The thermodynamics of some reactions in the Gd–Ba–Cu–O system

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Abstract

In this study, enthalpies of solution for Gd_2O_3, CuO, $BaCO_3$ and $GdBa_2Cu_3O_{6.9}$ phases have been measured by solution calorimetry in 6N HCl at 323 K. Experimental and literature data have been used to calculate the enthalpy of the reaction $0.5Gd_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = GdBa_2Cu_3O_{6.9}$. $\Delta_r H$ was found to be -37.3 ± 8.2 kJ mol^{-1}. Based on these data, we came to the conclusion that the $GdBa_2Cu_3O_{6.9}$ phase appeared to be thermodynamically more favourable than the mixture of gadolinium oxide, copper oxide, and barium cuprate at room and lower temperatures. The experimental and literature data have allowed us to conclude that the $GdBa_2Cu_3O_{6.9}$ phase is thermodynamically stable, whereas the $YBa_2Cu_3O_{6.9}$ phase appears to be thermodynamically unstable at room and lower temperatures.

Keywords: Calorimetry; Quaternary system; Stability; Thermodynamics

1. Introduction

The aim of this paper is to elucidate the thermodynamic stability of the $GdBa_2Cu_3O_x$ superconducting phase.

The authors of a number of recent publications, using results obtained by solution calorimetry and EMF methods, have stated that at room and lower temperatures the $YBa_2Cu_3O_x$ phase is thermodynamically less stable than mixtures

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of several phases with the same nominal composition [1–5]. This is important because thermodynamic instability appears to be one explanation for the observed loss of superconducting properties of superconductors at low temperatures.
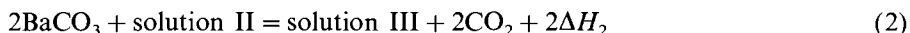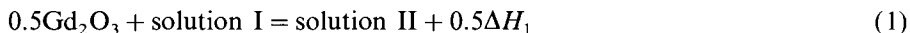
Thus, thermodynamically stable superconducting materials are required. There are several approaches to this problem. One is to investigate other superconducting phases in the Y–Ba–Cu–O system, for example $1:2:4$ phase. An alternative is to change the elements of the $YBa_2Cu_3O_x$ phase. There are many other ways as well. Using the method of comparative thermodynamic analysis, we have estimated that the superconducting phases seem to be more stable with Gd (or some other rare earth elements) in place of Y.

This research was undertaken both to substantiate our estimation and to get experimental information on the thermodynamical properties of the $GdBa_2Cu_3O_{6.9}$ phase, and to establish the stability of this phase at room and lower temperatures.
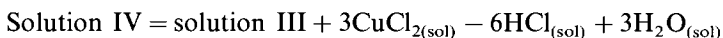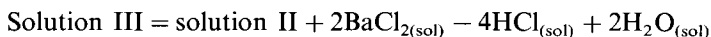
2. Method

Solution calorimetry was used as an investigation method. Calorimetric cycles were designed in such a way that it was possible to determine the formation enthalpy of the $1:2:3$ phase in the Gd–Ba–Cu–O system from gadolinium oxide (Gd_2O_3), copper oxide (CuO), and barium carbonate ($BaCO_3$) and then to calculate the formation enthalpy of the $GdBa_2Cu_3O_{6.9}$ phase from oxides and barium cuprate on the basis of experimental and literature data.

The dissolution processes are described by the equations

$$0.5Gd_2O_3 + \text{solution I} = \text{solution II} + 0.5\Delta H_1 \tag{1}$$

$$2BaCO_3 + \text{solution II} = \text{solution III} + 2CO_2 + 2\Delta H_2 \tag{2}$$

$$3CuO + \text{solution III} = \text{solution IV} + 3\Delta H_3 \tag{3}$$

$$GdBa_2Cu_3O_{6.9} + \text{solution I} = \text{solution IV}' + 0.2O_2 + \Delta H_4 \tag{4}$$

where

$$\text{Solution II} = \text{solution I} + GdCl_{3(sol)} - 3HCl_{(sol)} + 1.5H_2O_{(sol)}$$

$$\text{Solution III} = \text{solution II} + 2BaCl_{2(sol)} - 4HCl_{(sol)} + 2H_2O_{(sol)}$$

$$\text{Solution IV} = \text{solution III} + 3CuCl_{2(sol)} - 6HCl_{(sol)} + 3H_2O_{(sol)}$$

