

Thermochemistry of $\text{Gd}_2\text{BaCuO}_5$ and $\text{LuBa}_2\text{Cu}_3\text{O}_x$ Nata I. Matskevich,^{*,†} Thomas Wolf,[‡] and Yurii I. Pochivalov[§]

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Solution calorimetry, using 6.0 M HCl as a solvent, is used to study the thermochemistry of $\text{Gd}_2\text{BaCuO}_5$ and the high-temperature superconductor $\text{LuBa}_2\text{Cu}_3\text{O}_{6.92}$. For the first time, the standard formation enthalpies of these phases have been determined as follows: $\Delta_f H^\circ (\text{Gd}_2\text{BaCuO}_5, \text{s}, 298.15 \text{ K}) = -2618.6 \pm 7.4 \text{ kJ/mol}$; $\Delta_f H^\circ (\text{LuBa}_2\text{Cu}_3\text{O}_{6.92}, \text{s}, 298.15 \text{ K}) = -2693.1 \pm 11.9 \text{ kJ/mol}$. The thermodynamic stability at room temperature has been assessed. The results show that Gd211 and Lu123 are thermodynamically stable with respect to binary oxides and unstable with respect to interaction with CO_2 at ambient temperatures. Lu123 is thermodynamically stable with respect to assemblages containing combinations of Lu_2O_3 , CuO , and BaCuO_2 and thermodynamically unstable with respect to interactions with water.

1. Introduction

Since the discovery of high-temperature superconductors (HTSCs), a lot of investigations on physico-chemical properties and syntheses of new superconducting materials have been carried out.^{1–7} At present, a key research area is the development of second-generation HTSC devices, such as superconducting wires, magnetic bearings, motors and generators, and flywheel energy storage systems.^{6,7} Of the available HTSC materials, the REBCO (where RE = rare earth such as Nd, Sm, Gd, etc. or Y) family offers the greatest potential for application. It is known that $\text{RE}_2\text{BaCuO}_5$ (RE211), dispersed as secondary phase particles in bulk $\text{REBa}_2\text{Cu}_3\text{O}_x$ (RE123), has a strong influence on the micro-

structure and pinning properties in RE–Ba–Cu–O bulk materials. It is also known that one of the prospective technologies to prepare RE123 compounds is a partial melting process.⁸ This process is based on a peritectic reaction, in which the RE123 phase is formed from solid $\text{RE}_2\text{BaCuO}_5$ and a liquid phase containing Cu, Ba, and O. It is necessary to carry out physico-chemical investigations, in particular, thermodynamic studies, of all compounds in the RE_2O_3 –BaO–Cu–O system in order to understand the melting process in detail and to improve its technology. Especially, it is important to study the $\text{RE}_2\text{BaCuO}_5$ and $\text{REBa}_2\text{Cu}_3\text{O}_x$ phases, which are the main constituents in the melting process.

For technical applications, we should have stable materials for devices. Therefore, the study of the stability of these compounds is one of the important areas in the field of HTSC research. The study of thermodynamic stability involves at least three aspects: (1) stability with respect to internal reactions, for example, phase transformations; (2) stability with respect to other oxide phases, for example, the stability of RE123 phases with respect to mixtures of RE_2O_3 , BaCuO_2 , and CuO ; and (3) stability with respect to reactions with extraneous compounds such as H_2O , CO_2 , O_2 , H_2 , and so forth.

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Much work has been done in the RE₂O₃–BaO–Cu–O systems. However, there are some uncertainties regarding their thermochemistry. Thermochemical properties were investigated mainly for Y₂O₃–BaO–Cu–O,^{9–14} and to a lesser extent for other RE₂O₃–BaO–Cu–O systems.^{15,16} We determined the enthalpy of formation of GdBa₂Cu₃O_x previously.¹⁶ There are no thermochemical data for Gd₂BaCuO₅ and the superconductor LuBa₂Cu₃O_x. In this paper, for the first time, we report standard formation enthalpies of Gd₂BaCuO₅ and LuBa₂Cu₃O_x and discuss their thermodynamic stability.

