_{1-x}Ba_2Cu_4O_8$ phases ($x=1$; 0.5; 0.75) by special method from nitrates is described in this paper. Dissolution enthalpies of $YBa_2Cu_4O_8$, $Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8$, $Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8$, Y_2O_3, Gd_2O_3, CuO, $BaCO_3$ were measured in 6 N HCl at 323 K. On the basis of obtained experimental data, the enthalpies of some reactions with $Y_xGd_{1-x}Ba_2Cu_4O_8$ were determined. It was established that the above-mentioned 1 : 2 : 4 superconductors were thermodynamically more favourable than mixtures including CuO, $YBa_2Cu_3O_x$. It was also established that, according to the obtained data, these phases can react with CO_2. © 1998 Elsevier Science B.V.

Keywords: Calorimetry; Stability; Superconductors; (Y,Gd)–Ba–Cu–O system

1. Introduction

This work is a continuation of a series of earlier papers [1–7] on thermodynamic characteristics and stability study of compounds in the (Y,Gd)–Ba–Cu–O systems. As an analysis of the literature shows, YBa-CuO substances are widely investigated from the beginning of high T_c superconductivity discovery to the present, in particular, in the field of thermodynamics [8–23]. The reason for this popularity is the necessity to systematize the available background on the system for a deeper understanding of the mechanisms in high-temperature superconductors. The Y–Ba–Cu–O system can also be considered as a model system for further study of other lanthanoid–barium–copper complex oxides. The GdBaCuO phases are the other interesting objectives for investigation. As shown in Refs. [1,5,7], the superconducting phases seem to be more stable with Gd in place of Y.

In this study, the thermodynamic characteristics of the 1 : 2 : 4 phases and their reactions with different reagents are measured. Thermodynamic stabilities of the above-mentioned substances in the (Y,Gd)–Ba–Cu–O system have been studied from the viewpoint of their decomposition to the mixture, including 1 : 2 : 3 phase and CuO. The reason for investigating the 1 : 2 : 4 compounds is the following. It is reported in Refs. [4,5,8–23] that the YBaCuO-123 solid solutions are thermodynamically unstable. The problem of stability is an important one, both in applied and in fundamental sciences. For example, there is a conception in the theory of superconductivity that any superconductor is a thermodynamically unstable system

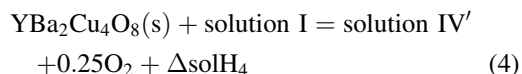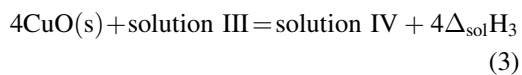*Corresponding author. Fax: +7-3832-34-4489; e-mail: nata@casper.che.nsk.su
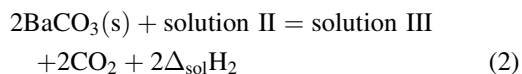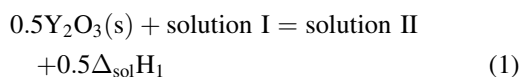
[24]. Data obtained on the thermodynamic stability of 1 : 2 : 3 phase in the Gd–Ba–Cu–O system particularly contradict this conclusion. Besides, the instability of high T_c superconductors seems to be one of the reasons of superconducting property losses, and thermodynamically stable superconducting materials are then required . One of the ways to solve this problem is to investigate other superconducting phases in the Y–Ba–Cu–O system, for example 1 : 2 : 4 or 1 : 2 : 3.5 phase. There are some discrepancies in the thermodynamic values of the 1 : 2 : 4 phase, and there are no thermodynamic data (i.e. formation enthalpies, entropies, heat capacities) for $(Y_xGd_{1-x})Ba_2Cu_4O_8$. The objective of this paper is to study the $(Y_xGd_{1-x})Ba_2Cu_4O_8$ phases with $x=1.0$; 0.5; 0.75.

2. Experimental

2.1. Investigation method

As in our earlier papers [1–7], solution calorimetry with 6 N HCl was chosen as the method for investigation. A selected set of thermochemical reactions allows us to obtain an internally closed system of thermochemical data for obtaining substance formation enthalpies from different mixtures.

