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The Y–Ba–Cu–O–Cl system: thermodynamic characteristics of 1:2:3 phases, thermodynamic stability

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Abstract

In this study, the solution enthalpy for the $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phase has been measured by solution calorimetry in 6 N HCl at 323 K. On the basis of experimental and literature data the following values were obtained:

the formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ from the mixture of $0.433\ Y_2O_3 + 0.133\ YCl_3 + 3\ CuO + 2\ BaCO_3$ ($\Delta_r H^0$ (323.15 K) $= +\ 309.20 \pm 7.79$ kJ mol^{-1});

the standard formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ ($\Delta_r H^0$ (323.15 K) $= -\ 2756.6 \pm 11.5$ kJ mol^{-1});

the formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ from the mixture of $0.433\ Y_2O_3 + 0.133\ YCl_3 + 2\ BaCuO_2 + CuO$ ($\Delta_r H^0$ (323.15 K) $= -\ 92.98 \pm 8.24$ kJ mol^{-1}).

The calculated values permitted us to conclude that $YBa_2Cu_3O_{6.5}Cl_{0.4}$ reacted with CO_2 giving the mixture of Y_2O_3, YCl_3, CuO, $BaCO_3$.

Comparing two values of reaction enthalpies of 1:2:3 phases (with chlorine or without chlorine) showed that the formation of the Y123 phase from the $0.5\ Y_2O_3 + CuO + 2\ BaCuO_2$ mixture was thermodynamically unfavourable, but the formation of the Y123 phase with chlorine from the $0.433\ Y_2O_3 + 0.133\ YCl_3 + 2\ BaCuO_2$ mixture was thermodynamically favourable. The reason of the stability increase has been discussed. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Calorimetry; Y–Ba–Cu–O–Cl system; Stability; Thermodynamics

1. Introduction

The aim of this paper is to measure thermodynamic characteristics of the $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phase.

The Y–Ba–Cu–O–Cl system is of interest due to its application in high temperature superconductors. The authors of a number of publications [1–6] have stated that the $YBa_2Cu_3O_x$ phase is thermodynamically less stable than mixtures of several phases with the same nominal composition at room and lower temperatures. Hence, thermodynamically stable superconducting materials are required. There are several ways to solve this problem. One is to investigate other superconducting phases in the Y–Ba–Cu–O system, for example, the 1:2:4 phase. As it was reported in some papers [2,7–10] the 1:2:4 phase was more stable than the 1:2:3 one. An alternative is to change elements of the $YBa_2Cu_3O_x$ phase.

It is known that superconducting phase stability is increased when replacing oxygen by chlorine. There are no thermodynamical data for the $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phase in literature.

This research was undertaken both to obtain thermodynamic characteristics of $YBa_2Cu_3O_{6.5}Cl_{0.4}$, and

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to discuss reasons of the phase stability basing on obtained experimental data.

2. Preparation of samples

The following samples were used in calorimetric measurements: Y_2O_3, CuO, $BaCO_3$, $BaCuO_2$, $YBa_2Cu_3O_x$, $YBa_2Cu_3O_{6.5}Cl_{0.4}$.

Y_2O_3, CuO, $BaCO_3$ samples were treated by a special temperature regime before using as described in papers [6,7].

The preparation of $BaCuO_2$, $YBa_2Cu_3O_x$ was described in paper [6]. $YBa_2Cu_3O_{6.9}$ was prepared from Y_2O_3, $BaCO_3$, CuO. A stoichiometric mixture of these substances was thoroughly mixed, ground, pressed into pellets and fired in oxygen at 1200 K. The grinding and pressing procedures were repeated several times. During the final stage of synthesis the temperature was decreased and the sample was kept in oxygen at 1000 K for 16 h, then at 600 K for 6 h. $BaCuO_2$ was synthesised from stoichiometric amounts of $BaCO_3$ and CuO. The components were thoroughly mixed and ground in ethanol (C_2H_5OH), using a ‘‘Pulverizette’’ mill. After ethanol was evaporated the reactants were heated in air at 1113 K for 24 h. Then the sample was cooled, ground repeatedly, pressed, and heated in air again at 1173 K for 120 h.