2. Experimental Section

A. Samples Preparation and Characterization. Reagents Gd₂O₃ (99.99% Alfa), Lu₂O₃ (99.999% Alfa), Lu (99.999% Alfa), BaCO₃ (99.999% Cerac), and CuO (99.999% Alfa) were used for synthesis of oxide compounds in the Gd₂O₃–BaO–CuO and Lu₂O₃–BaO–Cu–O systems and for the calorimetric experiments.

All starting materials were annealed at high temperatures before solid-state reactions. Gd₂O₃ and Lu₂O₃ were annealed at 1023 K in the air for 10 h; CuO was heated in an O₂ atmosphere for 15 h ($T = 900$ K); BaCO₃ was annealed at 650 K in the air for 4 h for the preparation of Gd₂BaCuO₅. For the preparation of LuBa₂Cu₃O_x, BaCO₃ was calcined at 1123 K for 20 h and then at 1173 K for 65 h in a continuously pumped vacuum. At the end of this process, the pressure was less than 3×10^{-5} bar. From weight loss, a complete decomposition to BaO could be confirmed.

The LuBa₂Cu₃O_x samples were prepared from Lu₂O₃, CuO, and BaO powder at the appropriate stoichiometry. The reactants were carefully weighed and mixed in a planetary mill, and then pressed and heated at 1123 K for 150 h and then at 1173 K for 101 h in an atmosphere of 100 mbar of oxygen flow. Lu123 samples with an oxygen content of $x = 6.92$ were obtained by annealing at 723 K for 23 h in 1 bar of O₂. T_c was 92.1 ± 1.1 K.

Gd₂BaCuO₅ was synthesized from Gd₂O₃, CuO, and BaCO₃ at 1273 K for 70 h with several intermediate grindings.

The samples were characterized using powder X-ray diffraction (STADI-P, Stoe diffractometer, Germany, Cu K_{α1} radiation). The powder patterns agree well with the patterns known from the literature.^{17,18} X-ray diffraction analysis confirmed that Gd₂BaCuO₅ and LuBa₂Cu₃O_x were single-phase. The Lu123 phase has space group *Pmmm* and Gd₂BaCuO₅ space group *Pnma*.^{17,18}

All compounds were also characterized by chemical analysis. For the analysis of Gd and Lu, a spectrophotometric method (spectropho-

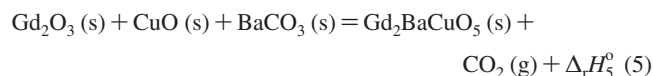
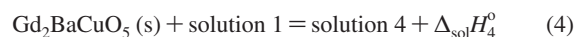
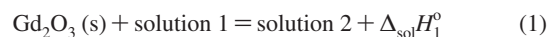
tometer SF-46) was used. Ba was determined by flame photometry, and Cu by atomic absorption (air–acetylene, Hitachi Z-8000). The content of impurities was determined by spectral methods (mass-spectrometer “Element”, Finnigan Mat, Germany).^{12,16} The analyses indicated that impurities of Ho, Dy, Eu, Yb, La, Tm, Er, Nd, Pr, Sm, Ce, Te, Ca, Mg, Mn, Pb, and Ag metals were present at a level of 10^{-3} to 10^{-4} atom %. The oxygen contents were determined by iodometric titration using 0.01 N Na₂S₂O₃·5H₂O according to the method described in ref 19. The results of the chemical analysis for Gd₂BaCuO₅ and LuBa₂Cu₃O_x allow us to conclude that these phases have the following compositions: LuBa_{1.98±0.03}Cu_{2.98±0.05}O_{6.92±0.03} and Gd₂Ba_{0.98±0.02}Cu_{1.01±0.03}O_{5.02±0.03}.

The microstructure of Lu123 was analyzed by transmission electron microscopy (transmission electron microscope EMB-100, Russia). It was found that the powder size was in the range from 0.28 up to 1.2 μm.