Here, an example of the dissolution processes to obtain formation enthalpies of the $YBa_2Cu_4O_8$ phase from Y_2O_3, $BaCO_3$, CuO is given:

$$0.5Y_2O_3(s) + \text{solution I} = \text{solution II} + 0.5\Delta_{sol}H_1 \tag{1}$$

$$2BaCO_3(s) + \text{solution II} = \text{solution III} + 2CO_2 + 2\Delta_{sol}H_2 \tag{2}$$

$$4CuO(s) + \text{solution III} = \text{solution IV} + 4\Delta_{sol}H_3 \tag{3}$$

$$YBa_2Cu_4O_8(s) + \text{solution I} = \text{solution IV}' + 0.25O_2 + \Delta_{sol}H_4 \tag{4}$$

Here: solution I=6N HCl; solution II=solution I+YCl_3+1.5H_2O−3 HCl; solution III=solution I+YCl_3+2$BaCl_2$−7HCl+3.5H_2O; solution IV= solution I+YCl_3+2$BaCl_2$+4$CuCl_2$−15 HCl+7.5 H_2O; solution IV'=solution I+YCl_3+2$BaCl_2$+4$CuCl_2$−15HCl+7.5H_2O.

In the foregoing, it is mentioned that solution IV', obtained after dissolution of YBaCuO-124 phase, includes $CuCl_2$. But this is not obvious because it is possible to assume the existence of copper of three types of valence, Cu^{+1}, Cu^{+2}, Cu^{+3} in $LnBa_2Cu_{3+n}O_x$. We have performed some experiments which allow us to conclude that there is Cu^{+1} in $YBa_2Cu_4O_8$. The experiment was the following. We pass Ar (gas) through the HCl solution to evaluate O_2 dissolved in HCl. Then, we dissolved $YBa_2Cu_4O_8$, and immediately recorded spectra of the solution (spectra I). There was a certain peak in the range of 10^4 to 3×10^4 cm^{-1}, which belongs to Cu^{+2} as checked previously. Thereafter, the solution was kept for some time in air and the spectra were recorded again (spectra II). The peak had increased. The spectra were recorded repeatedly over a period of 2 h. Then, O_2 (gas) was passed through the solution and the spectra were recorded (spectra III). The spectra obtained 10 min after completion of the dissolution were the same as spectra III. The difference between spectra I and spectra III was about 33%. The above-mentioned facts gave us the possibility to confirm the existence of Cu^{+1} in samples because Cu^{+3} is a highly unstable state of copper and transforms to Cu^{+2} immediately. We have also performed experiments with Cu_2O and noted the same kinetic transformation of Cu^{+1} to Cu^{+2}.

The above-mentioned facts enabled us the possibility to draw the following conclusions:

1. there was Cu^{+1} in solution; and
2. solutions obtained by different means, namely, after dissolution of $1/2Y_2O_3$+$4CuO$+$2BaCO_3$ mixture and those obtained after dissolution of $YBa_2Cu_4O_8$ became identical 10 min after dissolution was completed.

Taking in account the facts of identity of solutions obtained by different means (solution IV and solution IV') the following equation can be written on the basis of the combination of reactions (1)–(3):

$$0.5Y_2O_3(s) + 2BaCO_3(s) + 4CuO(s) + 0.25O_2(g) = YBa_2Cu_4O_8(s) + 2CO_2(g) + \Delta_RH_5 \tag{5}$$
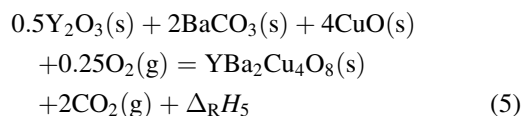
$$\Delta_RH_5 = 0.5\Delta_{sol}H_1 + 2\Delta_{sol}H_2 + 4\Delta_{sol}H_3 - \Delta_{sol}H_4$$

It is thus possible to construct the analogous cycle for the $(Y_xGd_{1-x})Ba_2Cu_4O_8$ solid solution to determine the substance formation enthalpy as well.

The experiments were performed in an automatic dissolution calorimeter, described elsewhere [25], with an isothermal shield at 323 K. The device was checked by dissolution of standard substance, namely, KCl. The dissolution value obtained ($\Delta_{sol}H$(KCl, 298.15 K) =17 529±0.009 kJ mol^{-1}) is in a good agreement with literature recommended data ($\Delta_{sol}H$(KCl, 298.15 K)=17 524±0.007 kJ mol^{-1}) [26].

