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Thermochimica Acta 292 (1997) 9–12

thermochimica acta

Formation enthalpy and thermodynamic stability of 247 compound in the Y–Ba–Cu–O system

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Received 19 August 1996; accepted 4 November 1996

Abstract

Solution calorimetry (6 N HCl solvent, 323 K) was used to obtain the enthalpies of certain reactions including the 247 substance ($Y_2Ba_4Cu_7O_{15}$) on the basis of solution enthalpies of Y_2O_3, $BaCO_3$, CuO, Y_2BaCuO_5 and $Y_2Ba_4Cu_7O_{15}$. It was established that $Y_2Ba_4Cu_7O_{15}$ was thermodynamically more favourable than $Y_2O_3 + 4BaCuO_2 + 3CuO$, $Y_2BaCuO_5 + 3BaCuO_2 + 3CuO$ mixtures at room and lower temperatures, whereas, in accordance with our earlier papers, the 123 phase in the Y–Ba–Cu–O system was metastable. This work continues our research on thermodynamic stability of superconducting phases in the Y(Gd, Ho)–Ba–Cu–O systems. © 1997 Elsevier Science B.V.

Keywords: Calorimetry; Stability; Superconductors; Y–Ba–Cu–O system

1. Introduction

In spite of the fact that the Y–Ba–Cu–O system still remains to be extensively investigated, an analysis of literature shows that there are no thermodynamic data on certain substances in the system. These data are necessary to establish the direction of chemical reaction, to predict stability and to optimize thermal processing in high T_c ceramic superconductors.

In our recent papers [1–3] and in those of other authors [4–8], it has been established that the $YBa_2Cu_3O_x$ phase is thermodynamically unstable at room and lower temperatures. The phase diagram of the Y–Ba–Cu–O system, including 123, 124 and 247 compounds, was studied in depth, as already reported (e.g. in [4–6,8–10]). There are some discrepancies on the thermodynamic stability of $YBa_2Cu_4O_8$ [8–11]; also no direct thermochemical investigations of $Y_2Ba_4Cu_7O_{15}$ at all are available.

In the present study, solution enthalpies of several compounds of the Y–Ba–Cu–O system, including 247 phase, have been measured. Enthalpies of certain reactions and 247 formation enthalpies have been obtained. Data on the $Y_2Ba_4Cu_7O_{15}$ thermodynamic stability are reported.

2. Experimental

To solve the problem of thermodynamic stability of superconductors in the Y–Ba–Cu–O system, we decided to start our research with the $YBa_2Cu_{3.5}O_{7.5}$

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0040-6031/97/$17.00
PII S0040-6031(96)03118-8

($Y_2Ba_4Cu_7O_{15}$) compound but without 124 phase for the following reasons. It has already been shown [2] that the $YBa_2Cu_3O_{6.9}$ phase is more thermodynamically stable than 123 samples with $6.4 < x < 6.8$. The enthalpy of reaction, $0.5Y_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = YBa_2Cu_3O_{6.9}$ ($\equiv$+13.0 ± 4.0 kJ mol^{-1}), is small enough to assume that certain phases can be thermodynamically stable on slightly increasing the oxygen content.

We used the same technique and the same procedure for preparing and performing calorimetric reactions as described in previous papers [2,12]. The dissolution of different compounds was carried out in an automatic solution calorimeter [12] in 6 N HCl at 323 K.

Y_2O_3, CuO, $BaCO_3$, Y_2BaCuO_5 and $Y_2Ba_4Cu_7O_{15}$ were used in direct calorimetric experiments. An example of a calorimetric cycle is given below:

$$Y_2BaCuO_5 + [(10+n)HCl]_{p-pI} = [2YCl_3 + BaCl_2 + CuCl_2 + 5H_2O + nHCl]_{p-pII} + \Delta H_1 \quad (1)$$

$$3BaCO_3 + [2YCL_3 + BaCl_2 + CuCl_2 + 5H_2O + nHCl]_{p-pII} = [2YCl_3 + 4BaCl_2 + CuCl_2 + 8H_2O + (n-6)HCl]_{p-pIII} + 3CO_2 + 3\Delta H_2 \quad (2)$$

$$6CuO + [2YCl_3 + 4BaCl_2 + CuCl_2 + 8H_2O + (n-6)HCl]_{p-pIII} = [2YCl_3 + 4BaCl_2 + 7CuCl_2 + 14H_2O + (n-18)HCl]_{p-pIV} + 6\Delta H_3 \quad (3)$$

$$Y_2Ba_4Cu_7O_{15} + [(10+n)HCl]_{p-pI} = [2YCl_3 + 4BaCl_2 + 7CuCl_2 + 14H_2O + (n-18)HCl]_{p-pIV'} + 0.5O_2 + \Delta H_4 \quad (4)$$