B. Experimental Technique. The calorimetric experiments were performed in an automatic dissolution calorimeter with an isothermal shield. The main part of the calorimeter was a Dewar vessel with a brass cover ($V = 200$ mL). The platinum thermometer, calibration heater, cooler, mixer, and 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.²⁰ Dissolution of potassium chloride in water was performed to calibrate the calorimeter. The obtained dissolution heat of KCl was 17.41 ± 0.04 kJ mol⁻¹ (the molality of the final solution was 0.028 mol kg⁻¹, $T = 298.15$ K). The literature data are 17.42 ± 0.02 kJ mol⁻¹²¹ and 17.47 ± 0.07 kJ mol⁻¹.²²

The experiments were performed at 323.15 K. At lower temperatures, the rate of dissolution of CuO is small, which results in a low precision of the measurements. The amounts of substances used were LuBa₂Cu₃O_{6.92}, about 0.13 g; Gd₂BaCuO₅, about 0.2 g; CuO, about 0.04 g; BaCO₃, about 0.07 g; Lu, about 0.03 g; and Gd₂O₃, about 0.13 g. All compounds were stored in a dry box to prevent interaction with moisture or CO₂.

C. Thermochemical Cycles. Gd₂BaCuO₅. To obtain the thermochemical data of Gd₂BaCuO₅, we designed a calorimetric cycle in such a way that the solution enthalpy of Gd₂BaCuO₅ was compared with the dissolution enthalpies of Gd₂O₃, BaCO₃, and CuO. The dissolution processes are described by the following equations



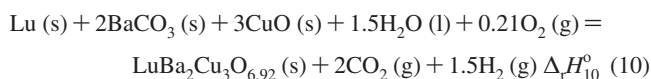
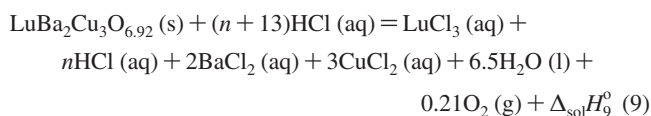
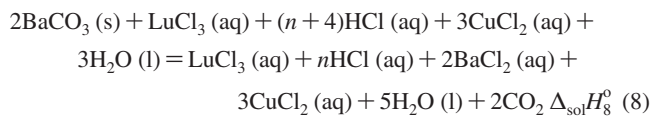
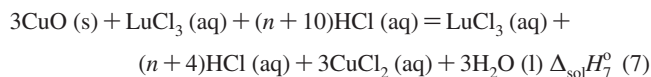
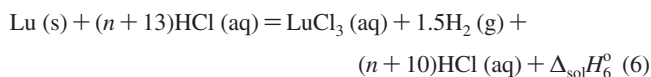
where solution 1 is a 6 M solution of HCl, $\Delta_rH_5^{\circ} = \Delta_{\text{sol}}H_1^{\circ} + \Delta_{\text{sol}}H_2^{\circ} + \Delta_{\text{sol}}H_3^{\circ} - \Delta_{\text{sol}}H_4^{\circ}$.

LuBa₂Cu₃O_x. To determine the enthalpies of reactions with LuBa₂Cu₃O_x, we initially tried to dissolve Lu₂O₃ in different concentrations of HCl, which, however, was not possible. For this reason, we chose thermochemical cycles, in which we dissolved

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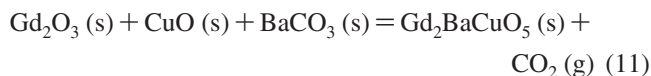
Lu, BaCO₃, CuO, and LuBa₂Cu₃O_x. A detailed scheme of the thermochemical reactions for LuBa₂Cu₃O_{6.92} is given below:



3. Results and Discussion

Gd₂BaCuO₅ is called the “green phase” and is often found as an impurity phase in 123 samples. The solution enthalpies of reactions (1–4) were $\Delta_{\text{sol}}H_1^{\circ}$ (Gd₂O₃, s, 323.15 K) = -411.4 ± 3.6 kJ/mol, $\Delta_{\text{sol}}H_2^{\circ}$ (CuO, s, 323.15 K) = -51.1 ± 2.1 kJ/mol, $\Delta_{\text{sol}}H_3^{\circ}$ (BaCO₃, s, 323.15 K) = -15.3 ± 2.5 kJ/mol, and $\Delta_{\text{sol}}H_4^{\circ}$ (Gd₂BaCuO₅, s, 323.15 K) = -675.2 ± 3.4 kJ/mol. The dissolution enthalpies of reactions 1–4 were calculated from the average values of six experiments. Errors were calculated for the 95% confidence interval using the Student’s coefficients.

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

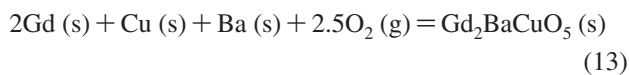


$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = +197.4 \pm 5.9\text{kJ/mol}$$

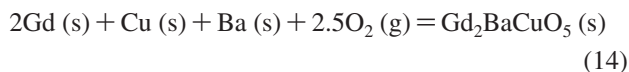
Literature data for the heat of reaction BaO + CO₂ = BaCO₃; formation enthalpies of BaO, CuO, and Gd₂O₃; and heat capacities²² were used to calculate the enthalpy of formation of Gd₂BaCuO₅ from binary oxides and standard formation enthalpy as follows:



$$\Delta_{\text{ox}}H^{\circ} (323.15\text{K}) = -75.2 \pm 6.0\text{kJ/mol}$$



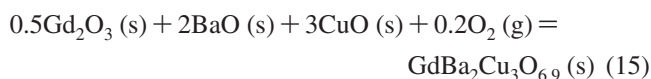
$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = -2618.7 \pm 7.4\text{kJ/mol}$$



$$\Delta_{\text{f}}H^{\circ} (298.15\text{K}) = -2618.7 \pm 7.4\text{kJ/mol}$$

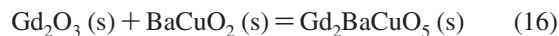
It is necessary to note that in this paper the enthalpies of formation refer to 1 mol of formula and not to a mole of atoms.

We have measured previously¹⁶ the thermodynamic properties of the GdBa₂Cu₃O_{6.92} phase as follows:

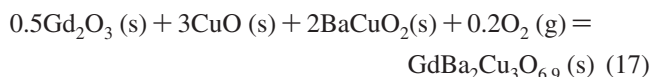


$$\Delta_{\text{ox}}H^{\circ} (323.15\text{K}) = -174.1 \pm 12.6\text{kJ/mol}$$

Data for the enthalpies of reactions 12 and 15 and our data on the enthalpy of reaction of BaO + CuO = BaCuO₂¹⁶ were used to calculate the enthalpies of reactions:

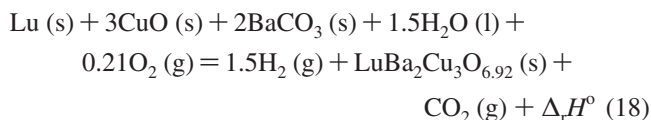


$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = -3.9 \pm 6.3\text{kJ/mol}$$



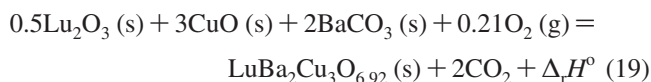
$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = -31.5 \pm 13.2\text{kJ/mol}$$