2.2. Sample preparation

The following materials were used in the experiments:

– Y_2O_3 (high purity) which before use was held at 1023 K in air for 10 h;
– CuO (high purity) which was heated in O_2 for 15 h (T=900 K); and
– $BaCO_3$ (high purity) which was held at 650 K in air for 4 h.

High-purity (HP) samples used in our experiments were marked as HP 16–5. It means that 16 elements were controlled in the samples and the level of impurity was 10^{-5}%.

The samples of $YBa_2Cu_4O_8$, $Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8$, $Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8$ were prepared from $Y(NO_3)_3 \cdot nH_2O$, $Ba(NO_3)_2$ and $Cu(NO_3)_2 \cdot nH_2O$ in Chalmers University of Technology and University of Gothenburg, Gothenburg, Sweden [27]. Synthesis procedure included the following two simple steps:

1. the formation of metal citrate chelates in a mixed solvent of ethylene glycol and water without ageing and pH adjustment; and
2. the subsequent thermal decomposition of the gel to obtain a powder precursor.

The required amounts of nitrate salts were dissolved in H_2O, and citric acid and ethylene glycol were added in the ratio of 1 and 30 mol, respectively, to each mole of metal. The solution was heated at 393 K, and then heated at 463 K until a brown-black gel was obtained. The gel was decomposed to a powder at 573 K. The powdered precursor was calcined at 1073 K for 24 h under an atmosphere of flowing oxygen. The resultant 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 an oxygen pressure of one atmosphere. Further sintering at 1093 K for 4 days was necessary to obtain a single phase material.

All compounds were characterised by X-ray powder diffraction, chemical analysis and by Raman scattering. The X-ray powder diffraction pattern matches the orthorhombic $1:2:4$ structure, except for very weak lines seen only after a long X-ray exposure at 35.46 and 35.56°. These extra lines correspond to the 002 and -111 reflections of CuO. Special experiments were performed to find the dependence between values of reflections and the quantity of CuO. On the basis of these experiments, the amount of CuO in the sample is estimated to be below 1%. No traces of $YBa_2Cu_3O_x$, Y_2BaCuO_5, $Y_2Cu_2O_5$, $BaCuO_2$ are detected by X-ray powder diffraction and by Raman scattering. The lower limit of impurity detection for these compounds by the Raman technique is typically about 0.5 wt.%. We thus conclude that our sample is nearly pure $Y_xGd_{1-x}Ba_2Cu_4O_8$ with about 1 wt.% impurity phases.

A least-squares fit of 33 diffraction peaks ($20<2\theta<90°$) within space group Ammm gave the following lattice parameters for $YBa_2Cu_4O_8$ phases: a=3.8387(6), b=3.8710(7), c=27.269(2). The onset and midpoint temperatures of the superconducting transition were 82.6 and 78 K, respectively, and the transition width (10–90%) is 4.5 K. The transition width is much smaller than those reported in a previous investigation of the 124 phase [28]. The results of chemical analysis for YBaCuO-124 phase allow us to conclude that $1:2:4$ phase has the composition: $Y_{0.99}Ba_{1.98}Cu_{4.00}O_{8.01}$.

3. Results and discussion

The enthalpies of reactions (1)–(4) were:

$$\Delta_{sol}H(Y_2O_3, \ 323.15\,K)$$
$$= -382.71 \pm 1.84\,kJ/mol$$

$$\Delta_{sol}H(Gd_2O_3, \ 323.15\,K)$$
$$= -411.41 \pm 3.56\,kJ/mol$$

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

$\Delta_{sol}H(BaCO_3,\ 323.15\,K)$
$\quad = -15.27 \pm 2.51\,kJ/mol$

$\Delta_{sol}H(YBa_2Cu_4O_8,\ 323.15\,K)$
$\quad = -790.83 \pm 2.92\,kJ/mol$

$\Delta_{sol}H(Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8\,323.15\,K)$
$\quad = -802.21 \pm 4.92\,kJ/mol$

$\Delta_{sol}H(Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8,\ 323.15\,K)$
$\quad = -792.63 \pm 5.55\,kJ/mol$

The presented dissolution enthalpies were calculated as average values of six calorimetric experiments. Errors were calculated for 95% confidence interval using Students coefficients.

