

THERMODYNAMIC PROPERTIES OF THE SYSTEMS $Y(Ln)Ba_2Cu_3O_x$

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Abstract. The enthalpies of formation of $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0; 0,5$) have been determined at 298K by solution calorimetry. These values were shown for $YBa_2Cu_3O_x$ to depend on the oxygen stoichiometry of a sample. The results of thermodynamic investigations were found to be in good agreement with the data of the kinetic investigations of the $Y(Ln)Ba_2Cu_3O_x$ formation reactions. This agreement is explained in the aspect of electronic structure of lanthanide atoms.

1. INTRODUCTION

Discovery of superconductivity above the boiling point of liquid nitrogen in $Y(Ln)Ba_2Cu_3O_x$ (123) has aroused considerable interest in these compounds. Although the 123-oxides have been widely studied, the problem of their synthesis without other phases as impurities have not been solved. It is well known that the presence of impurity phases and oxygen stoichiometry of $Y(Ln)Ba_2Cu_3O_x$ arising out of post-synthesis treatment influence on their superconducting properties. Hence a need for a high quality and well characterized single phase sample, both for applications and for study of basic physical properties, can never be over emphasized. A good understanding of thermodynamic stability of $Y(Ln)Ba_2Cu_3O_x$ with respect to initial components and to changes in oxygen stoichiometry is essential for finding the optimum synthesis conditions and for discovering the solid state reaction mechanisms in these systems.

2. THERMODYNAMIC PROPERTIES OF THE $Y(Ln)$ -Ba-Cu-O SYSTEMS

There are a few data on the investigation of thermodynamic properties for the $Y(Ln)$ -Ba-Cu-O systems. As to the Ln-Ba-Cu-O systems thermodynamic parameters obtained by experimental way are absent in literature. The point is that the thermody-

amic investigation demands a monophasic sample. The $Y(Ln)Ba_2Cu_3O_x$ compounds are very difficult to synthesize without impurity phases. Moreover the 123-phases are unstable with respect to attack by H_2O , CO_2 and the substrate material. This being so, the thermodynamic investigations of $Y(Ln)Ba_2Cu_3O_x$ are very complicated and depend on many factors. Table 1 shows the formation enthalpy and entropy from the simple oxides. As seen from the Table, there is some discordance in the data. It can be explained by the various synthesis conditions yielding different quantities of impurities and oxygen in the 123-phase. The standard enthalpies of formation of the complex oxides in Y-Ba-Cu-O system were measured [4-8, 10] with the solution calorimetry in $HClO_4$ or HCl (Table 1). Depending upon the oxygen stoichiometry the value of $\Delta_f H^\circ$ ($YBa_2Cu_3O_x$, 298K) obtained in [4] ranges from (-29,9) kJ/mol to (-43,8) kJ/mol. Using the EMF method [1-3,9,11,12] made it possible to obtain ΔH and ΔS for the reactions of formation from simple oxides at elevated temperatures. As can be seen in Table, these results are not in accordance with the calorimetric ones. It should be kept in mind that higher than 1000K the melting and polymorphism transformation processes influence on $\Delta_f H^\circ$ for the compounds of the $Y(Ln)$ -Ba-Cu-O systems. The discordance between these data might be also caused not only by a systematic error in the deter-

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Table 1. Enthalpy (kJ/mol) and entropy (J/(mol·K)) changes on formation of compounds from simple oxides.