The derivation of the enthalpy of formation of LuBa₂Cu₃O_{6.92} from the solution calorimetric data was done using the dissolution of lutetium metal, CuO, BaCO₃, and LuBa₂Cu₃O_{6.92} in hydrochloric acid. The solution enthalpies of reactions 6–9 $-\Delta_{\text{sol}}H_6^{\circ}$ (Lu, s, 323.15 K) = -702.7 ± 2.3 kJ/mol, $\Delta_{\text{sol}}H_7^{\circ}$ (CuO, s, 323.15 K) = -51.1 ± 2.1 kJ/mol, $\Delta_{\text{sol}}H_8^{\circ}$ (BaCO₃, s, 323.15 K) = -15.3 ± 2.5 kJ/mol, and $\Delta_{\text{sol}}H_9^{\circ}$ (LuBa₂Cu₃O_{6.92}, s, 323.15 K) = -730.7 ± 3.1 kJ/mol—allow one to calculate the enthalpy of the reaction:

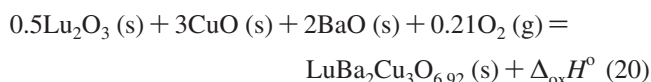


$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = -156.0 \pm 9.0\text{kJ/mol}$$

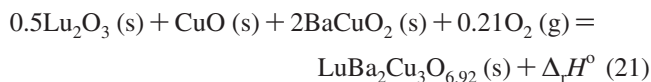
The heat of formation of LuBa₂Cu₃O_{6.92} from binary oxides, or mixtures including BaCuO₂ or barium carbonate, and the standard formation enthalpy were calculated from our calorimetric data as well as from literature data using enthalpies of H₂O, Lu₂O₃, BaO, CuO, BaCO₃, CO₂, and BaCuO₂ and the heat capacities of the used compounds:²²



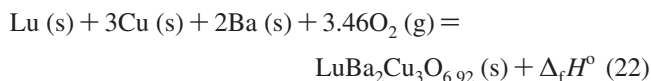
$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = +354.4 \pm 9.2\text{kJ/mol}$$



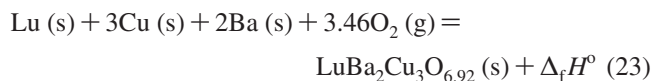
$$\Delta_{\text{ox}}H^{\circ} (323.15\text{K}) = -190.9 \pm 9.4\text{kJ/mol}$$



$$\Delta_{\text{f}}H^{\circ} (323.15\text{K}) = -47.8 \pm 10.1\text{kJ/mol}$$



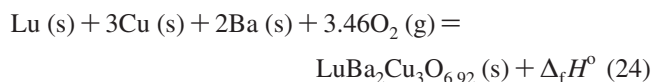
$$\Delta_{\text{f}}H^{\circ} (298.15\text{K}) = -2692.7 \pm 11.9\text{kJ/mol}$$



$$\Delta_f H^\circ (298.15\text{K}) = -2693.1 \pm 11.9\text{kJ/mol}$$

It is necessary to note the following. The reference state for the formation enthalpy is called the standard formation enthalpy. For solids, the standard state is the thermodynamically stable state at a pressure of 1 atm and a temperature of 298.15 K. To transfer the standard formation enthalpy from 323.15 to 298.15 K, we have performed the following. We have calculated the formation enthalpies from oxides for Gd211 and Lu123 (reactions 12 and 20) at 323.15 K. Using heat capacities of the compounds of reactions 12 and 20,²² we have calculated the formation enthalpies from oxides for the same reactions at 298.15 K. Then, on the basis of standard formation enthalpies of Lu₂O₃, BaO, CuO, and Gd₂O₃, we have calculated the standard formation enthalpies, that is, enthalpies at $P = 1 \text{ atm}$, $T = 298.15 \text{ K}$.