The 1:2:3 phase doped by chlorine in the Y–Ba–Cu–O system ($YBa_2Cu_3O_{6.5}Cl_{0.4}$) was prepared from $YBa_2Cu_3O_{6.9}$ and PCl_5 (1:0.5) in evacuated ampoule at 433 K for 4 h. After the reaction volatile products were removed at 300 K (10^{-2}).

Samples were characterised by X-ray powder diffraction and chemical analysis. The content of all the metallic components was determined by atomic absorption method [6]. The oxygen content was analysed by iodometric titration [6]. According to analysis results compounds employed were found to be single phases. The chemical analysis allows one to write the following formulas for samples: $BaCu_{0.98 \pm 0.04}O_{2.01 \pm 0.03}$, $YBa_{2.01 \pm 0.03}Cu_{2.98 \pm 0.05}O_{6.91 \pm 0.02}$, $YBa_{1.98 \pm 0.03}Cu_{2.96 \pm 0.05}O_{6.51 \pm 0.03}Cl_{0.41 \pm 0.04}$.

3. Solution calorimetry

Solution calorimetry was used as an investigation method. Experiments were performed in an automatic dissolution calorimeter with an isothermal shield. 6 N HCl was chosen as a solvent. The procedure of performing calorimetric experiments is described in our earlier papers [6,7,11]. Calorimetric cycles were designed in such a way that it was possible to determine the formation enthalpy of the $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phases from yttrium chloride (YCl_3), yttrium oxide (Y_2O_3), copper oxide (CuO), and barium carbonate ($BaCO_3$).

The dissolution processes are described by the equations:

$$\begin{aligned}&0.133\ \mathrm{YCl_3(s)} + \text{solution 1}\\&\quad = \text{solution 2} + 0.133\ \Delta_{\mathrm{sol}}H_1^0,\end{aligned}\tag{1}$$

$$\begin{aligned}&0.433\ \mathrm{Y_2O_3(s)} + \text{solution 2}\\&\quad = \text{solution 3} + 0.433\ \Delta_{\mathrm{sol}}H_2^0,\end{aligned}\tag{2}$$

$$\begin{aligned}&2\ \mathrm{BaCO_3(s)} + \text{solution 3}\\&\quad = \text{solution 4} + 2\ \mathrm{CO_2(g)} + 2\ \Delta_{\mathrm{sol}}H_3^0,\end{aligned}\tag{3}$$

$$3\ \mathrm{CuO(s)} + \text{solution 4} = \text{solution 5} + 3\ \Delta_{\mathrm{sol}}H_4^0,\tag{4}$$

$$\begin{aligned}&\mathrm{YBa_2Cu_3O_{6.5}Cl_{0.4}(s)} + \text{solution 1}\\&\quad = \text{solution 5} + 0.1\ \mathrm{O_2(g)} + \Delta_{\mathrm{sol}}H_5^0,\end{aligned}\tag{5}$$

Here: s — solid; g — gas.

Using the following data such as the mass of Y_2O_3 which is 0.06 g, the volume of calorimetric vessel which is 230 ml and 6 N HCl it is possible to get the following relations for the above mentioned solutions:

Solution 1: nHCl + a H_2O = 10 451 HCl:84 625 H_2O or 1 HCl:8.0973 H_2O

Assuming that solution 5 and solution 5’ are identical the following reaction can be written:

$$\begin{aligned}&0.433\ \mathrm{Y_2O_3(s)} + 0.133\ \mathrm{YCl_3(s)}\\&\quad + 2\ \mathrm{BaCO_3(s)} + 3\ \mathrm{CuO(s)} + 0.1\ \mathrm{O_2(g)}\\&= \mathrm{YBa_2Cu_3O_{6.5}Cl_{0.4}(s)} + \Delta_{\mathrm{r}}H_6^0,\end{aligned}\tag{6}$$

where $\Delta_{\mathrm{r}}H_6^0 = 0.133\ \Delta_{\mathrm{sol}}H_1^0 + 0.433\ \Delta_{\mathrm{sol}}H_2^0 + 2\Delta_{\mathrm{sol}}H_3^0 + 3\Delta_{\mathrm{sol}}H_4^0 - \Delta_{\mathrm{sol}}H_5^0$.

