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Thermal analysis of mercury superconductor $HgBa_2CuO_{4+x}$ and its precursor Ba_2CuO_{3+y} [☆]

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Abstract

The superconducting compound $HgBa_2CuO_{4+x}$ and its precursor Ba_2CuO_{3+y} have been studied in an oxygen atmosphere by TG–DTA in the temperature interval 20–1100°C. It was supposed that the succession of chemical processes taking place during the heating (20° min^{-1}, 1 atm O_2) of $HgBa_2Cu_{1.05}O_{4.12}$ is as follows:

$$HgBa_2Cu_{1.05}O_{4.12} \xrightarrow[20-240°C]{-H_2O,\ -CO_2} HgBa_2Cu_{1.05}O_{4.12} \xrightarrow[240-706°C]{-Hg_aO_b}$$

$$Hg_{1-a}Ba_2Cu_{1.05}O_{4.12-b} \xrightarrow[706-822°C]{-Hg,\ -O_2} Ba_2CuO_{3.1}$$

It was supposed that the $Ba_2CuO_{3.23}$ compound during heating (1° min^{-1}, 0.21 atm O_2) and cooling (20° min^{-1}, 0.21 atm O_2) undergoes following stages:

$$Ba_2CuO_{3.2} \xrightarrow[220-430°C]{+O_2} BaO_2 + Ba_2Cu_3O_{5.76} + Ba_2CuO_{3.3} \xrightarrow[430-640°C]{-O_2}$$

$$BaO_{1.85} + Ba_2Cu_3O_{5.73} + Ba_2CuO_{3.3} \xrightarrow[640-770°C]{-O_2} Ba_2CuO_{3.1} \xrightarrow[770-890°C]{-O_2}$$

$$Ba_2CuO_{3.0} \xrightarrow[890-20°C]{+O_2} Ba_2CuO_{3.2}$$

Keywords: Ba_2CuO_{3+y}; $HgBa_2CuO_{4+x}$; Mercury superconductor; TG–DTA; Thermal analysis

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1. Introduction

The mixed oxide $HgBa_2CuO_{4+x}$ (Hg[1201]) is the first compound in a series of mercury high-temperature superconductors discovered in 1993 [1,2]. The closeness of structures of Hg[1201] and of Ba_2CuO_{3+y} [021] easily enables introduction of a supplementary layer of Hg^{2+} cations between the two BaO layers in the Ba_2CuO_{3+y} structure in order to obtain $HgBa_2CuO_{4+x}$.

There is no description of thermochemical investigations of mercury superconductors in the literature.

The Ba_2CuO_{3+y} compound has been studied [3–6]. It was demonstrated that with an oxygen pressure of 0.21 atm a drastic change of the quantity y (from 0.32 to 0.09) takes place in the interval 760–827°C and a change of crystal structure with a transition temperature of 810°C also occurs [3]. While describing the phase Ba_2CuO_{3+y} the authors [7] supposed that it was a solid solution which appeared on the basis of two non-stoichiometric compounds: tetragonal phase $Ba_2CuO_{3.1} = [021]_{3.1}$ (here and further on the subscript figures represent a gross index for oxygen) and orthorhombic phase $Ba_2CuO_{3.3} = [021]_{3.3}$.

2. Experimental

2.1. Synthesis and analysis of samples

For preparing the materials we used solid state synthesis. Quantitative contents of the components were determined by wet chemical analysis. A determination of oxygen was carried out by means of iodometric titration [8]. A determination of the cation contents was carried out by technique described elsewhere [9]. A test portion of the material, about 0.1–0.2 g, was dissolved in nitric acid. The resulting solution was diluted to 100 ml with water. Barium was determined in the form of $BaSO_4$ by gravimetry, copper content by iodometric titration (an excess of KI was required to form a mercury complex) and determination of mercury was carried out using compleximetric titration. Relative standard deviation in stoichiometric index was about 0.01 for Ba and Hg and 0.02 for Cu.

The phase composition of the preparations was controlled by the method of X-ray phase analysis in a Guinier–de Wolff camera (CuKα radiation) with Ge as internal standard in conditions of complete isolation of the substance from the outer environment.