If solution IV, obtained after dissolution of $0.5Gd_2O_3 + 2BaCO_3 + 3CuO$ mixture, and solution IV', obtained after dissolution of the $GdBa_2Cu_3O_{6.9}$ phase, are assumed to be identical, the following equation can be written

$$0.5Gd_2O_3 + 2BaCO_3 + 3CuO + 0.2O_2 = GdBa_2Cu_3O_{6.9} + 2CO_2 + \Delta H_5 \tag{5}$$
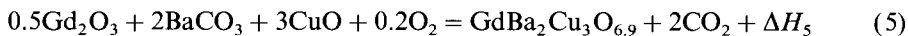
where

$$\Delta H_5 = 0.5\Delta H_1 + 2\Delta H_2 + 3\Delta H_3 - \Delta H_4$$

It should be noted that in the experiments we used different sequences of dissolving phases, not only those described by reactions (1)–(3). This was to avoid systematic errors. It was found that, within the accuracy of the measurements, the total amounts of heat liberated were independent of the dissolution sequence.

A selected set of thermochemical reactions can provide values of the formation enthalpy of the $GdBa_2Cu_3O_{6.9}$ phase, with very limited use of literature reference data.

3. Sample preparation

The following materials were used in the experiments: Gd_2O_3 (high purity) which before use was kept at 1023 K in air for 10 h; CuO (high purity) which was heated in O_2 atmosphere for 15 h ($T = 900$ K); $BaCO_3$ (high purity) which was kept at 650 K in air for 4 h. The sample of $GdBa_2Cu_3O_{6.9}$ was prepared from Gd_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. The total firing time was 72 h. 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. The prepared orthorhombic phase had $T_c = 92$ K and $\Delta T_c = 1$ K.

All compounds were characterized by X-ray powder diffraction analysis, chemical analysis and differential solution. The content of all the metallic components was determined by the atomic absorption method. For the $GdBa_2Cu_3O_{6.9}$ phase, the analysis was: Gd, 21.0%; Ba, 36.1%; Cu: 25.1%. According to the results of the analyses the involved compounds were found to be single phases with an accuracy of about 1%. The oxygen content was determined by measuring crystal lattice parameter values. The accuracy of the determination was 0.1. The sample with an oxygen content of 6.9 was investigated in this paper. The analyses performed indicated that impurities of Ho, Dy, Eu, Yb, La, Lu, Tm, Er, Nd, Pr, Sm, Ce, Te, Ca, Mg, Mn, Pb, Ag metals were present at the level 10^{-3}–10^{-4} at%.

4. Experimental technique

The experiments were performed in an automatic dissolution calorimeter with an isothermal shield. The main part of the calorimeter was a glass Dewar vessel with a brass cover ($V = 200$ ml). The thermistor, calibration heater, cooler, mixer, and the device to break the ampules were mounted on the lid closing the Dewar vessel. The construction of the solution calorimeter and the experimental procedure are described elsewhere [6]. A device, designed according to the CAMAC standard, was created to connect the calorimeter heater and thermistor to an Electronika-60 computer. Automatic calibration of the calorimeter was used. The reproducibility of the heat equivalent of the calorimeter with the automatic calibration system was 0.03%. To check the precision of the calorimeter, dissolution of a standard
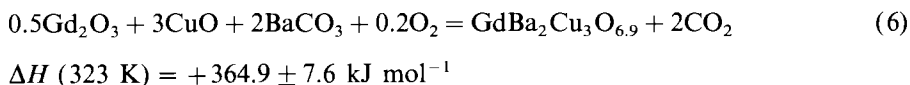
substance, potassium chloride, was performed. The obtained dissolution heat of KCl ($17.529 + 0.009$ kJ mol^{-1}) is in good agreement with the value recommended in the literature [7].

The experiments were performed at 323 K. At lower temperatures the rate of Gd_2O_3 dissolution is small, which results in a low precision of the measurements. The amounts of substances used were 0.06–0.3 g. All compounds were stored in a dry box to prevent interaction with moisture or CO_2. The identical state of the solution obtained by dissolution of the $GdBa_2Cu_3O_{6.9}$ phase and dissolution of $0.5Gd_2O_3 + 3CuO + 2BaCO_3$ mixture was proved by measuring the electronic spectra of these solutions in the range $10^4 - 3 \times 10^4$ cm^{-1}. It was shown that in experiments conducted in air, the spectra of the solutions became identical 1–2 min after dissolution was finished.

