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Optimization of the Solution-Free Process for the Preparation of Superconducting Materials from $SmBa_2Cu_3O_y$: Thermodynamic Aspects

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Abstract

Thermochemistry of the decomposition reactions of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions ($x = 0–0.8$) has been studied by solution calorimetry (2M HCl, 23.15 K). Dependences of the formation enthalpies of these compounds on the samarium content have been obtained. Analysis of the experimental data shows that the $Sm_{1+x}Ba_{2-x}Cu_3O_y$ phases can decompose into mixtures of variable composition in both inert and oxygen atmospheres. In an inert atmosphere, decomposition reactions can form mixtures of solid solutions with high samarium contents and barium cuprate. Under oxygen, decomposition can lead either to mixtures of phases with higher and lower samarium contents or to mixtures with high samarium contents and barium cuprate. Decomposition reactions of solid solutions are assumed to increase the critical current. For samples prepared under oxygen, the critical current is admitted to be stronger than for samples synthesized under an inert atmosphere. The results of thermochemical studies will permit optimization of the solution-free process for sample preparation from $SmBa_2Cu_3O_y$, which is currently the most promising and widely used technology.

INTRODUCTION

Recent progress in the application of 3D high-temperature superconductors (HTSCs) as permanent magnets, load transport systems, hysteresis motors, *etc.* calls for innovation and optimization in the field of superconductor technologies [1–3]. Systems currently employed for these purposes include RE–Ba–Cu–O (RE = Y, Sm, Nd, and other rare-earth elements). To understand processes that take place during synthesis of superconductor samples demands comprehensive physicochemical (in particular, thermodynamic) investigation of cuprates.

In recent decades, compounds of the Y–Ba–Cu–O (YBCO) system have become the key material for HTSC articles. However, wide use of these phases is hindered by the low magnitude of the trapped magnetic field. The pinning ability of YBCO may be improved by using neutron radiation. After an yttrium system has been irradiated at 77 K, the trapped magnetic field is 3.1 T *vs.* ~1 T before irradiation [4, 5]. For comparison, for nonirradiated Sm–Ba–Cu–O (SmBCO), the trapped magnetic field is 2.1 T at 77 K; *i. e.*, this is one of the best candidates for growing textured samples.

The goal of the present work is to study the thermodynamic properties of compounds of the Sm–Ba–Cu–O system for rationalizing processes that affect the superconducting characteristics of these materials. This study will make possible optimization of solution-free technology, which is currently widely employed for sample preparation from $SmBa_2Cu_3O_y$.

EXPERIMENTAL

Preparation of superconducting materials in Sm—Ba—Cu—O

One of the most widespread techniques for sample preparation from $SmBa_2Cu_3O_y$ to be used for manufacturing superconducting articles is as follows. A mixture of $SmBa_2Cu_3O_y$ and Sm_2BaCuO_5 phases with minor additions of metallic platinum and silver oxide is heated to a temperature close to the melting point (~1100 °C) in atmospheric conditions or in an atmosphere with a low oxygen pressure (oxygen mixed with argon). The temperature is slowly decreased at first to ~1000 °C and then to room temperature. In some cases, high-temperature annealing (at ~900 °C) is conducted for a few hours. The thus prepared samples are oxidized at 300–400 °C. The critical current measured for the samples depends on the atmosphere (air or argon with a low oxygen content) in which heating of $SmBa_2Cu_3O$ and Sm_2BaCuO_5 was conducted and on the use of sample annealing before high-temperature oxidation. A comprehensive physicochemical study of the Sm–Ba–Cu–O system is needed to examine the influence of these parameters on the superconducting characteristics. Here the following is worth noting. As is known [1–5], $YBa_2Cu_3O_y$ solid solutions (y = 6.0–7.0) are formed in YBCO, but barium is not replaced by yttrium. X-ray phase analysis and various other techniques were used to show [6–8] that this kind of substitution leads to $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions with a homogeneity region of $x = 0$ to 0.8. The existence of solid solutions permits one to smoothly adjust the superconducting properties; on the other hand, it occasionally leads to lower superconducting transition temperatures. Therefore, it is important to investigate the $Sm_{1+x}Ba_{2-x}Cu_3O_y$ phases.

