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Thermodynamic characteristics of compounds in the Sm–Ba–Cu–O system

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Abstract

Dissolution enthalpies of Sm_2O_3, $BaCO_3$, CuO, $SmBa_2Cu_3O_{6.92}$, $BaCuO_2$ at 323.15 K in 2N HCl were measured by solution calorimetry. On the basis of these data, the enthalpies of the following reactions were obtained: (1) $0.5Sm_2O_3 + 2BaCO_3 + 3CuO + 0.21O_2 = SmBa_2Cu_3O_{6.92} + 2CO_2$; (2) $0.5Sm_2O_3 + 2BaO + 3CuO + 0.21O_2 = SmBa_2Cu_3O_{6.92}$; (3) $0.5Sm_2O_3 + 2BaCuO_2 + CuO + 0.21O_2 = SmBa_2Cu_3O_{6.92}$. It was established that $SmBa_2Cu_3O_{6.92}$ was thermodynamically unstable with respect to the interaction with CO_2 and thermodynamically stable with respect to the mixture including $BaCuO_2$. The standard formation enthalpy of $SmBa_2Cu_3O_{6.92}$ was calculated as following: $\Delta_f H^\circ$ ($SmBa_2Cu_3O_{6.9}$, s, 323.15 K) $= -2672.30 \pm 5.01$ kJ/mol.

Keywords: Thermodynamics; Sm–Ba–Cu–O system; Calorimetry; Stability

1. Introduction

At present cuprate systems including high temperature superconductors (HTSC) are widely studied. A good understanding of thermodynamic characteristics of HTSC is essential to optimise synthesis, to determine stability, to create basis for the understanding of the mechanism of high T_c oxide superconductors. The Sm–Ba–Cu–O system is one of the technologically promising systems. Unfortunately, there are lacking thermodynamic data for the compounds of this system in literature.

The aim of the present paper is to determinate the formation enthalpy of $SmBa_2Cu_3O_x$, to measure the thermodynamic characteristics of some reactions including $SmBa_2Cu_3O_x$ and to study the stability of this phase. This work continues a series of author's previous papers [1–10] on thermodynamic characteristics determination of compounds in the RE–Ba–Cu–O systems (RE = Y, Ho, Gd, Nd, Dy).

2. Investigation methods

Solution calorimetry was applied in this investigation. The experiments were performed in an automatic dissolution calorimeter with an isothermal shield. The calorimeter design and the experimental procedure are partially described in paper [11]. The volume of the calorimetric vessel (Dewar vessel) was 200 ml. The temperature of the calorimeter was measured by the thermistor (R(298.15 K) $= 33$ kΩ). The calibration

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was carried out after each calorimetric experiment using a heater ($R = 20\,\Omega$) mounted on the lid closing the Dewar vessel. The uncertainty of power measurement was ±0.003%. The reproducibility of the heat equivalent of the calorimeter with the automatic calibration system amounts to ±0.03%. The precision of the calorimeter was checked dissolving KCl as a standard substance. The dissolution heat of KCl (17.529 ± 0.009 kJ/mol) was found to be in a good agreement with the value recommended in the literature [12].

The 2N HCl solution was used as a solvent. The thermochemical cycle to calculate the $SmBa_2Cu_3O_{6.92}$ formation enthalpy is based on the determination of dissolution enthalpies of Sm_2O_3, $BaCO_3$, CuO, $SmBa_2Cu_3O_x$. The sequence of thermochemical reactions is represented by Eqs. (1)–(4):

$$0.5Sm_2O_3(s) + \text{solution }1 = \text{solution }2,\quad \Delta_{sol}H = 0.5\Delta_{sol}H_1^{\circ} \tag{1}$$

$$2BaCO_3(s) + \text{solution }2 = \text{solution }3 + 2CO_2(g),\quad \Delta_{sol}H = 2\Delta_{sol}H_2^{\circ} \tag{2}$$

$$3CuO(s) + \text{solution }3 = \text{solution }4,\quad \Delta_{sol}H = 3\Delta_{sol}H_3^{\circ} \tag{3}$$

$$SmBa_2Cu_3O_{6.92}(s) + 0.21\,O_2(g) + \text{solution }1 = \text{solution }4',\quad \Delta_{sol}H = \Delta_{sol}H_4^{\circ} \tag{4}$$

Here: solution 1 is a solution of HCl with concentration of 2N; s: solid; g: gas; $\Delta_{sol}H_{an}^{\circ}$: the molar enthalpy of solution.