5. Experimental results

The enthalpies of reactions (1)–(4) were: ΔH_1 (323 K) $= -411$ kJ mol^{-1}; ΔH_2 (323 K) $= -51$ kJ mol^{-1}; ΔH_3 (323 K) $= -15$ kJ mol^{-1} and ΔH_4 (323 K) $= -754$ kJ mol^{-1}.

The measured enthalpies of dissolution were used for calculating the enthalpy of the reaction

$$0.5Gd_2O_3 + 3CuO + 2BaCO_3 + 0.2O_2 = GdBa_2Cu_3O_{6.9} + 2CO_2 \tag{6}$$

$$\Delta H \text{ (323 K)} = +364.9 \pm 7.6 \text{ kJ mol}^{-1}$$

The dissolution enthalpies of Gd_2O_3, CuO, $BaCO_3$, $GdBa_2Cu_3O_{6.9}$ used for calculation of the enthalpy of reaction (6) were calculated as average values of six experiments. Errors were calculated for the 95% confidence interval using the Students coefficient.

Literature data for the heat of the reaction $BaO + CO_2 = BaCO_3$ [8] were used to calculate the enthalpy of formation of $GdBa_2Cu_3O_{6.9}$ from the oxides

$$0.5Gd_2O_3 + 3CuO + 2BaO + 0.2O_2 = GdBa_2Cu_3O_{6.9}$$

$$\Delta H \text{ (323 K)} = -174.1 \pm 12.6 \text{ kJ mol}^{-1} \tag{8}$$
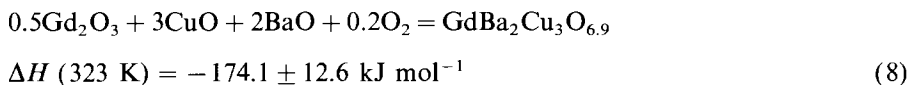
According to our estimation, this value is -158 kJ mol^{-1}.

Our data and the entropies of all the substances employed in reaction (8) allow us to conclude that the formation of the 1:2:3 phase from the oxides is thermodynamically favourable at room and higher temperatures.

This conclusion is similar to that for the Y–Ba–Cu–O system.

Data for the enthalpy of reaction (6) and literature data on the enthalpy of formation of $BaCuO_2$ were used to calculate the enthalpy of the reaction

$$0.5Gd_2O_3 + CuO + 2BaCuO_2 + 0.2O_2 = GdBa_2Cu_3O_{6.9}$$

$$\Delta H \text{ (323 K)} = -37.3 \pm 8.2 \text{ kJ mol}^{-1} \tag{9}$$
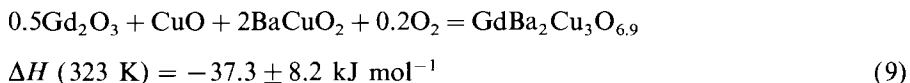
Literature data on the entropies of $GdBa_2Cu_3O_{6.9}$, Gd_2O_3, CuO and $BaCuO_2$, and the value of the enthalpy of reaction (9) allow us to conclude that the $1:2:3$ superconducting phase in the $Gd-Ba-Cu-O$ system is thermodynamically more favourable than the mixture of barium cuprate, and gadolinium and copper oxides at room and lower temperatures.

6. Conclusion

The results reported here obtained by solution calorimetry and additional information on the entropies of different substances confirm the stability of the $GdBa_2Cu_3O_{6.9}$ phase with respect to gadolinium oxide, copper oxide, and barium cuprate at room and lower temperatures. A contrasting result was obtained for the $Y-Ba-Cu-O$ system. The $YBa_2Cu_3O_x$ phase was reported to be thermodynamically less stable [1–5] than $0.5Y_2O_3 + CuO + 2BaCuO_2$, $0.5Y_2BaCuO_5 + 1.5BaCuO_2 + 0.5CuO$ and $0.5Y_2Cu_2O_5 + 2BaCuO_2$ mixtures. These results must be taken into account in the application and investigation of high-temperature superconducting materials.

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