4. Results and discussion

4.1. Stability of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ at interaction with CO_2

The dissolution enthalpy of the $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phase obtained in the paper was the following:

$$\Delta_{sol}H^0(323.15\,K) = -678.28 \pm 5.49\,kJ\,mol^{-1}.$$

Experimental data for dissolution enthalpies of Y_2O_3, $BaCO_3$, CuO were taken from our paper [7] and given below:

$$\Delta_{sol}H^0(Y_2O_3,\ 323.15\,K) = -382.71 \pm 1.84\,kJ\,mol^{-1},$$

$$\Delta_{sol}H^0(BaCO_3,\ 323.15\,K) = -15.27 \pm 2.57\,kJ\,mol^{-1},$$

$$\Delta_{sol}H^0(CuO,\ 323.15\,K) = -51.13 \pm 2.13\,kJ\,mol^{-1}.$$

The dissolution enthalpy of YCl_3 was calculated, as done in paper [12], on the basis of $\Delta_fH^0(Y_2O_3$, 323.15 K), $\Delta_fH^0(YCl_3$, 323.15 K), $\Delta_fH^0(HCl{:}8\ H_2O$, 323.15 K) [13] and $\Delta_{sol}H^0(Y_2O_3$, 323.15 K) [7] as the following value: $\Delta_{sol}H^0(YCl_3$, 323.15 K) = − 146.15 ± 4.13 kJ mol^{-1}.

The dissolution enthalpies were calculated as average values of six calorimetric experiments. The errors were calculated for the 95% confidence interval using the Students coefficient.

Solution enthalpies of Y_2O_3, YCl_3, $BaCO_3$, $YBa_2Cu_3O_{6.5}Cl_{0.4}$, CuO were used to get the enthalpy of the following reaction:

$$\begin{aligned}&0.433Y_2O_3(s) + 0.133YCl_3(s)\\&\quad + 2BaCO_3(s) + 3CuO(s)\\&= YBa_2Cu_3O_{6.5}Cl_{0.4}(s) + 0.1O_2(g)\\&\quad + 2CO_2(g) + \Delta_rH_7^0,\end{aligned} \tag{7}$$

$$\begin{aligned}&\Delta_rH_7^0(323.15\,K)\\&= 0.433\Delta_{sol}H^0(Y_2O_3,\ 323.15\,K)\\&\quad + 0.133\Delta_{sol}H^0(YCl_3, 323.15\,K)\\&\quad + 2\Delta_{sol}H^0(BaCO_3,\ 323.15\,K)\\&\quad + 3\Delta_{sol}H^0(CuO,\ 323.15\,K)\\&\quad - \Delta_{sol}H^0(YBa_2Cu_3O_{6.5}Cl_{0.4})\\&= +309.20 \pm 7.79\,kJ\,mol^{-1}.\end{aligned}$$

These data and entropies of all the substances employed in reaction (7) [13] allow us to conclude that $YBa_2Cu_3O_{6.5}Cl_{0.4}$ reacts with CO_2 forming Y_2O_3, YCl_3, $BaCO_3$, CuO at room and lower temperatures.

4.2. Formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$

For other calculations it is necessary to have the formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$. To calculate this value we used literature data taken from [13,14] and experimental data for reaction (7). It gave us a possibility to calculate the formation enthalpy of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ from the following equation:

$$\begin{aligned}\Delta_rH^0 &= 2\Delta_fH^0(CO_2) + \Delta_fH^0(YBa_2Cu_3O_{6.5}Cl_{0.4})\\&\quad -3\Delta_fH^0(CuO) - 2\Delta_fH^0(BaCO_3)\\&\quad -0.133\Delta_fH^0(YCl_3) - 0.433\Delta_fH^0(Y_2O_3).\end{aligned}$$

The following data were used for the calculation: $\Delta_fH^0(CO_2,\ 323.15\,K) = -393.17 \pm 0.05$ kJ mol^{-1} [14] $\Delta_fH^0(BaCO_3,\ 323.15\,K) = -1213.8 \pm 5.0$ kJ mol^{-1} [13] $\Delta_fH^0(Y_2O_3,\ 323.15\,K) = -1904.8 \pm 4.0$ kJ mol^{-1} [13] $\Delta_fH^0(YCl_3,\ 323.15\,K) = -997.7 \pm$ 2.7 kJ mol^{-1} [13] $\Delta_fH^0(CuO,\ 323.15\,K) = -155.7$ ±2.1 kJ mol^{-1} [14].