This work reports on the thermodynamic characteristics of solid solutions with different samarium contents and studies the transport properties of the textured samples prepared from the $SmBa_2Cu_3O_y$ phase. The ceramic materials under study ($Sm_{1+x}Ba_{2-x}Cu_3O_y$) were synthesized from samarium (III) oxide, copper (II) oxide, and barium carbonate at 1173 K with subsequent annealing in oxygen. $SmBa_2Cu_3O_{6.91}$ was also obtained from nitrates by the sol-gel method. The samples were characterized by X-ray phase and chemical analyses. According to the data obtained, all substances under study are individual phases.

Thermodynamic studies of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions

The thermodynamic characteristics of the $Sm_{1+x}Ba_{2-x}Cu_3O_y$ phases were determined by the solution calorimetry technique, yielding the formation enthalpies of compounds at room temperature. The thermochemical cycle was arranged in such a way that the solution enthalpy of the substance was compared with that of a mixture of samarium (III) oxide, copper (II) oxide, and barium carbonate. Thermochemical reaction conditions and details of measurement procedures are found in previous publications [9–12]. The samples under study included $SmBa_2Cu_3O_{6.92}$, $Sm_{1.1}Ba_{1.9}Cu_3O_{6.91}$, $Sm_{1.4}Ba_{1.9}Cu_3O_{6.96}$, $Sm_{1.6}Ba_{1.4}Cu_3O_{7.16}$ and $Sm_{1.8}Ba_{1.2}Cu_3O_{7.18}$. Reaction enthalpies were calculated from the solution enthalpies of Sm_2O_3, CuO, $BaCO_3$, and $Sm_{1+x}Ba_{2-x}Cu_3O_y$ measured in a 2 M HCl solution for the following general reactions:

$$0.5(1 + x)Sm_2O_3 + 3CuO + (2 - x)BaCO_3 + aO_2 = Sm_{1+x}Ba_{2-x}Cu_3O_y + (2 - x)CO_2 \quad (1)$$

Table 1 lists the formation enthalpies for reaction (1).

The experimental data obtained were used along with the reference values taken from [13, 14] to calculate the formation enthalpies of solid solutions according to the reaction scheme

$$0.5(1 + x)Sm_2O_3 + 3CuO + (2 - x)BaO + aO_2 = Sm_{1+x}Ba_{2-x}Cu_3O_y \quad (2)$$

In terms of thermochemistry, the enthalpy of this process is called the enthalpy of formation from oxides and is denoted as $\Delta_{ox}H^o$ [15]. Based on experimental data one can evaluate $\Delta_{ox}H^o$ for solid solutions for which the oxygen contents are indicated in Table 1. Then the formation enthalpies of solid solutions with the same oxygen content but with different values of x are calculated in order to trace the dependence of the formation enthalpy on the cation content alone. For this, the enthalpies of formation from oxides were calculated using the mean oxidation enthalpy [9, 16, 17] for $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions where

TABLE 1

Enthalpies of formation of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ from Sm_2O_3, CuO and $BaCO_3$

Compound	$\Delta_{car}H^\circ$ (323.15 K), kJ/mol
$SmBa_2Cu_3O_{6.92}$	+367.45 ± 5.01
$Sm_{1.1}Ba_{1.9}Cu_3O_{6.91}$	+350.22 ± 4.48
$Sm_{1.4}Ba_{1.6}Cu_3O_{6.96}$	+282.59 ± 5.86
$Sm_{1.6}Ba_{1.4}Cu_3O_{7.16}$	+238.54 ± 5.80
$Sm_{1.8}Ba_{1.2}Cu_3O_{7.18}$	+208.29 ± 5.06

$y = 6$ and 7. The dependences of these quantities are plotted in Fig. 1.

Analysis of the data obtained showed that when $x = 0.4$, the straight lines have a bending, possibly corresponding to a transition of the orthorhombic modification to the tetragonal one. For $Sm_{1+x}Ba_{2-x}Cu_3O_y$ phases ($x = 0.3-0.4$), a transition of this kind was observed by Japanese scientists [16], and it was also reported in a study of lattice parameters [18].

