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Solid solution in the system $BaCuO_2$–CuO–O_2 [☆]

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Abstract

The existence of an homogenity range of $BaCu_{1+y}O_{2+x}$ in respect of copper was established by EMF measurement and DTA, and the nonstoichiometry index (x_t) of oxygen versus temperature (t) was measured by TG in static dry oxygen. The values obtained for x and y were:

$$0 \leq y(\pm 0.02) \leq 0.15$$

$0.05\,(1000°C) \leq x_t(pO_2 = 1\text{ atm}, y = 0.15) \pm 0.03 < 0.25\,(450°C)$ significant attention was paid to phase and composition analysis of samples synthesized.

Keywords: $BaCuO_2$–CuO–O_2; Cation non-stoichiometry; DSC–TG; DTA; EMF measurement; High-temperaure superconductor; Oxygen non-stoichiometry; Solid solution; TG

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1. Introduction

The compound ($BaCuO_2$ (011) is an intermediate phase in the synthesis of high-temperature superconductors (HTSC) (in the system YBaCuO) and is also a product of its degradation. The compound has been investigated in many studies; the results obtained for the crystal structure [1–3], for oxygen non-stoichiometry [4–6], for the heat of formation [7–9], and for the estimation of stability [10, 11] seem to be reliable. The phase relations between $BaCuO_2$ and CuO have been studied [5, 12–15] mainly by X-ray analysis and DTA. The composition of the eutectic is 70 ± 3 mol% CuO and its temperature is between 920 and 937°C, depending on the heating rate. The temperature

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of congruent melting of pure $BaCuO_2$ is between 1015 and 1045°C. Such differences in temperatures cannot be explained only by the experimental conditions (heating rate, oxygen pressure), but by the elements' concentration in the samples investigated. No one has ever reported non-stoichiometry of cations. In our work an attempt has been undertaken to determine the cation homogeneity range of $BaCuO_2$ by DTA and to confirm the results by EMF measurement.

2. Experimental and results

2.1. Synthesis and analysis of samples

The samples of gross formula $BaCu_zO_{2+x}$ were synthesized by the ceramic method ($1 \leq z \leq 11$, $0.015 \leq x \leq 0.025$). An initial mixture (total weight 8–10(±0.1) mg of $BaCO_3$ and CuO (Reakhim, Russia, 99.0% purity) thoroughly ground in an agate mortar with ether for better homogenization and then pressed into pellets under a pressure of 2 kbar. The pellets were sintered for 24 h at 800°C then ground and sintered again at 890°C for 90 h in air. We believed that the sample was in the state of equilibrium if after 2 consecutive sinterings the phase composition of the sample did not change. For some experiments we used mechanical mixtures of $(z-1)CuO + BaCuO_2$.

The electrodes of galvanic cells for the EMF method were equilibrium mixtures of the oxides under investigation with BaF_2, previously sintered in a vacuum of 10^{-4} mm Hg at 900°C. As solid electrolyte we used a monocrystal of BaF_2 and as reference electrode a mixture of $CaO + CaF_2$.

The element compositions of the samples synthesized were determined by wet chemical analysis (WCA) with an accuracy of 0.01 in indices for cations and of 0.02 in index for oxygen. X-ray analyses were performed by use of a Guinier camera (Cu-Kα radiation with Ge as internal standard). The samples under investigation were overlaid with petrolatum. DSC–TG analysis conducted by the method described in Ref. [6] showed the absence of such impurities as $BaCO_3$, hydroxy groups and moisture.

2.2. Thermoanalytical investigations

All thermoanalytical experiments were carried out on an STA-409 thermoanalyser (Netzsch, Germany) in dry static oxygen at heating rates of 1 or 20° min^{-1} with sintered kaoline as a reference material. Typical thermoanalytical curves are represented in Figs. 1 and 2; the onset temperatures of phase transitions are listed in Table 1.

