

Short communication

Formation enthalpies and thermodynamic stability of the $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solutions

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Abstract

Enthalpies of solution of Sm_2O_3 , BaCO_3 , CuO , $\text{Sm}_2\text{BaCuO}_5$, and $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solutions ($x = 0.1, 0.7$) were measured by solution calorimetry using 2 N HCl solvent at 323 K. The obtained values were used to give thermodynamic data for reactions of formation of $\text{Sm}_2\text{BaCuO}_5$, $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$, $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$ from the mixture including BaCO_3 . The enthalpies of reactions were determined as $+185 \pm 3$ kJ/mol for $\text{Sm}_2\text{BaCuO}_5$, $+357 \pm 5$ kJ/mol for $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$, $+216 \pm 5$ kJ/mol for $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$. The data obtained showed that the above mentioned phases were thermodynamically stable with respect to mixture with BaCuO_2 , Sm_2O_3 , CuO .

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Keywords: Calorimetry; Sm–Ba–Cu–O system; Thermodynamic stability

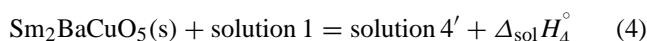
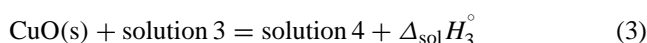
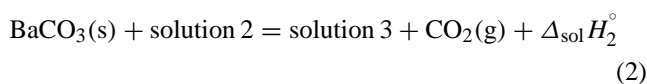
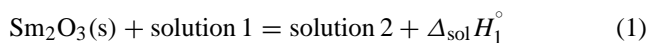
1. Introduction

As it is known, experimental results with $\text{SmBa}_2\text{Cu}_3\text{O}_y$ (Sm123) demonstrate the high potential of these high temperature superconductors (HTSC) materials for bulk application [1–3]. Due to a partial substitution of Ba by Sm, Sm123 forms a solid solution $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ where the solid solubility extends up to $x = 0.8$. The existence of a range of solid solutions makes it more difficult to control the physical properties of materials based on Sm123 [4]. The superconducting properties of samples depend strongly on temperatures of synthesis and annealing. A good understanding of thermodynamic stability of solid solutions with respect to different mixtures is essential for finding the optimum synthesis conditions of $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$.

The aim of this paper is to measure thermodynamic characteristics of the $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_x$, $\text{Sm}_2\text{BaCuO}_5$ phases and to study thermodynamic stability of solid solutions in the Sm–Ba–Cu–O system with respect to different mixtures. There are no thermochemical data for these compounds in literature.

2. Investigation methods and experimental technique

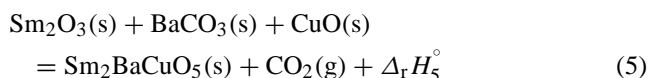
Solution calorimetry was used as an investigation method. Calorimetric cycles were designed in such a way that it was possible to determine the formation enthalpy of phases in the Sm–Ba–Cu–O system from samarium oxide (Sm_2O_3), copper oxide (CuO), and barium carbonate (BaCO_3). The dissolution processes to calculate the formation enthalpy of $\text{Sm}_2\text{BaCuO}_5$ are described by the equations



Here: s: solid; g: gas; $\Delta_{\text{sol}}H_{\text{an}}^\circ$: the molar enthalpy of solution; solution 1: solution of 2 N HCl; solution 2: solution 1 + $2\text{SmCl}_3(\text{sol}) + 3\text{H}_2\text{O}(\text{sol}) - 6\text{HCl}(\text{sol})$; solution 3: solution 1 + $2\text{SmCl}_3(\text{sol}) + \text{BaCl}_2(\text{sol}) + 4\text{H}_2\text{O}(\text{sol}) - 8\text{HCl}(\text{sol})$; solution 4: solution 1 + $2\text{SmCl}_3(\text{sol}) + \text{BaCl}_2(\text{sol}) + \text{CuCl}_2(\text{sol}) + 5\text{H}_2\text{O}(\text{sol}) - 10\text{HCl}(\text{sol})$.

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If solution 4, obtained after dissolution of $\text{Sm}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$ mixture, and solution 4', obtained after dissolution of the $\text{Sm}_2\text{BaCuO}_5$ phase, are assumed to be identical, the following equation can be written



where

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

The identical state of the solution obtained by dissolution of the $\text{Sm}_2\text{BaCuO}_5$ phase and dissolution of $\text{Sm}_2\text{O}_3 + \text{BaCO}_3 + \text{CuO}$ mixture was proved in paper [5] by measuring the electronic spectra of these solutions in the range $10^4 - 3 \times 10^4 \text{ cm}^{-1}$.