Ba_2CuO_3 was synthesized from $BaCO_3$ and CuO (Reakhim, 99.0% purity) previously sintered at temperatures of 900°C and 500°C, respectively. Mixtures (1:1) thoroughly ground in a dry camera were placed in a quartz reactor in the form of pellets and vacuum-treated at a temperature of 790°C. Purified oxygen was introduced into the reactor and then pumped out and introduced again periodically 2–3 times a day in order to remove completely CO_2 formed as a result of decomposition of $BaCO_3$. The total sintering time amounted to 350–400 h. The specimen was cooled to room temperature by furnace cooling. The quantitative wet chemical analysis revealed the composition of the synthesized material to be as follows:

$Ba_{2.00\pm0.01}Cu_{1.02\pm0.02}O_{3.23\pm0.02}([021]_{3.23})$.

$HgBa_2CuO_{4+x}$ was synthesized from HgO (Reakhim, 99.8% purity), BaO_2 and CuO (Reakhim, 99.0% purity). The mixture (1:2:1) was thoroughly ground and pressed into pellets. All the operations were conducted in a dry camera. Samples were sintered in evacuated quartz capsules at a temperature of 550°C for 36 h, then cooled by furnace cooling. The composition of the synthesized sample was as follows:

$Hg_{1.00\pm0.01}Ba_{2.00\pm0.01}Cu_{1.05\pm0.02}O_{4.12\pm0.02}$ ($[Hg(1201)_{4.12}]$)

The X-ray diffraction patterns of the compounds produced were in agreement with those published [1,4]. The lines of admixed phases were not detected (accuracy was about 2 mass%).

The presence of some possible admixed phases ($BaCO_3$, water and hydrogen carbonates) was controlled also by way of TG-DTA simultaneous thermoanalysis (Netzsch STA-409 thermoanalyser) following the method described elsewhere [10, 11]. If not mentioned specifically, no peculiarities typical of these compounds were to be seen on the thermograms (accuracy: 0.5 mass%).

2.2. *Thermoanalysis*

Simultaneous TG-DTA investigations were carried out on an STA-409 thermoanalyser with oxygen pressures of 1 or 0.21 atm in the temperature interval 20-1180°C and with heating rates of 1 or 20° min^{-1}. Alundum crucibles were used; the masses of previously weighed samples ranged from 30 to 70 mg.

For description of the processes taking place during heating and cooling of $[021]_{3.23}$ we used information obtained by supplementary experiments:

1) sintering at 430°C for 10 h $pO_2 = 0.21$ atm (point 2 Fig. 2) did not cause a change of the sample mass (gross composition: Ba:Cu:O = 2:1:3.77) and so, using the scheme of phase relationship of the $BaO-Cu_2O-O_2$ system, proposed by Voronin and Degtiarev [7], the composition at point 2 (Figs. 2 and 3) has been calculated as 52 mol% $[021]_{3.3}$ + 10 mol% $[023]_{5.76}$ + 38 mol% BaO_2;

2) thermoanalysis of the $BaO-BaO_2$ mixture in dry oxygen at pressures of 0.21 or 1 atm conducted with scanning rates of 1 or 20° min^{-1} was used for qualitative phase analysis and confirmed formation at the beginning and then a partial degradation of BaO_2 in the compound in the interval 220-640°C;

3) cooling (20° min^{-1}, $pO_2 = 0.21$ atm) from 890°C (point 3 Figs. 2 and 3) after a 10 h sintering at this temperature brough us back to the starting mass and to the initial composition of the sample (point 1 Figs. 2 and 3).

3. Results and discussion

The thermoanalytical curves obtained for $Hg[1201]_{4.12}$ (Fig. 1) and $[021]_{3.23}$ (Fig. 2) can be divided into several sections.