We also used another scheme of calorimetric reactions to calculate the standard formation enthalpy of LuBa₂Cu₃O_x and to confirm the reliability of our data. The scheme is described in ref 11 in detail for calculation of the formation enthalpy of Y₂Ba₄Cu₇O_x. In this case, the calorimetric cycle is based on using experimental data for solution enthalpies of rare earth metals, complex oxides, and literature data of formation enthalpies of BaCl₂, CuCl₂, H₂O, and HCl taken from refs.22–24 Calculation of $\Delta_f H^\circ$ (LuBa₂Cu₃O_{6.92}, 298.15 K) on the basis of the cycle of ref 11 with our data for solution enthalpies of Lu and LuBa₂Cu₃O_{6.92} allows one to obtain



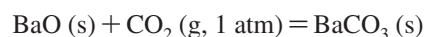
$$\Delta_f H^\circ (298.15\text{K}) = -2690.6 \pm 12.3\text{kJ/mol}$$

As we can see, we have good agreement for calculation of the same value [$\Delta_f H^\circ$ (LuBa₂Cu₃O_{6.92}, 298.15 K)] using different thermochemical schemes. This testifies in favor of the reliability of our thermochemical data.

The large exothermic enthalpies of Gd₂BaCuO₅, GdBa₂Cu₃O_{6.9}, and LuBa₂Cu₃O_{6.92} calculated from binary oxides imply that these reactions are spontaneous and that Gd211, Gd123, and Lu123 are probably thermodynamically more stable than their component oxides at room temperature. A comparison of enthalpies of reactions of Gd₂BaCuO₅ with GdBa₂Cu₃O_{6.9} and of GdBa₂Cu₃O_{6.9} with LuBa₂Cu₃O_{6.92} shows the following. Gd123 is probably more stable than Gd211, and Lu123 is more stable than Gd123 with respect to decomposition to binary oxides. It is necessary to note that the direction of any chemical transformation is deter-

mined by the sign of the Gibbs energy $\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$. It was shown in ref 16 for the RE123 phase that the term $T\Delta S^\circ$ was not so large for reactions of types 12, 15, and 20 (the order is about 10 kJ/mol). So, it is possible to justify the thermodynamic stability on the basis of the enthalpies of reactions.

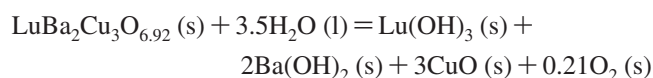
If barium oxide reacts with copper oxide before the Lu123 phase is formed, the reaction (eq 17) is also spontaneous (exothermic heat). However, the situation is different in the Y₂O₃–BaO–Cu–O system. The large endothermic heat of reaction between Y₂O₃, BaCuO₂, and CuO forming YBa₂Cu₃O_{6.92} (9, 11, and 12) suggests that the Y123 compound is unstable with respect to a mixture of Y₂O₃, CuO, and BaCuO₂. In ref 25, the entropy of carbonation of BaO was determined as follows:



$$\Delta S = -173.7 \pm 5.2 \text{ J/K mol}$$

Combining these data with the data of reactions 11 and 19 and assuming that the entropies of formation of Lu123 and Gd211 from binary oxides are close to zero, it is possible to conclude that the Lu123 and Gd211 phases are thermodynamically unstable with respect to the reaction with CO₂.

Hydration products of the 123 phases depend on the conditions under which the reaction with H₂O takes place. For example, when the 123 phase interacted with H₂O at 313 K for 312 h, Ba(OH)₂, RE(OH)₃, and CuO were found in the hydration product⁹ according to the reaction:



$$\Delta G = -234.7 \pm 22.0 \text{ kJ/mol}$$

This free energy is calculated using our experimental data and the free energy of formation from elements at room temperature taken from the literature.^{22,23} Data for the enthalpy of formation of Lu(OH)₃ were taken from ref 26.

4. Conclusion

In this paper, for the first time, we measured the standard formation enthalpies of Gd₂BaCuO₅ and LuBa₂Cu₃O_{6.92}. It was established on the basis of our experimental data that Gd₂BaCuO₅ and LuBa₂Cu₃O_{6.92} are thermodynamically stable with respect to mixtures of binary oxides at ambient temperature. The Lu123 phase is also thermodynamically stable with respect to the decomposition of mixtures of Lu₂O₃, BaCuO₂, and CuO. The standard free energies of interaction of Gd211 and Lu123 with carbon dioxide and water have been assessed. The large exothermic values show that the degradation of these phases at ambient conditions is thermodynamically favorable.

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