Calorimetric cycles for $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ were similar to above described equations.

The experiments were performed in an automatic dissolution calorimeter with an isothermal shield. The construction of the solution calorimeter and the experimental procedure are described elsewhere [5]. The volume of the calorimetric vessel was 200 ml. 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) is in good agreement with the value recommended in the literature [6]. The experiments were performed at 323 K. The amounts of substances used were 0.06–0.3 g.

3. Sample preparation

The following materials were used in the experiments: Sm_2O_3 (high purity) that before use was kept at 1023 K in air for 10 h; CuO (high purity) that was heated in O_2 atmosphere for 15 h ($T = 900 \text{ K}$); BaCO_3 (high purity) that was kept at 650 K in air for 4 h. The sample of $\text{Sm}_2\text{BaCuO}_5$ was prepared from Sm_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. We investigated two single crystals: $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$ and $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$. Sample of $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$ were grown from CuO – BaO flux in an atmosphere of 300 mbar air in a ZrO_2/Y crucible by method described in paper [7]. They have been oxidized between 390–290 °C during 300 h in 1 bar O_2 . Their T_c value is 77 K. $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$ has been grown in 1 bar air in ZrO_2/Y crucible. The crystals have been oxidized in 1 bar O_2 between 600 and 400 °C for about 650 h. All compounds were characterized by X-ray power diffraction and chemical analysis [8]. The content of copper 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 relative standard deviation (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 . According to the results of the analyses the involved compounds were found to be single phases with an accuracy of about 1%.

4. Experimental results

We measured the following values of the molar dissolution enthalpies:

$$\Delta_{\text{sol}} H^\circ (\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}, 323.15 \text{ K}) = -783 \pm 4 \text{ kJ/mol};$$

$$\Delta_{\text{sol}} H^\circ (\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}, 323.15 \text{ K}) = -757 \pm 3 \text{ kJ/mol};$$

$$\Delta_{\text{sol}} H^\circ (\text{Sm}_2\text{BaCuO}_5, 323.15 \text{ K}) = -663 \pm 2 \text{ kJ/mol};$$

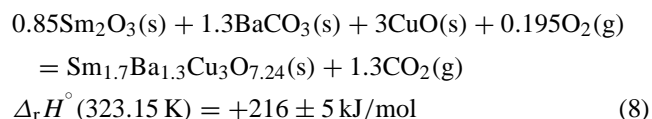
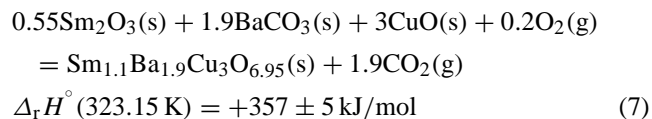
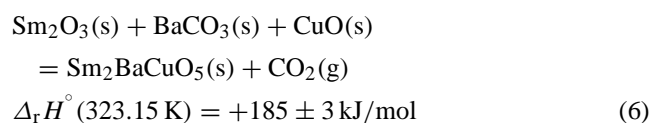
$$\Delta_{\text{sol}} H^\circ (\text{Sm}_2\text{O}_3, 323.15 \text{ K}) = -407 \pm 3 \text{ kJ/mol};$$

$$\Delta_{\text{sol}} H^\circ (\text{BaCO}_3, 323.15 \text{ K}) = -10 \pm 1 \text{ kJ/mol};$$

$$\Delta_{\text{sol}} H^\circ (\text{CuO}, 323.15 \text{ K}) = -60.8 \pm 0.7 \text{ kJ/mol}.$$

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

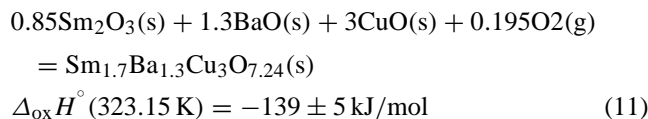
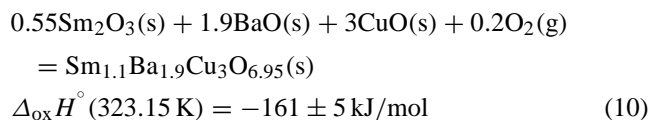
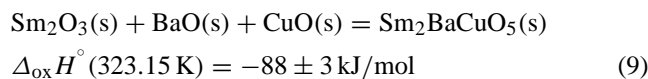
The measured enthalpies of dissolution were used for calculating the enthalpies of the reactions



The experimental data were also used to study the thermodynamic phase stability with respect to the phase mixtures with the same nominal composition.