Compound	T, K	$\Delta_f H^0$	$\Delta_f S^0$	method	Reference
Y ₂ Cu ₂ O ₅	1173-1340	20,7±3	22,8±2	EMF	[1]
	1097-1292	10,9	13,4	EMF	[2]
	1100-1250	12,2±2	17,8±1	EMF	[3]
	298	-18,6		calorimetry	[4]
	298	12,1±2,7		calorimetry	[5]
BaCuO ₂	1000-1100	-53,8±12,1	-17,9±3	EMF	[3]
	298	-49,1		calorimetry	[4]
	298	-93,3±6		calorimetry	[6]
	298	-76		calorimetry	[7]
	298	-85,2±2,4		calorimetry	[5]
	298	-82,0±3		calorimetry	[8]
	298	-51		EMF	[9]
Y ₂ BaCuO ₅	1073-1173	-48,4±11,9	-6,6±2,1	EMF	[3]
	298	-26,1		calorimetry	[4]
	298	-92		calorimetry	[7]
	298	-48,6±3		calorimetry	[5]
	298	-38		EMF	[9]
YBa ₂ Cu ₃ O _{6,5}	298	-143		calorimetry	[10]
YBa ₂ Cu ₃ O ₇₋₈	1073-1173	-66,6±20,2	-9,4±7,6	EMF	[3]
	298	(-29,9)÷(-43,8)		calorimetry	[4]
YBa ₂ Cu ₃ O _{6,5}	298	(-93±28)÷(-101±32)		EMF	[11]
	298	-96±15		EMF	[12]

mination of thermodynamic functions of the components of the reaction of YBa₂Cu₃O_x formation from oxides, but in the separation of Gibbs' energy into enthalpy and entropy and by the uncertainty of the thermodynamic state of quenched samples in calorimetric experiments as well. The last circumstance is essential also because of the fact that all the oxide high-temperature superconducting phases are metastable with respect to the decomposition into more simple phases (especially into the binary oxides) [4].

3. EXPERIMENTAL

The synthesis of the R_yR'_{1-y}Ba₂Cu₃O_x (R, R' = Y, Nd, Eu; y=0,5; 1,0) was carried out at 950 °C with the intermediate homogenization. The phase compositions was identified by the X-ray

diffractometry which confirmed the monophasicity of the obtained samples. The oxygen content x in synthesized samples was determined by the method of iodometry*.

To determine the enthalpies of formation of the R_yR'_{1-y}Ba₂Cu₃O_x from oxides the heat-conducting differential calorimeter of Calve's type was used [13]. The instrument has two identical cells connected according to the differential scheme [14]. The temperature stability of the thermostatically controlled block was about 5·10⁻⁴ degree for a long time.

The voltage value of the thermocouple battery ends is proportional to the temperature gradient and therefore to the heat stream passing through. The investigation of this signal per time during the experience gives the value proportional to the energetic effect passing in the sell:

$$Q = k \iint U dt dS, \quad (1)$$

* Iodometry analysis performed by N.P.Baranskaya in analytical laboratory ISC RAS.

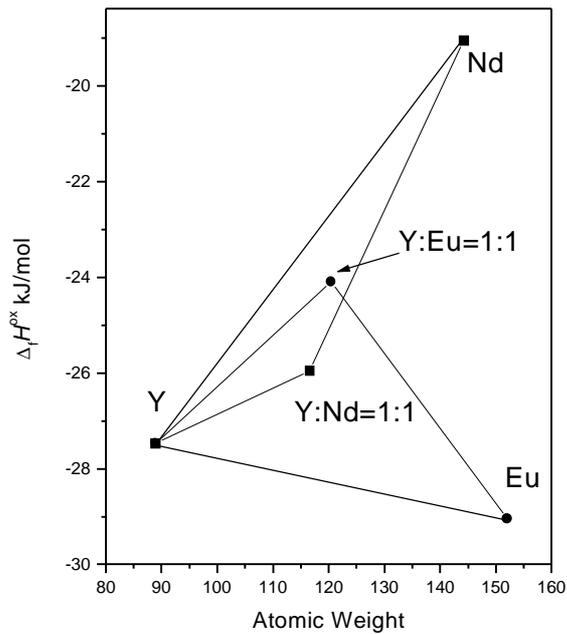


Fig. 1. Enthalpy (± 1.5 kJ/mol) of the $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0; 0,5$) formation from simple oxides vs atomic weight of rare-earth element.

where τ – is the time of the solution reaction, U – the voltage value of the thermocouple battery, S – the surface square of calorimeter cell. Further the heat effect of the solution reaction is calculated:

$$\Delta H_{sol} = \frac{QM}{P}, \quad (2)$$

where Q – is the heat stream of the solution, M is the molecular weight of the matter, P is the mass of portion.