If solution 4 obtained according to reaction (3) and solution 4′ obtained according to reaction (4) are assumed to be identical, the following equation can be written:

$$0.5Sm_2O_3(s) + 2BaCO_3(s) + 3CuO(s) + 0.21O_2(g) = SmBa_2Cu_3O_{6.92}(s) + 2CO_2(g),\quad \Delta r H_5^{\circ} \tag{5}$$

The corresponding enthalpy ($\Delta_r H_5^{\circ}$) of reaction (5) can be calculated providing the identity of solutions 4 and 4′:

$$\Delta_r H_5^{\circ} = 0.5\Delta_{sol}H_1^{\circ} + 2\Delta_{sol}H_2^{\circ} + 3\Delta_{sol}H_3^{\circ} - \Delta_{sol}H_4^{\circ}$$

The identity of solutions 4 and 4′, however, needs some proof due to the presence of various oxidation states of Cu (Cu^{+}, Cu^{2+}, Cu^{3+}) in $SmBa_2Cu_3O_x$ [13]. If $SmBa_2Cu_3O_x$ includes Cu^{3+}, Cl_2 is formed by the interaction with HCl. In [14], the formation of oxygen instead of chlorine was observed in dissolving $REBa_2Cu_3O_x$ and $REBa_2Cu_3O_8$. In the present study, the electronic spectra of solutions 4 and 4′ have been investigated in the range of (1–3) × $10^4\,cm^{-1}$ in air atmosphere. The spectra of solution 4 became identical to the spectra of solution 4′ within 10 min after dissolution was completed. This result indicates that the amount of oxygen which is partially dissolved in solution 4′ and partially contained in the air interlayer above the calorimeter is sufficient to transfer Cu^{+} to Cu^{2+}. Therefore, all calorimetric experiments were performed at 323 K, with the main period time being more than 10 min. At lower temperatures, the rate of Sm_2O_3 dissolution is small, resulting in a low precision of the measurements. The masses of substances used were 0.06–0.3 g. The heat evolved in calorimetric experiments was 100–200 J.

3. Sample preparation

The samples used in the calorimetric experiments were pre-treated as follows: Sm_2O_3 was kept at 1023 K in air for 10 h; CuO was heated in O_2 atmosphere for 15 h ($T = 900$ K); $BaCO_3$ was kept at 650 K in air for 4 h. The samples of $SmBa_2Cu_3O_{6.92}$ and $BaCuO_2$ were prepared from Sm_2O_3, $BaCO_3$, CuO by solid state reactions followed by annealing in oxygen at 673 K.

All compounds were characterised by X-ray power diffraction (Cu Kα radiation) and chemical analysis [9,10]. The sensitivity of X-ray analysis is about 2–3% according to [9]. The content of copper in the samples was determined by atomic absorption spectrometry in the flame of air–acetylene, whereas the content of barium was determined by photometric method in the flame of nitrogen dioxide–acetylene. The R.S.D. was 0.006–0.007. The content of samarium was determined by the spectrophotometry. The R.S.D. was 0.004–0.005. The stoichiometric coefficient of oxygen was determined by iodometric titration with an accuracy better than ±0.03. Within the resolution of the analyses, the involved compounds were found to be single phase. The spectral analysis indicated that the metal impurities were at the level 10^{-3} to 10^{-4} at.%.