On the basis of enthalpies of reactions (6)–(8) and literature data for the heat of the reaction $\text{BaO} + \text{CO}_2 = \text{BaCO}_3$ (–272.40 kJ/mol) [9] we calculated the enthalpies of formation of $\text{Sm}_2\text{BaCuO}_5$, $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$,

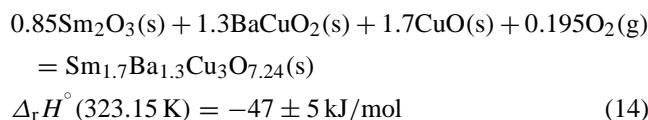
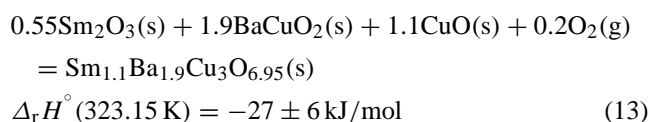
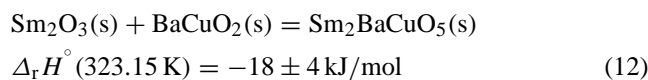
$\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$ from the oxides



These data and entropies of all the substances employed in reactions (9–11) allow us to conclude that the formation of Sm_{211} and $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ ($x = 1.1; 1.7$) from the oxides is thermodynamically favourable at room and higher temperature.

Experimental results on synthesis of the $\text{Sm}_{1+x}\text{Ba}_{2-x}\text{Cu}_3\text{O}_y$ solid solutions showed that the main impurity phase was BaCuO_2 . So, it is interesting to study the thermodynamic stability with respect to mixtures involved this phase.

Using experimental data for the reactions (6–8) obtained in this paper, and our earlier data for the reaction $\text{BaCO}_3 + \text{CuO} = \text{BaCuO}_2 + \text{CO}_2$ ($\Delta_r H^\circ = +202.01 \pm 1.9 \text{ kJ/mol}$ [5]), it is possible to obtain thermodynamical data for the stability of $\text{Sm}_2\text{BaCuO}_5$, $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$, $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$ with respect to mixtures including BaCuO_2 . The results are given below.



Literature data on the entropies of Sm_2O_3 , CuO , BaCuO_2 , $\text{Sm}_2\text{BaCuO}_5$, $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$, $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$ [5,10], and the values of the enthalpies of reactions (12–14) allow us to conclude that Sm_{123} solid solutions with $x = 1.1, 1.7$ are thermodynamically more favourable than

the mixture of barium cuprate, and samarium and copper oxides at room temperatures.

5. Conclusions

Solution calorimetry was used to measure dissolution enthalpies of phases: Sm_2O_3 , CuO , BaCO_3 , $\text{Sm}_2\text{BaCuO}_5$, $\text{Sm}_{1.1}\text{Ba}_{1.9}\text{Cu}_3\text{O}_{6.95}$, $\text{Sm}_{1.7}\text{Ba}_{1.3}\text{Cu}_3\text{O}_{7.24}$. Basing on the above data the enthalpies of the following reactions with $\text{Sm}_{123\text{ss}}$ and $\text{Sm}_2\text{BaCuO}_5$ were calculated:

1. formation enthalpies of $\text{Sm}_2\text{BaCuO}_5$ and $\text{Sm}_{123\text{ss}}$ ($x = 1.1, 1.7$) from the mixture of Sm_2O_3 , CuO , BaCO_3 ;
2. formation enthalpies of $\text{Sm}_2\text{BaCuO}_5$ and $\text{Sm}_{123\text{ss}}$ ($x = 1.1, 1.7$) from the mixture of binary oxides;
3. formation enthalpies of $\text{Sm}_2\text{BaCuO}_5$ and $\text{Sm}_{123\text{ss}}$ ($x = 1.1, 1.7$) from the mixture of Sm_2O_3 , CuO , BaCuO_2 .

Data obtained by solution calorimetry and additional information on the entropies of different substances show the thermodynamical stability of $\text{Sm}_2\text{BaCuO}_5$ and $\text{Sm}_{123\text{ss}}$ with respect to the mixture of Sm_2O_3 , CuO , BaCuO_2 .

Acknowledgements

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