The DTA curve for $BaCuO_2$ (Table 1 #1, 2) had one endothermic peak of peritectic melting at an onset temperature of 1042 ± 2°C (1 atm O_2, heating rate 1° min^{-1}). With increasing CuO content ($1.01 < z \leq 1.14$) the peak became more complicated and looked like superposition of two curves of independent transitions. The temperatures of these transitions were determined by a construction of the measured curve for independent events. The typical thermogram for this area of compositions is presented

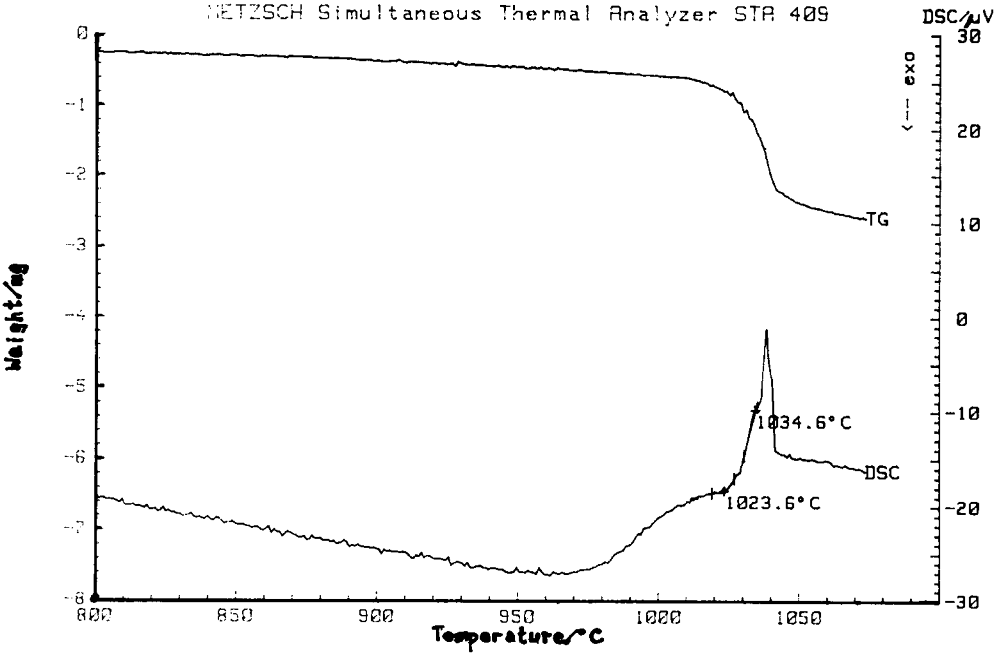

Fig. 1. The TG–DTA curves for $BaCu_{1.14}O_{2+x}$. Heating rate 1 K min^{-1}, pO_2 = 1 atm.

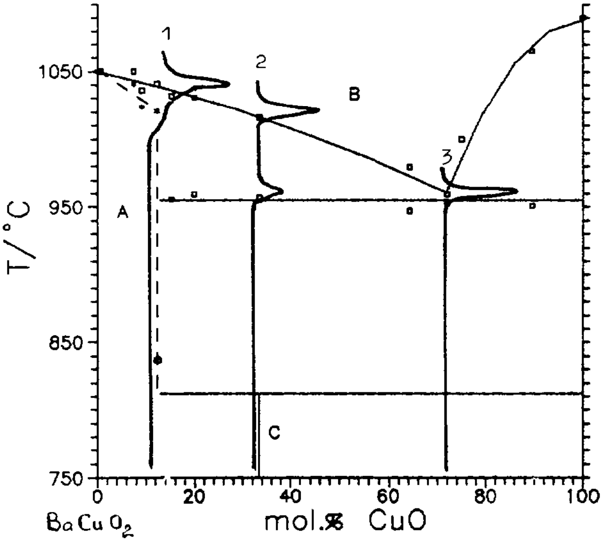

Fig. 2. Scheme of phase relations in the system $BaCuO_2$–CuO–(Cu_2O) and thermograms at rate 20° min^{-1} in 1 atm O_2 1–for $BaCu_{1.14}O_{2+x}$, 2—for $BaCu_{1.14}O_{2+x}$ + CuO, 3—for eutectic mixture, ●—a phase boundary obtained by EMF, A—the monophase region of $BaCu_{1+y}O_{2+x}$, B—liquid phase containing Cu^{1+}, C—phase $Ba_2Cu_3O_{2+n}$, ○, □—experimental points.