According to Hess law:

$$\Delta H_f = \Delta H_3 - (\Delta H_1 + \Delta H_2). \quad (3)$$

where ΔH_3 is the enthalpy of solution of the final product, ΔH_1 and ΔH_2 are the enthalpies of solution of the initial products of reaction.

To carry out the calorimetric measurements the synthesized singlephase samples of $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0; 0,5$) were grinded in the agate mortar, put into the ampoules of fluoroplastic and dissolved in the 6N HCl. The solvent was chosen based on the following principles:

- i) the samples under study must dissolve as fast as possible and without any sediment;
- ii) during the solution none secondary process must take place, and always the same products must be obtained;

iii) the kinetics of the solution reaction must not be slow [14].

The heats of solution of a number of samples of the same chemical composition obtained in the calorimetric experiment can be considered as the measure of energy of the crystal lattices of samples counted off the conditional zero level which is the diluted solution of chlorides in 6N HCl. In case of a polycrystal sample the heat of solution includes along with the energy of the lattice with all the defects also and the surface energy of the grain contact boundaries, but we didn't estimate its contribution. In such a manner comparing the solution heats of samples with distinct history, one can estimate the influence of all the factors on the energetics of the $R_yR'_{1-y}Ba_2Cu_3O_x$ phases, compare it with the oxygen contents or other factors and on the basis of that it's possible to formulate first of all the recommendations for the synthesis regime of samples and on the other hand, to estimate the ways of their structure stabilization.

4. RESULTS

Fig. 1 represents the standard enthalpies of formation of $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0,5; 1,0$) calculated from the enthalpies of solution as the functions of the rare-earth elements' atomic weights. For the of $R_{0,5}R'_{0,5}Ba_2Cu_3O_x$ compositions the atomic weights of $R_{0,5}R'_{0,5}$ were calculated as arithmetical mean values. From Fig. 1 one can see that the obtained $\Delta_f H^{ox}$ are exothermic. This fact confirms that the $R_yR'_{1-y}Ba_2Cu_3O_x$ compounds ($R, R'=Y, Nd, Eu$) are quite stable with respect to the oxides Y_2O_3 (Ln_2O_3), BaO and CuO. As shown in Fig.1, the substitution Y for Nd in $YBa_2Cu_3O_x$ instabilizes the 123 structure. On the other hand, $EuBa_2Cu_3O_x$ with $\Delta_f H^{ox}$ close to that of $YBa_2Cu_3O_x$ is slightly more stable than $YBa_2Cu_3O_x$. The oxide $Y_{0,5}Eu_{0,5}Ba_2Cu_3O_x$ appears to be less stable than the combination of $YBa_2Cu_3O_x$ and $EuBa_2Cu_3O_x$.

It is interesting to compare the results of our work with those of the kinetic investigation of the Y(Ln)-Ba-Cu-O systems reported in [15]. In that work the apparent activation energies (E_a) of reactions between Y_2O_3 (Ln_2O_3), $BaCO_3$ and CuO during the synthesis of $Y(Ln)Ba_2Cu_3O_x$ were determined from the Arrhenius equation. For the reactions of $RBa_2Cu_3O_x$ formation ($R=Nd, Eu, Yb, Y$) the apparent activation energies were estimated as 540, 380, 390 and 400 kJ/mol, respectively. From these results it's clearly seen that the reactions proceeding in the Nd-Ba-Cu-O system in the course of the