Summing all these reactions and assuming the identity of IV and IV′ solutions we obtain:

$$Y_2BaCuO_5 + 3BaCO_3 + 6CuO + 0.5O_2 = Y_2Ba_4Cu_7O_{15} + 3CO_2 + \Delta H_5 \quad (5)$$

where: $\Delta H_5 = \Delta H_1 + 3\Delta H_2 + 6\Delta H_3 - \Delta H_4$

The procedure for establishing the identity of IV and IV′ solutions was described earlier [2].

It is possible to create the analogous cycle for $Y_2O_3 + 4BaCO_3 + 7CuO + 0.5O_2 = Y_2Ba_4Cu_7O_{15} + 4CO_2$, $Y_2O_3 + BaCO_3 + CuO \equiv Y_2BaCuO_5 + CO_2$ and other reactions.

The samples of substances used in direct calorimetric experiments weighed 0.06–0.3 g.

3. Sample preparation

Y_2O_3, CuO, $BaCO_3$, Y_2BaCuO_5 and 247 phase were used for direct dissolution reactions.

CuO and $BaCO_3$ (both of high purity) were treated as described in our earlier paper [13] prior to use.

Y_2O_3 (high purity) was kept at 650 K in air for 4 h.

Y_2BaCuO_5 phase was synthesized from $BaCO_3$, CuO and Y_2O_3, in air, at 1200 K for 120 h by solid-state phase synthesis.

The synthesis of 247 phase was as follows:

1. Calcination of high purity powder of Y_2O_3, $BaCO_3$ and CuO in flowing oxygen at 1 bar between 1153 K and 1223 K with intermediate regrounding.
2. Annealing of cold pressed pellets at 1273 K under 20 bar of O_2 during 36 h.

The density of 247 samples obtained was about 85% of the theoretical value. The temperature of superconducting transition was measured by AC susceptibility (80 Hz, 0.1 Oe RMS) as it was described previously [14,15]. T_c was defined as the maximum of the temperature derivative of the AC susceptibility curve. The field cooling effect of sample 247 was measured in a 20 Oe field, the Meissner fraction reached 40% at 10 K. Short characterizations of two samples used in calorimetric experiments are given in Table 1.

All the foregoing samples were characterized by X-ray powder diffraction and chemical analysis. They were found to be single phases. The analysis of impurities in samples indicated that Gd, Ho, Dy, Eu, Yb, La, Lu, Tm, Er, Nd, Pr, Sm, Ce, Tl, Ca, Mg, Pb and Ag were present in amounts of 10^{-2}–10^{-3}%.

Table 1
Lattice parameters and temperatures of superconducting transitions of 247 phase

Code	247-A	247-B
a, Å	3.8302 ± 0.0007	3.8329 ± 0.0005
b, Å	3.8779 ± 0.0006	3.8780 ± 0.0004
c, Å	50.604 ± 0.008	50.604 ± 0.005
T_c/K	90.3	88.3
ΔT_c/K	1.5	1.7

4. Results

The measured dissolution enthalpies of Y_2O_3, $BaCO_3$, CuO, Y_2BaCuO_5 and $YBa_2Cu_{3.5}O_{7.5}$ are as follows:

$$\Delta_s H(Y_2O_3) = -390 kJmol^{-1};$$
$$\Delta_s H(BaCO_3) = -15 kJmol^{-1};$$
$$\Delta_s H(CuO) = -50 kJmol^{-1};$$
$$\Delta_s H(Y_2BaCuO_5) = -640 kJmol^{-1};$$
$$\Delta_s H(YBa_2Cu_{3.5}O_{7.5}) = -785 kJmol^{-1}$$