Table 1
The onset temperatures of the phase transitions at 1 atm O_2

#	Composition $BaCuO_2$:CuO /mol%	Cation relation, $z(\pm 0.02)$ Ba:Cu = 1:z	Temp/°C of phase trans. t_{sol}, t_{liq}	Heating rate (min^{-1})
Sintered samples				
1	99.3:0.7	1.01	– 1042	1
2	99.3:0.7	1.01	– 1050	20
3	92.59:7.41	1.08	(1041), 1050	20
4	90.9:9.11	1.10	1024, 1036	20
5	87.73:12.27	1.14	1023, 1041	20
6	84.74:15.26	1.18	956, 1032	20
7	80:20	1.25	960, 1031	20
8	66.6:33.4	1.50	957, 1016	20
9	66.6:33.4	1.50	933, 1003	1
10	45.66:64.34	2.19	947, 980	20
11	28:72	3.57	960, 960	20
Mechanical mixtures				
12	90.9:9.11	1.10	957, 1034	20
13	40:60	2.50	957, 982	20
14	25:75	4.00	960, 1000	20
15	10.48:89.52	9.54	951, 1069	20
16	10.48:89.52	9.54	942, 1066	5
17	10.48:89.52	9.54	934, 1063	1
18	10.48:89.52	9.54	930[a], 1032[a]	1

[a] 0.21 atm O_2.

in Fig. 1 and 2 (curve 1). The first temperature (t_{sol}) corresponds to the appearance of liquid phase and the second (t_{liq}) to full melting (Table 1 #3, 4, 5, for #3 approximately).

For compositions with $z \geq 1.18$ the DTA curves had two peaks the temperatures of which are presented in Table 1 #6–10, and in Fig. 2 (curve 2), but for $z = 3.57$ one peak (Table 1 #11, Fig. 2, curve 3) because this composition is very close to the eutectic one [14]. All compositions, produced by simple mixture of $BaCuO_2$ with CuO, showed the DTA curves with two peaks (Table 1 #12–18).

On the basis of this data we suggest that the compound $BaCuO_2$ has a homogenity range not only in respect of oxygen (this fact is well known) but also in respect of copper (hitherto unknown) with a boundary between $z = 1.14$ and $z = 1.18$; the phase rich in copper may be produced only by long heating (about 100 h). A possible phase relation is reflected in Fig. 2 together with the thermograms observed.

To confirm the results and to define more precisely the boundary of non-stoichiometry in respect of copper we carried out a series of electrochemical investigations.

2.3. Electrochemical investigations

A good test of the validity of our suggestion is determination of the dependence of the chemical potential on sample composition. For measurement of the chemical potential of BaO in samples we studied the EMF = f(*z*) of the cells:

$$\mathrm{Pt, O_2 | BaCu_zO_{2+x}, BaF_2 | BaF_2 | CaO, CaF_2 | Pt, O_2}, \quad \ldots E_1, \mathrm{mV}$$

with the reaction

$$1/\delta\,\mathrm{BaCu_zO_{2+x} + BaF_2 + CaO} \rightleftarrows 1/\delta\,\mathrm{Ba_{1+\delta}Cu_zO_{2+x+\delta} + CaF_2}, \quad \delta \to 0$$

Combining the results obtained with literature information [16] for the cell:

$$\mathrm{Pt, O_2 | BaO, BaF_2 | BaF_2 | CaO, CaF_2 | Pt, O_2} \quad \ldots E_2, \mathrm{mV}$$

in which the following reaction takes place:

$$\mathrm{BaO + CaF_2} \rightleftarrows \mathrm{BaF_2 + CaO}$$

We calculated $\Delta\mu_{\mathrm{BaO}}(z) = -2FE_{\mathrm{calc}} = 2F(E_2 - E_1)$ for the reaction:

$$1/\delta\,\mathrm{BaCu_zO_{2+x} + BaO} \rightleftarrows 1/\delta\,\mathrm{Ba_{1+\delta}Cu_zO_{2+x+\delta}}$$

The experiments were carried out in a quartz reactor at $pO_2 = 1$ atm at 837°C by the method described in Ref. [16]. The results are presented in Table 2. As one can see from this table, there is a dependence between the chemical potential of BaO and its content in samples in the range $1 < z < 1.15$. This means that in this range ($t = 837°\mathrm{C}$, $pO_2 = 1$ atm) the samples are monophases and at $z > 1.15$ they consist of two phases ($\Delta\mu = \mathrm{const}$). These results confirm the scheme of phase relations suggested above (Fig. 2). Then the composition of the range of monophases can be described by the formula $\mathrm{BaCu_{1+y}O_{2+x}}$, where $0 \leq y(\pm 0.02) \leq 0.15$.