4. Experimental results

The molar dissolution enthalpies of $BaCO_3$, CuO, Sm_2O_3, $BaCuO_2$, $SmBa_2Cu_3O_{6.92}$ in 2N HCl are given below.

$$\Delta_{sol}H^\circ(BaCO_3,\ 323.15\,K) = 10.42 \pm 1.30\,kJ/mol$$

$$\Delta_{sol}H^\circ(CuO,\ 323.15\,K) = 60.84 \pm 0.67\,kJ/mol$$

$$\Delta_{sol}H^\circ(Sm_2O_3, 323.15\,K) = 406.66 \pm 2.74\,kJ/mol$$

$$\Delta_{sol}H^\circ(SmBa_2Cu_3O_{6.92},\ 323.15\,K) = 774.14 \pm 3.52\,kJ/mol$$

$$\Delta_{sol}H^\circ(BaCuO_2,\ 323.15\,K) = 273.26 \pm 1.21\,kJ/mol$$

All dissolution enthalpies were calculated as average values of 5–6 calorimetric experiments. The errors were calculated for the 95% confidence interval using the Students coefficient.

The dissolution enthalpies were used to calculate the enthalpy of the following reaction:

$$0.5Sm_2O_3(s) + 2BaCO_3(s) + 3CuO(s) + 0.21O_2(g) = SmBa_2Cu_3O_{6.92}(s) + 2CO_2(g),$$
$$\Delta_r H^\circ_5(323.15\,K) = 367.45 \pm 5.01\,kJ/mol \qquad (5)$$

Since the direction of any chemical transformation is determined by the sign of the Gibbs energy, $\Delta G^\circ = \Delta H^\circ – T\Delta S^\circ + RT\ln P$ the value of the enthalpy change $\Delta_r H_5$ is not sufficient to evaluate whether $SmBa_2Cu_3O_x$ is stable or not with respect to reaction (5) at room temperature. Here P is a function of the fugacities of volatile components representing the different chemical potentials appearing in the initial and final state, respectively. However, it was shown in [1,2] for a number of cuprate phases that the term $T\Delta S$ was not so large as to change the sign of ΔG (the order is 100 kJ/mol for reaction 5), and the term ($-RT\ \ln P$ is estimated to be even less for the reaction proceeding in air (30 kJ/mol if the CO_2 level at steady state is approximately 10^2 Pa). Therefore, it can be concluded from the large endothermic heat of reaction (5) that Sm123 is not a thermodynamically stable phase at room temperature with respect to interaction with CO_2.

Table 1
Literature data on formation enthalpies used for calculation of reaction enthalpies

Compound	$\Delta_f H^\circ$ (kJ/mol) ($T = 323.15\,K$)
CO_2 (g)	−393.53
$BaCO_3$(s)	−1213.85
BaO (s)	−547.92
CuO (s)	−161.91
Sm_2O_3(s)	−1826.76

The formation enthalpy of the $SmBa_2Cu_3O_{6.92}$ phase from binary oxides ($\Delta_{ox}H$) was calculated using the enthalpy of reaction (5) and literature data [15] as follows:

$$\Delta_{ox}H^\circ(SmBa_2Cu_3O_{6.92},\ s,\ 323.15\,K) = \Delta_r H^\circ_5(323.15\,K) + 2\Delta_f H^\circ(BaCO_3,\ s,\ 323.15\,K) - 2\Delta_f H^\circ(BaO,\ s,\ 323.15\,K) - 2\Delta_f H^\circ(CO_2\ g,\ 323.15\,K)$$

The literature data used for calculation are given in Table 1 [15]. The value of formation enthalpy from binary oxides is presented below.

$$0.5Sm_2O_3(s) + 2BaO(s) + 3CuO(s) + 0.21O_2(g) = SmBa_2Cu3O6.92(s),$$
$$\Delta_{ox}H^\circ(323.15\,K) = -177.35 \pm 5.01\,kJ/mol \qquad (6)$$

The formation enthalpy of the Sm123 phase from Sm(s), Ba(s), Cu(s), O_2(g) ($T = 323.15\,K$) was calculated as follows:

$$\Delta_f H^\circ(SmBa_2Cu_3O_{6.92},\ s,\ 323.15\,K) = \Delta_r H^\circ_5(323.15\,K) + 2\,\Delta_f H^\circ(BaCO_3,\ s,\ 323.15\,K) - 2\Delta_f H^\circ(CO_2,\ g,\ 323.15\,K) + 0.5\Delta_f H^\circ(Sm_2O_3\ s,\ 323.15\,K) + 3\Delta_f H^\circ(CuO,\ s,\ 323.15\,K)$$

The values used for calculation are given in Table 1 [15].