Using the foregoing data, the calculation of the following reaction enthalpies gave:

$$0.5Y_2O_3 + 2BaCO_3 + 3.5CuO + 0.25O_2 = YBa_2Cu_{3.5}O_{7.5} + 2CO_2 \quad (6)$$
$$\Delta_r H = +381.7 \pm 6.0 kJ$$

$$0.5Y_2BaCuO_5 + 1.5BaCO_3 + 3CuO + 0.25O_2 = YBa_2Cu_{3.5}O_{7.5} + 1.5CO_2 \quad (7)$$
$$\Delta_r H = +286.5 \pm 5.7 kJ$$

and

$$Y_2O_3 + CuO + BaCO_3 = Y_2BaCuO_5 + CO_2 \quad (8)$$
$$\Delta_r H = +193.4 \pm 4.7 kJ$$

The dissolution enthalpies of Y_2O_3, CuO, Y_2BaCuO_5, $BaCO_3$ and $YBa_2Cu_{3.5}O_{7.5}$, used to calculate the reaction enthalpies in Eqs. (6)–(8), were average values of four-to-eight calorimetric experiments. Errors were calculated for the 95% confidence interval using Student's coefficients. Two samples of 247 phase were used in calorimetric experiments. The dissolution enthalpies of both samples were equal within the accuracy of measurements and so, they were treated as one.

Taken from the literature [16] the enthalpy of $BaCO_3 = BaO + CO_2$ reaction allowed to evaluate the $YBa_2Cu_{3.5}O_{7.5}$ and Y_2BaCuO_5 enthalpies from oxides:

$$0.5Y_2O_3 + 2BaO + 3.5CuO + 0.25O_2 = YBa_2Cu_{3.5}O_{7.5} \quad (9)$$
$$\Delta_r H = -157.3 \pm 6.0 kJ$$

$$Y_2O_3 + CuO + BaO = Y_2BaCuO_5 \quad (10)$$
$$\Delta_r H = -76.1 \pm 4.7 kJ$$

As it was shown in our earlier papers [2,3], in order to solve the problem of thermodynamic stability it is necessary to investigate the reaction including $BaCuO_2$ phase. Hence, our data on thermodynamics of the reaction [2,3]: $BaCO_3 + CuO = BaCuO_2 + CO_2$ were used to calculate the values presented below:

$$0.5Y_2O_3 + 2BaCuO_2 + 1.5CuO + 0.25O_2 = YBa_2Cu_{3.5}O_{7.5} \quad (11)$$
$$\Delta_r H = -22.3 \pm 4.1 kJ$$

$$0.5Y_2BaCuO_5 + 1.5BaCuO_2 + 1.5CuO + 0.25O_2 = YBa_2Cu_{3.5}O_{7.5} \quad (12)$$
$$\Delta_r H = -16.5 \pm 4.3 kJ$$

and

$$Y_2O_3 + BaCuO_2 = Y_2BaCuO_5 \quad (13)$$
$$\Delta_r H = -8.6 \pm 3.5 kJ$$

From the data and entropies of all substances employed in reactions (11) and (12) [12–14], it is possible to conclude that the 247 superconductor, with an oxygen content equal to 15, was thermodynamically more stable than the following mixtures: (1) Y_2O_3, $BaCuO_2$ and CuO; and (2) Y_2BaCuO_5, $BaCuO_2$ and CuO at room and lower temperatures.

5. Conclusion

In this paper, we obtained an alternative result in respect to the $YBa_2Cu_3O_x$ phase which was metastable at room and lower temperatures. The 247 phase, with an oxygen content equal to 15, was found to be thermodynamically stable under similar conditions. As already mentioned, the Y–Ba–Cu–O system phase diagram, including that of 123, 124 and 247, has been extensively studied [4–6,8–10] at high temperature. In order to compare our result with those of [4–6,8–10], it is necessary to obtain high temperature heat capacities for the 247, 123 and 124 phases and the thermodynamic data for the 124 substance. This will be a subject of our further investigations.

Acknowledgements

Calorimetric measurements were supported by the Scientific Council of the Russian Scientific – Technical Program 'Superconductivity' direction, section 'Basis of chemistry and technology of superconductors' (Grant N 93205 'System').

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