The dependences presented in Fig. 1 suggest that a reaction forming phases with higher or lower samarium contents can occur under oxygen:

$$aSm_{1+x}Ba_{2-x}Cu_3O_y + bO_2 = cSm_{1+x+d}Ba_{2-x-d}Cu_3O_{y1} + dSm_{1+x-d}Ba_{2-x-d}Cu_3O_{y2} \qquad (3)$$

We can arrive at this conclusion if we admit that the total entropy of solid solutions ($cSm_{1+x+d}Ba_{2-x-d}Cu_3O_{y1}$, $dSm_{1+x+d}Ba_{2-x-d}Cu_3O_{y2}$) formed by reaction (3) equals the entropy of the starting products. The available experimental data [19] support this assumption, since the entropy of complex oxides (in particular, HTSCs) may be evaluated (with a high degree of accuracy) as the sum of the entropies of binary oxides.

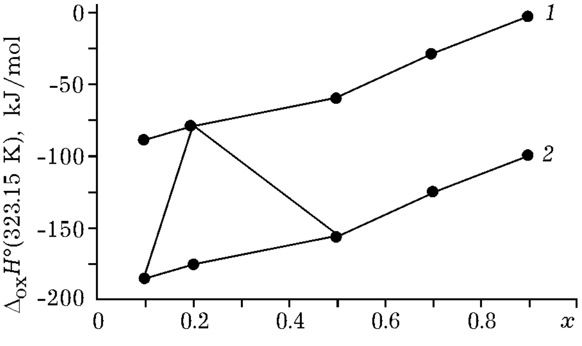

Fig. 1. Dependences of the formation enthalpies of $Sm_{1+x}Ba_{2-x}Cu_3O_6$ (*1*) and $Sm_{1+x}Ba_{2-x}Cu_3O_7$ (*2*) solid solutions obtained from oxides on the cation composition.

Evidence in support of feasibility of reaction (3) is interesting from the viewpoint of the number of defects and structure nonhomogeneity, presumably increased by reaction (3). These effects, in turn, can increase the peak effect and hence the critical current in superconductors.

Furthermore, it was interesting to compare the formation enthalpies of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions with the formation enthalpy of barium cuprate. As the $SmBa_2Cu_3O_y$ phase is employed for synthesis of superconductors, it is important to examine the decomposition products of the phase. For this, it is necessary to investigate the decomposition of $SmBa_2Cu_3O_y$ into mixtures of phases including barium cuprate. For thermochemical analysis of reactions with $BaCuO_2$ we took the formation enthalpy $\Delta_{ox}H^\circ$ (323.15 K, $BaCuO_2$) = −71.4 ± 1.9 kJ/mol [20]. The dependences of the formation enthalpies of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ on the composition are plotted in Fig. 2 using data for barium cuprate.

It can be seen that under oxygen the $Sm_{1+x}Ba_{2-x}Cu_3O_y$ phases can form solid solutions with higher samarium contents and barium cuprate; *i. e.*, the following process can occur:

$$aSm_{1+x}Ba_{2-x}Cu_3O_y + bO_2 = cSm_{1+x+d}Ba_{2-x-d}Cu_3O_{y1} + dBaCuO_2 \qquad (4)$$

Moreover, the dependence shown in Fig. 2 suggests that solid solutions with higher samarium contents and barium cuprate can also form in reactions of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ with low contents of oxygen ($x = 0-0.4$) in an inert atmosphere. This process is represented by the following scheme:

$$aSm_{1+x}Ba_{2-x}Cu_3O_y = bSm_{1+x+d}Ba_{2-x-d}Cu_3O_{y1} + cBaCuO_2 \qquad (5)$$

Thus thermochemical analysis has demonstrated that solid solutions with high samarium contents and barium cuprate can