2.4. *Thermogravimetric investigations*

Determination of oxygen non-stoichiometry x (T, $pO_2 = 1$atm) in $\mathrm{BaCu_{1.14}O_{2+x}}$ was carried out by TG (static dry oxygen, total mass of sample 30–60 mg, scanning rate 1° $\mathrm{min^{-1}}$, accuracy of weight change measurement 10^{-2} mg). For calculation of x we used the formula:

$$x(T) = x_0 + \Delta m(\%)M/M_0/100$$

Table 2
Chemical potential of BaO($\Delta\mu$) for the reaction $1/\delta\ \mathrm{BaCu_zO_{2+x} + BaO} \to 1/\delta\ \mathrm{Ba_{1+\delta}Cu_zO_{2+x+\delta}}$, $\delta \to 0$ at 1110 K (837°C)

$z(\pm 0.02)$	E_1/mV(± 0.5)	E_{calc}/mV(± 0.5)	$-\Delta\mu$/(kJ mol^{-1})(± 0.1)
1.01	209.7	95.5	18.4
1.03	201.0	104.2	20.1
1.10	165.8	139.4	26.9
1.13	147.8	157.4	30.4
1.15	134.0	171.2	33.0
1.20	130.4	174.8	33.7
3.00	133.6	171.6	33.1

where M is the molecular mass of initial substance $BaCu_{1+y}O_{2+x_0}$, M_0 is the molecular mass of oxygen, and Δm(%) is the dependence of the change of mass on temperature. The values of x_0 and y were checked by wet chemical analysis (WCA). The results are listed in Table 3. It is easy to see that the oxygen non-stoichiometry of this compound is close to the additive value ($BaCuO_{2+y} + yCuO = BaCu_{1+y}O_{2+y+y}$) up to about 800°C, but smaller than it is at higher temperatures and vanishes near the solidus temperature t_{sol}. At temperatures higher than t_{sol} a considerable loss of sample mass was observed (for example Fig. 1). In such a fusion cake cooled at a rate of 99° min^{-1} the existance of Cu^{+1} was detected by WCA.

3. Discussion

In some investigations [16, 17] of the system BaO–CuO such phases as $BaCuO_{2.5}$, $BaCuO_{2.64}$, $BaCuO_{2.3-2.4}$ were detected. All this work suffered from lack of cation analysis. It is now reliably established [6] that the oxygen index of barium cuprate cannot be more than 2.11 ± 0.02, so the homogeneity range for (011) is rather small. Our results enable explanation of the appearance of the large value of oxygen nonstoichiometry in these works [16, 17]. We suggest that the appearance of a large excess of oxygen is connected with interaction between $BaCuO_2$ and CuO with production of the monophase sample $BaCu_{1+y}O_{2+x}$ with a wide oxygen homogeneity range and also with a formation of intermediate phases [9].

Also we have to remark that we did not find a difference between eutectic temperatures measured for sintered samples and for mechanical mixtures. So the average eutectic temperature is 956 ± 4°C for a heating rate 20° min^{-1} in 1 atm O_2.

Table 3

Change of mass and oxygen index for a sample with initial composition $BaCu_{1.14}O_{2.25}$ in dependence on temperature in static oxygen $pO_2 = 1$ atm Heating rate 1° min^{-1}

T/°C	Δm/% (±0.2)	$2+x$ (±0.03)
410	0.01	2.25
450	0.06	2.24
500	0.12	2.23
550	0.19	2.22
600	0.26	2.21
650	0.37	2.19
700	0.48	2.18
750	0.68	2.15
800	0.78	2.13
850	0.88	2.12
880	0.94	2.11
920	1.04	2.09
970	1.19	2.07
1000	1.31	2.05

4. Conclusions

1. By use of DTA and EMF measurement it has been shown that barium cuprate has non-stoichiometry in respect of copper, so the formula of this compound may be written as $BaCu_{1+y}O_{2+x}$.

2. The compound with excess copper may be produced only by long heating (100 h) of the mixture of $BaCuO_2$ and CuO in oxygen.

3. The oxygen non-stoichiometry is less than the additive value at temperatures higher than 800°C.

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