The measured enthalpies of dissolution were used to calculate the reaction enthalpies of the $1:2:4$ phase formation from mixtures including $BaCO_3$, CuO, Y_2O_3, Y_2BaCuO_5 using the calorimetric cycle presented above (reactions (1)–(4)). The dissolution enthalpies of $Y(Gd)_2BaCuO_5$ were taken from Ref. [6] ($\Delta_{sol}H(Y_2BaCuO_5,\ 323.15\,K)=-639.525\pm2.761\,kJ/mol$), $\Delta_{sol}H\ (Gd_2BaCuO_5,\ 323.15\,K)=-675.202\pm3.389\,kJ/mol$).
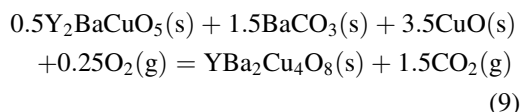
The results are presented below. Data taken from [29] were used to recalculate formation enthalpy from 323.15 up to 298.15 K:

$$0.5Y_2O_3(s) + 2BaCO_3(s) + 4CuO(s)$$
$$+0.25O_2(g) = YBa_2Cu_4O_8(s) + 2CO_2(g) \tag{6}$$
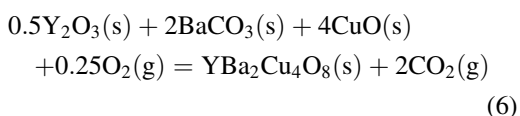
$\Delta_R H_6(298.15\,K) = +364.7 \pm 6.4\,kJ/mol$

$$0.25Y_2O_3(s) + 0.25Gd_2O_3 + 2BaCO_3(s)$$
$$+4CuO(s) + 0.25O_2(g)$$
$$= Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8(s) + 2CO_2(g) \tag{7}$$

$\Delta_R H_7(298.15\,K) = +359.4 \pm 8.1\,kJ/mol$

$$0.375Y_2O_3(s) + 0.125Gd_2O_3 + 2BaCO_3(s)$$
$$+4CuO(s) + 0.25O_2(g)$$
$$= Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8(s) + 2CO_2(g) \tag{8}$$

$\Delta_R H_8(298.15\,K) = +372.6 \pm 7.6\,kJ/mol$

$$0.5Y_2BaCuO_5(s) + 1.5BaCO_3(s) + 3.5CuO(s)$$
$$+0.25O_2(g) = YBa_2Cu_4O_8(s) + 1.5CO_2(g) \tag{9}$$

$\Delta_R H_9(298.15\,K) = +269.3 \pm 6.1\,kJ/mol$

$$0.25Y_2BaCuO_5(s) + 0.25Gd_2BaCuO_5(s)$$
$$+1.5BaCO_3(s) + 3.5CuO(s) + 0.25O_2(g)$$
$$= Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8(s) + 1.5CO_2(g) \tag{10}$$

$\Delta_R H_{10}(298.15\,K) = +262.3 \pm 7.8\,kJ/mol$

$$0.375Y_2BaCuO_5(s) + 0.125Gd_2BaCuO_5$$
$$+1.5BaCO_3(s) + 3.5CuO(s) + 0.25O_2(g)$$
$$= Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8(s) + 1.5CO_2(g) \tag{11}$$

$\Delta_R H_{11}(298.15\,K) = +276.4 \pm 7.3\,kJ/mol$

Our data [1–4] and data on reactions (6)–(11) allow us to calculate the $1:2:4$ phase formation enthalpies from mixtures including $YBa_2Cu_3O_x$ and CuO. Thus, it was possible to consider the stability of the $1:2:4$ compound with respect to the $1:2:3$ phase. Data for $x=6.9;\ 6.5$ in $YBa_2Cu_3O_x$ are given below.

$$YBa_2Cu_3O_{6.9} + CuO + 0.05O_2 = YBa_2Cu_4O_8 \tag{12}$$
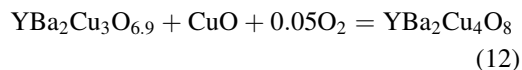
$\Delta_R H_{12}(298.15\,K) = -52.5 \pm 8.1\,kJ/mol$

$$YBa_2Cu_3O_{6.9} + 0.25Gd_2O_3 + CuO + 0.05O_2$$
$$= 0.25Y_2O_3 + Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8 \tag{13}$$