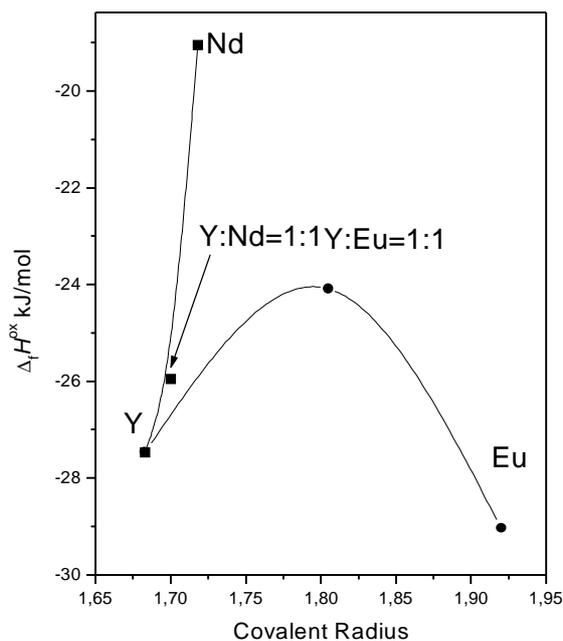


Fig. 2. Enthalpy (± 1.5 kJ/mol) of the $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0; 0,5$) formation from simple oxides vs covalent radius of rare-earth element (nm).

$NdBa_2Cu_3O_x$ synthesis are less active. The values of the activation energies determined for the other systems are very close and increase a bit in the line Eu-Yb-Y. So one can conclude that the results of thermodynamic and kinetic investigations of the Y(Ln)-Ba-Cu-O systems are in satisfactory accordance. It should be noted that thermodynamic and kinetic parameters are partially independent. They are interrelated, but one can not calculate thermodynamic parameters from the values of kinetic parameters, and vice versa. These parameters reflect different levels of the process description. Thermodynamics reflects the potential possibility of a reaction. Kinetics describes the reaction passing with regard to the influence of various "difficulties". Nevertheless, in the present work the results of thermodynamic and kinetic investigations show obviously that europium takes a particular place among the rare-earth elements. The least values of $\Delta_f H^\circ$ and E_a obtained for the samples containing Eu_2O_3 allow to make a conclusion about more activity of the processes in the Eu-Ba-Cu-O system as compared with the other rare-earth elements' systems. This conclusion appears to be true also for the Yb-Ba-Cu-O system.

Evidently, the specific electronic structure of the europium and ytterbium atoms is a likely reason for the anomalous behavior of the compounds containing

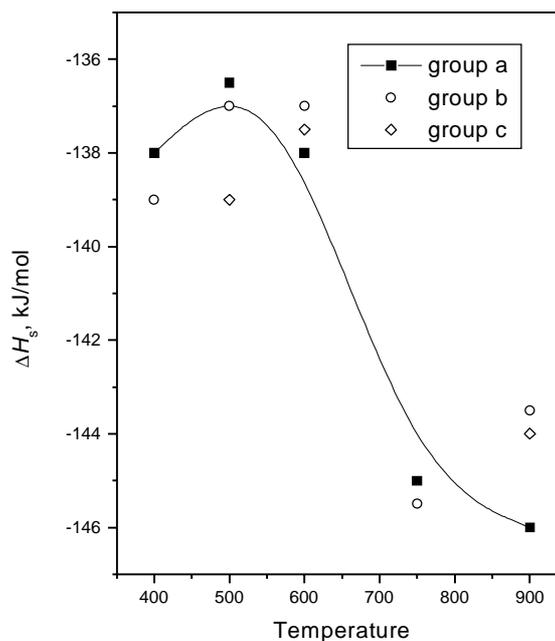


Fig. 3. Enthalpy of solution (± 1.5 kJ/mol) of the $YBa_2Cu_3O_y$ compounds vs quenching temperature ($^\circ C$).

these elements. A number of electrons on the 4f-orbital of europium and ytterbium may be both even and odd in dependence on their oxidations states. In particular, for "0" and "3+" oxidations states these values are 7 and 6 for Eu and 14 and 13 for Yb while for the other lanthanides these values are identical. The peculiarity of atomic electronic structure influences on some physico-chemical properties of the europium and ytterbium compounds: on the enthalpies of Ln_2O_3 formation from elements [16], on the values of ionic, atomic [17] and covalent radii of rare-earth elements [18] and other properties. This fact suggests an insignificant role of "geometrical" factors in the formation of the 123-oxides investigated in the present work. The supposition was confirmed when the values of the enthalpies of formation calculated for $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu; y=0,5; 1,0$) have been plotted against the values of rare-earth covalent radii (Fig.2). From this figure one can observe that an insignificant difference in the values of covalent radii (Nd and Y) can be accompanied by a significant difference in $\Delta_f H^\circ$ for $NdBa_2Cu_3O_x$ and $YBa_2Cu_3O_x$, and vice versa (Y and Eu).