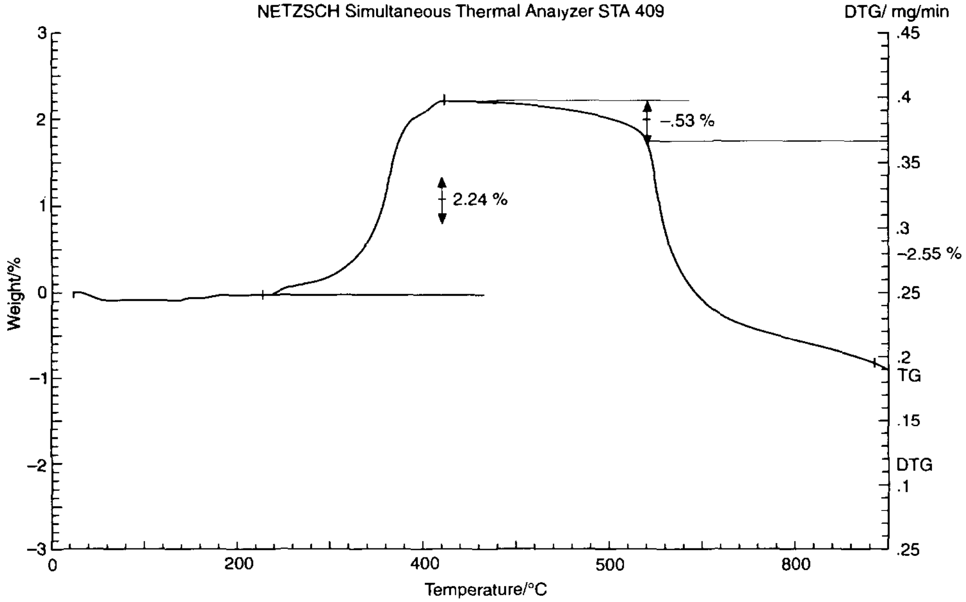

Fig. 1. Thermogram of the sample $Hg_{1.00\pm0.01}Ba_{2.00\pm0.01}Cu_{1.05\pm0.02}O_{4.12\pm0.02}$; $pO_2 = 1$ atm, heating rate = 20° min^{-1}.

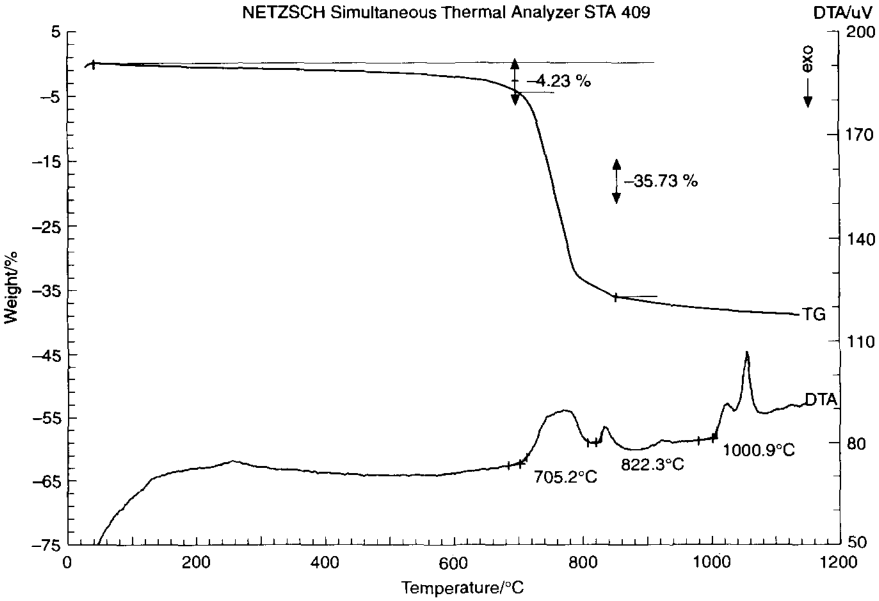

Fig. 2. Thermogram of sample $Ba_{2.00\pm0.01}Cu_{1.02\pm0.02}O_{3.23\pm0.02}$; $pO_2 = 0.21$ atm, heating rate = 1° min^{-1}, cooling rate = 20° min^{-1}.