On the basis of these data the following value for Δ_fH^0 of 123 phase in the Y–Ba–Cu–O–Cl system was calculated:

$$\Delta_fH^0(YBa_2Cu_3O_{6.5}Cl_{0.4},\ 323.15\,K) = -2756.6 \pm 11.5\,kJ\,mol^{-1}.$$

4.3. Stability of $YBa_2Cu_3O_{6.5}Cl_{0.4}$ with respect to mixture with $BaCuO_2$

Data on the enthalpy of reaction (7) and our data [6] on the formation enthalpy of $BaCuO_2$ from $BaCO_3$ and CuO (Δ_rH^0(323.15 K) = + 201.09 ± 1.90 kJ mol^{-1}) were used to calculate the enthalpy of the reaction:

$$\begin{aligned}&0.433Y_2O_3(s) + 0.133YCl_3(s)\\&\quad +2BaCuO_2(s)CuO(s) = YBa_2Cu_3O_{6.5}Cl_{0.4}(s)\\&\quad +0.1O_2(g) + \Delta_rH_8^0\end{aligned} \tag{8}$$

Here: $\Delta_rH_8^0(323.15\,K) = -92.98 \pm 8.24$ kJ mol^{-1}.

In our earlier papers we investigated the stability of the 1:2:3 phase in the Y–Ba–Cu–O system. The results obtained showed that the 1:2:3 phase is thermodynamically unstable in respect to the mixture of 0.5 Y_2O_3 + CuO + 2 $BaCuO_2$ [6]. For example, Δ_rH^0(3.15 K) = + 15.12 ± 5.33 kJ mol^{-1} for the $YBa_2Cu_3O_{6.9}$ phase.

Comparing two values of reaction enthalpies of 1:2:3 phases (with chlorine or without chlorine) showed that the formation of the Y123 phase from the 0.5 $Y_2O_3 + CuO + 2\ BaCuO_2$ mixture was thermodynamically unfavourable, but the formation of the Y123 phase with chlorine from the 0.433 $Y_2O_3 + 0.133\ YCl_3 + 2\ BaCuO_2$ mixture was thermodynamically favourable. To explain the situation we tried to establish the correlations between thermodynamic values and structural parameters.

We assume that the crystal network of $YBa_2Cu_3O_{6.9}$ ($YBa_2Cu_3O_{6.5}Cl_{0.4}$) is an epitaxial structure. It is possible to suppose, as done by Goodenough and Manthiram [15], that if lattice parameters of two layers match, the structure is very favourable and stable. Cell parameters of CuO, BaO, $BaCl_2$, $CuCl_2$ are given in Table 1.

According to literature data [16] some part of chlorine is in CuO layers. The other part of chlorine is in BaO layers. The relative difference $[\delta = (a_1 - a_2) \times 100\%{:}a_1]$ of lattice parameters of $BaCl_2$ and CuO layers is 1%. The same value for CuO, BaO layers is 8%. Here: a_1 is the cell parameter of $BaCl_2$ or BaO, a_2 is the cell parameter of CuO. It is noteworthy that the increase of the formation enthalpy from the mixture of binary oxides and $BaCuO_2$ in the absolute value correlates with the decrease of the relative difference of lattice parameters.

5. Conclusion

In the paper thermodynamic data for $YBa_2Cu_3O_{6.5}Cl_{0.4}$ was determined by solution calorimetry. On the basis of experimental data the interaction of the above mentioned phase with CO_2 was studied. It was established that the 1:2:3 phase reacted with CO_2. The stability of $YBa_2Cu_3O_{6.9}$ and $YBa_2Cu_3O_{6.5}Cl_{0.4}$ phases in respect to the mixture including $BaCuO_2$ was investigated as well. It was established that the stability increased from $YBa_2Cu_3O_x$ up to $YBa_2Cu_3O_{6.5}Cl_{0.4}$. The reason for the stability increase was discussed.

Table 1
Cell parameters of compounds

Compound	*a* (nm)	*b* (nm)	*c* (nm)
$BaCl_2$	0.7823	0.9333	0.4705
$CuCl_2$	0.670	0.330	0.667
CuO	0.5108	0.3410	0.4653
BaO	0.5542		

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