Since the properties of high-temperature superconducting oxides are drastically modified by oxygen stoichiometry arising out of post-synthesis treat-

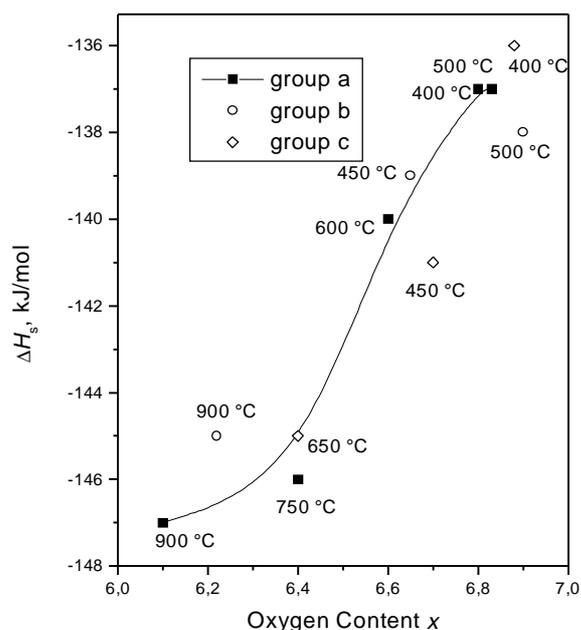


Fig. 4. Enthalpy of solution (kJ/mol) of the $YBa_2Cu_3O_x$ compounds vs oxygen content x .

ments, it was interesting to investigate for $YBa_2Cu_3O_x$ the influence its oxygen stoichiometry (x) on its enthalpies of solution (ΔH_{sol}). Three groups of samples were prepared in dependence on the regime of post-synthesis treatment:

- by quenching in liquid nitrogen from the temperature of synthesis;
- by annealing in reducing atmosphere at various temperature;
- by annealing in oxidizing atmosphere (O_2).

Fig. 3 shows the measured enthalpies of solution for $YBa_2Cu_3O_x$ (a-group) as a function of the quenching temperature. From this dependence one can suppose that all changes of the $YBa_2Cu_3O_x$ crystal structure energy take place in the range from 500 to 700 °C. At that the samples different essentially on their histories and initial states, show the identical dependence of ΔH_{sol} on quenching temperature. Thus the quenching of samples in controlled conditions can be an effective method to standardize the $Y(Ln)Ba_2Cu_3O_x$ ceramics and to smooth some initial difference in their properties.

It is the most surprisingly that the samples of all three groups give a similar dependence of ΔH_{sol} (and consequently crystal structure energies) on x (Fig.4). This dependence is in good quantitative agreement with the results reported in [19, 20]. It's necessary to mention that the results of [20] were obtained

under conditions of the direct oxidation of the $YBa_2Cu_3O_x$ sample in a high-temperature calorimeter. In all probability the heat or another history of the $YBa_2Cu_3O_x$ sample determines its energetics through the changes in its oxygen contents first of all (and also through the oxygen redistribution in the lattice positions, but we can't have controlled this factor yet). So one can conclude that various ways of changes of oxygen stoichiometry in the 123-phase have the same effect on its crystal lattice energetics determined in the calorimetric experiments.

5. CONCLUSION

It was shown that the values of the enthalpies of the $RBa_2Cu_3O_x$ ($R=Y, Nd, Eu$) formation from simple oxides were in good agreement with the ones of activation energies of the $RBa_2Cu_3O_x$ formation. Both thermodynamic and kinetic parameters of these reactions are determined by the peculiarities of electronic structure of lanthanide atoms. The enthalpies of formation of $R_yR'_{1-y}Ba_2Cu_3O_x$ ($R, R'=Y, Nd, Eu$; $y=0; 0,5$) connect closely with their oxygen stoichiometry.

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