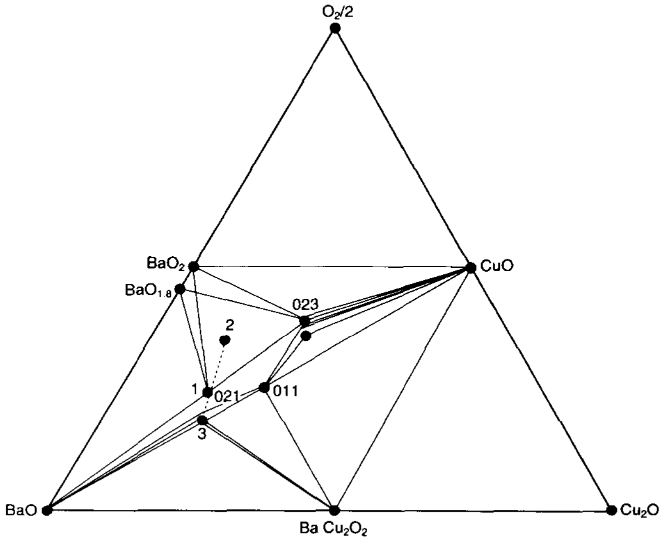

Fig. 3. Scheme of phase relationships in $BaO-Cu_2O-O_2$ system taking into account investigations of oxygen homogeneity sections for compounds [011] from Ref. [10], BaO_2 from Ref. [11], [023] from Ref. [12] and $[021]_{3.1}$ from this work. Points 1, 2 and 3 correspond to that presented on a thermoanalytical curve in Fig. 2. The phases [031], [013], [035] reported in the literature are not indicated because we did not detect them under our experimental conditions.

Gross values of oxygen index (y or x) were calculated by use of a formula:

$$y(\text{or } x) = y_O(\text{or } x_O) + [m\% \times M/(M_O \times 100\%)],$$

where: M—molecular mass of starting sample; $m\%$—change of mass in %; M_O—molecular mass of oxygen; and y_O(or x_O)— index value of oxygen in starting sample.

On the basis of the data obtained by DTA-TG and phase diagram theoretically estimated elsewhere [7] we propose a scheme of successive reactions taking place during heating and cooling $[021]_{3.23}$ (see Table 1). The equilibrium index z in BaO_z (stage II of Table 1) calculated has coincided—within tolerance limits—with the index value obtained at 630°C [11]. Oxygen indexes for phase [023] were taken from Ref. [12].

Table 1
Change of index for oxygen (y) in Ba_2CuO_{3+y} (0.21 atm O_2) during heating (1° min^{-1}) and cooling (20° min^{-1}) in the temperature interval 20–890°C and succession of chemical processes (I–V)

Process[a]	I	II	III	IV	V
Temperature/°C	220–430	430–640	640–770	770–890	890–20
Gross index for oxygen $3+y(\pm 0.02)$	3.23–3.77	3.77–3.64	3.64–3.10	3.10–3.01	3.01–3.23

[a] I $[021]_{3.2} \rightarrow BaO_2 + [023]_{5.76}$; II $BaO_2 \rightarrow BaO_{1.85}$ [11]; $[023]_{5.76} \rightarrow [023]_{5.73}$; III $[023]_{5.73} + BaO_{1.85} \rightarrow [021]_{3.3} \rightarrow [021]_{3.1}$; IV $[021]_{3.1} \rightarrow [021]_{3.0}$ (non-stoichiometry range); V $[021]_{3.0} \rightarrow [021]_{3.23}$.

Thermoanalysis of $HgBa_2Cu_{1.05}O_{4.12}$ carried out by heating from 20–1200°C at 20° min^{-1} in 1 atm of purified oxygen (Fig. 1) demonstrated the presence of traces of water and of CO_2 adsorbed by the samples during weighing and loading them into the thermoanalyser. These traces disappear completely at 240°C.