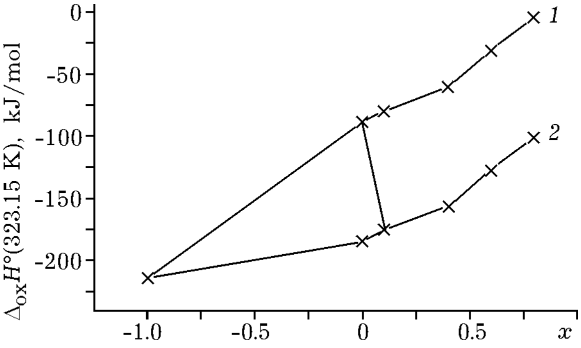

Fig. 2. Dependences of the formation enthalpies of $Sm_{1+x}Ba_{2-x}Cu_3O_6$ (*1*) and $Sm_{1+x}Ba_{2-x}Cu_3O_7$ (*2*) on x.

form from $Sm_{1+x}Ba_{2-x}Cu_3O_y$ when the reaction is performed in an inert atmosphere (reaction (5)). When the process is conducted under oxygen, these compounds can additionally decompose into solid solutions with higher and lower samarium contents and barium cuprate (reactions (3) and (4)). Analyzing the variation of the critical current caused by changes in the number of defects from the viewpoint of the results of this study, one can state the following.

1. High-temperature annealing, leading to decomposition of solid solutions, can cause an increase in the critical current.
2. For samples obtained under oxygen, the transport properties must be better than those for phases synthesized in an inert atmosphere.

Let us consider the available data on the transport properties of solid solutions in the Sm–Ba–Cu–O system in the context of the results of this study.

Transport characteristics of superconductors based on $SmBa_2Cu_3O_y$

The variation of the critical current was analyzed with allowance for data obtained from decomposition of solid solutions in the Sm–Ba–Cu–O system, and transport characteristics of textured samples subjected to thermal treatment in various gas phases were studied experimentally [17, 18]. The samples were synthesized from $SmBa_2Cu_3O_y$ and Sm_2BaCuO_5 phases taken in a ratio of 3 : 1 with additions of 0.5 % Pt and 10 % Ag_2O (by mass). Syntheses were conducted at T = 1353 K in air; the temperature was subsequently lowered to 1313, 1303, 1283, and 293 K. Then the compounds were annealed at 573–673 K in a pure oxygen atmosphere. For the resulting textured samples, the critical current was J_c = 1.5 10^4 A/cm^2. Annealing in argon (*i.e.*, in an inert atmosphere) at 1198 K increased J_c to 2.3 10^4 A/cm^2. For samples subjected to thermal treatment at 1198 K under oxygen (0.1 %), the critical current was 2.8 10^4 A/cm^2. These data, showing how different conditions of annealing affect the critical current, are comparable to experimental data obtained from decomposition of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions. That is, high-temperature annealing (at 1198 K in this case) under argon can lead to decomposition of solid solutions according to scheme (5), giving rise to nonhomogeneity and increasing the critical current, which was just observed in experiments. Thus assumption 1 is confirmed.

When the compounds $Sm_{1+x}Ba_{2-x}Cu_3O_y$ are annealed under oxygen, their decomposition can follow route (5) or any of routes (3) or (4). Therefore, we have an extra opportunity to increase the number of defects and structure nonhomogeneity. This should result in still higher values of J_c, which was confirmed by experiment. Consequently, assumption 2 is confirmed.

Thus data obtained by high-temperature decomposition of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions provided an explanation to the experimental facts. These studies also permit optimization of the process for the production of textured samples and enable one to develop the strategy of increasing the critical current in experiment.

CONCLUSIONS

1. The solution calorimetry technique was used to study the thermochemistry of the decomposition reactions of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ solid solutions (x = 0–0.8). The dependences of the formation enthalpies on x have been obtained for these compounds.
2. It has been shown that solid solutions based on the $SmBa_2Cu_3O_y$ phase can decompose into mixtures of variable compositions. Further decomposition reactions of $Sm_{1+x}Ba_{2-x}Cu_3O_y$ can take place when the reaction is conducted under oxygen (*versus* the inert atmosphere).

3. It is assumed that decomposition of solid solutions can increase the critical current. For samples obtained under oxygen, the critical current should exceed that of phases synthesized in an inert atmosphere.

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