According to [1,2] the formation enthalpies of a number of $REBa_2Cu_3O_x$ phases do not significantly depend on temperature. Therefore, the standard formation enthalpy [$\Delta_f H^\circ(SmBa_2Cu_3O_{6.92}$, s, 298.15 K] can be assumed to be equal to the formation enthalpy

Table 2
Literature and estimated data on entropies used for calculation of reaction enthalpies

Compound	S° (J/(K mol)) ($T = 323.15$ K)
$BaCuO_2$ (s)	125.3 ± 0.6
BaO(s)	75.82
CuO (s)	46.21
Sm_2O_3(s)	155.5
O_2(g)	207.4
$SmBa_2Cu_3O_{6.92}$(s)	368.0

$[\Delta_f H^{\circ}$ ($SmBa_2Cu_3O_{6.92}$, s, 323.15 K)] calculated at 323.15 K:

$$\Delta_f H^{\circ}(SmBa_2Cu_3O_{6.9},\ s,\ 323.15\,K) = -2672.30 \pm 5.01\,kJ/mol$$

Then, the enthalpy of the decomposition reaction of the $SmBa_2Cu_3O_{6.92}$ phase on the mixture including barium cuprate was calculated as follows.

$$0.5\,Sm_2O_3(s) + 2BaCuO_2(s) + CuO(s) + 0.21O_2(s) = SmBa2Cu3O_{6.92}(s)$$

$$\Delta_r H^{\circ}(323.15\,K) = -\,36.55 \pm 5.01\,kJ/mol$$

To understand whether the $SmBa_2Cu_3O_x$ phase decomposes to the 0.5 Sm_2O_3 + $2BaCuO_2$ + CuO mixture it is necessary to know the Gibbs energy. The values of entropies used for the calculation are given in Table 2. Entropies of Sm_2O_3, BaO, CuO, O_2 were taken from [15]. We measured the entropy of $BaCuO_2$ [3] using low-temperature adiabatic calorimetry and used this value for the Gibbs energy calculation. $S(BaCuO_2,\ s,\ 323.15\,K) = 125.3 \pm 0.6\,J/(K\,mol)$ [3].

There is no entropy of the $SmBa_2Cu_3O_x$ phase in literature. This value was estimated using entropies of Sm_2O_3, BaO, CuO (see Table 2).

$$S^{\circ}(Sm123,\ s,\ 323.15\,K) = 368.0\,J/(K\,mol).$$

Using the formation enthalpy of reaction (5) and data of Table 2 the Gibbs energy for the process (7) was estimated:

$$\Delta_r G^{\circ}(323.15\,K) = -21.03 \pm 5.01\,kJ/mol$$

On the basis of this value, it is concluded that the $SmBa_2Cu_3O_{6.92}$ phase is thermodynamically stable with respect to a decomposition according to reaction (7) at room temperature. Investigations performed by the authors [1,2,13] for 1:2:3 phases in the RE–Ba–Cu–O (RE = Y, Gd, Ho, Nd) systems showed that only phases with Gd and Nd are stable with respect to decomposition products including $BaCuO_2$ in contradiction to the 1:2:3 phases of Y and Ho.

5. Conclusion

The solution enthalpies of Sm_2O_3, $BaCO_3$, CuO, $SmBa_2Cu_3O_{6.92}$, $BaCuO_2$ at 323.15 K in 2N HCl were measured by solution calorimetry. On the basis of these data the following values were calculated:

1. the enthalpy of the reaction $0.5Sm_2O_3 + 2BaCO_3 + 3CuO + 0.21O_2 = SmBa_2Cu_3O_{6.92} + 2CO_2$;
2. the formation enthalpy of the $SmBa_2Cu_3O_{6.92}$ phase from binary oxide;
3. the $SmBa_2Cu_3O_{6.92}$ phase standard formation enthalpy;
4. the reactive enthalpy and Gibbs energy of reaction $0.5Sm_2O_3 + 2BaCuO_2 + CuO + 0.21O_2 = SmBa_2Cu_3O_{6.92}$.

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