The peak on the DTA curve at 706°C reflects the degradation of Hg[1201] in the 706–822°C interval accompanied by complete removal of HgO. With a change of temperature from 822 to 1180°C the thermogram of Hg[1201] coincides with the [021] thermogram in the same temperature interval (Fig. 4). On the basis of elaboration of thermoanalytical curves (Fig. 1) a possible succession of chemical processes of degradation of non-stoichiometric Hg[1201] was modelled:

$$HgBa_2Cu_{1.05}O_{4.12} \xrightarrow[20-240^\circ]{-H_2O,\ -CO_2} HgBa_2Cu_{1.05}O_{4.12} \xrightarrow[240-706^\circ]{-Hg_aO_b}$$

$$Hg_{1-a}Ba_2Cu_{1.05}O_{4.12-b} \xrightarrow[706-822^\circ]{-Hg,\ -O_2} Ba_2CuO_{3.1}$$

The heat (ΔH_1) produced by degradation of Hg[1201] was approximately determined on the basis of the DTA peak corresponding to the third stage. An hypothesis that $x = y$ was made to estimate the possible composition of Hg[1201] at 706°C. As the mass loss in temperature interval 240–706°C was 4.2%, the composition was $Hg_{0.88}Ba_2Cu_{1.05}O_{4.0}Hg[1_{0.88}201]$. The sensitivity index was found on the basis of the heat produced by the reaction of degradation of HgO. The value obtained for the sensitivity index was considered as constant in the temperature range 450–750°C. The

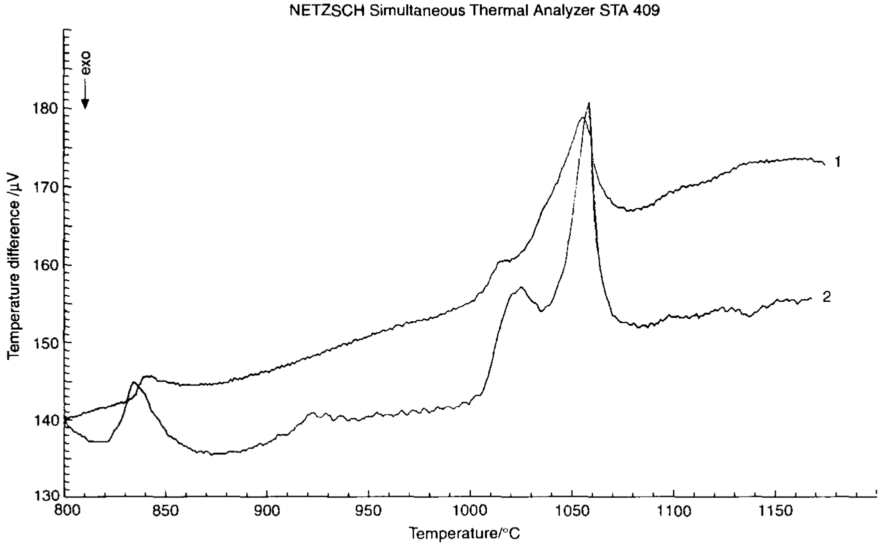

Fig. 4. A comparison of thermograms $pO_2 = 1$ atm, heating rate 20° min^{-1}) for [021] (curve 1) and [1201] (curve 2).

Table 2
Estimation of enthalpy of formation from oxides (ΔH_4) for $Hg_{0.88}Ba_2CuO_{4.0}$ at 706°C, $pO_2 = 1$ atm

1. $Hg_{0.88}Ba_2CuO_{4.0} \rightarrow 0.88Hg + 0.45O_2 + Ba_2CuO_{3.1}$ $\Delta H_1 = 74$ kJ mol^{-1} ± 20% (this work)
2. $Hg + 0.5O_2 \rightarrow HgO$ $\Delta H_2 = -144$ kJ mol^{-1} ± 5% [13]
3. $2BaO + CuO + 0.05O_2 \rightarrow Ba_2CuO_{3.1}$ $\Delta H_3 = -76.3$ kJ mol^{-1} [7]
4. $0.88HgO + 2BaO + CuO + 0.06O_2 \rightarrow Hg_{0.88}Ba_2CuO_{4.0}$ $\Delta H_4 = \Delta H_3 - 0.88\Delta H_2 - \Delta H_1 = -24$ kJ mol^{-1}

evaluation of the enthalpy of formation from oxides for $Hg[1_{0.88}201]$ at 706°C (ΔH_4) and all the other heats used are shown in Table 2.

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