$\Delta_R H_{13}(298.15\,K) = -57.8 \pm 9.5\,kJ/mol$

$$YBa_2Cu_3O_{6.9} + 0.125Gd_2O_3 + CuO + 0.05O_2$$
$$= 0.125Y_2O_3 + Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8 \tag{14}$$

$\Delta_R H_{14}(298.15\,K) = -44.6 \pm 9.1\,kJ/mol$

$$YBa_2Cu_3O_{6.5} + CuO + 0.25O_2 = YBa_2Cu_4O_8 \tag{15}$$

$\Delta_R H_{15}(298.15K) = -95.3 \pm 7.1\,kJ/mol$

$$YBa_2Cu_3O_{6.5} + 0.25Gd_2O_3 + CuO + 0.25O_2$$
$$= Y_{0.5}Gd_{0.5}Ba_2Cu_4O_8 + 0.25Y_2O_3 \tag{16}$$

$\Delta_R H_{16}(298.15\,K) = -100.6 \pm 8.6\,kJ/mol$

$$YBa_2Cu_3O_{6.5} + 0.125Gd_2O_3 + CuO + 0.25O_2$$
$$= 0.125Y_2O_3 + Y_{0.75}Gd_{0.25}Ba_2Cu_4O_8 \tag{17}$$

$\Delta_R H_{12}(298.15\,K) = -87.6 \pm 8.2\,kJ/mol$

The above data and data on entropies of all the compounds in reactions (6)–(11) [29] allow us to conclude that mixtures including Y_2O_3, Gd_2O_3, Y_2BaCuO_5, Gd_2BaCuO_5, $BaCO_3$ cannot react forming $Y_xGd_{1-x}Ba_2Cu_4O_8$ phases with $x=1.0$; 0.5; 0.75 at room temperatures. According to our calculation, the temperature at which reaction (6) takes place is ca. 1200 K. ΔG for reaction (6) at 298.15 K is +276.3 kJ/mol. At the same time, the reverse reaction, namely, reaction 1 : 2 : 4 phases with CO_2, can take place at room temperature as it is possible to see from our thermodynamic data. Experiments on holding 1 : 2 : 4 compound in air have shown that the decomposition time is ca. 2–3 weeks. After this period, the X-ray powder diffraction indicated $BaCO_3$ impurities.

The obtained experimental data permit us also to conclude that the 1 : 2 : 4 superconducting phases in the (Y,Gd)–Ba–Cu–O system are thermodynamically more favourable than mixtures of CuO and 1 : 2 : 3 phases.

Taking into account data on $YBa_2Cu_3O_7$ instability and the data of this paper, it is possible to assert that the substances in the Y–Ba–Cu–O system became more stable on moving from 1 : 2 : 3 to 1 : 2 : 4 phase. As it will be shown in our future work, the stability increases when oxygen is changed by chlorine, i.e. from $YBa_2Cu_3O_x$ to $YBa_2Cu_3O_xCl_y$.

According to available literature data, the thermodynamic characteristics and stability of $YBa_2Cu_4O_8$ phase were studied in Refs. [8–14]. There were (1) Navrotsky's research [9,10] performed by high-temperature reaction calorimetry using molten lead borate as a solvent, (2) investigation [12] obtained by solution calorimetry in 4 N $HClO_4$, (3) Voronin's research performed by EMF method and (4) Kaldis and Karpinski's [8] investigation, etc. All the authors established that the 1 : 2 : 4 phase is thermodynamically more stable than the 1 : 2 : 3 phase. The experimental data obtained by us are in good agreement with all the literature data.

4. Conclusion

Dissolution enthalpies of Y_2O_3, CuO, $BaCO_3$, $Y_xGd_{1-x}Ba_2Cu_4O_8$ were used to calculate enthalpies of some reactions with 1 : 2 : 4 phases. Data obtained allowed us to conclude that $Y_xGd_{1-x}Ba_2Cu_4O_8$ solid solutions were thermodynamically stable in respect to mixtures, including the 1 : 2 : 3 phase and CuO. Comparison with literature data showed that our data are in good agreement with all other literature data.

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