

Thermochemical characteristics of BaCuO₂

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Abstract

Using simultaneous thermal analysis (TG + DSC), the heat capacity and non-stoichiometry of BaCuO_{2+x} in O₂ atmosphere have been investigated. The results are formulated as $2.11 \pm 0.02 > 2 + x > 2.00 \pm 0.02$ for $600^\circ\text{C} < t < 900^\circ\text{C}$. The heat capacity $C_p = 0.405 + 1.05 \times 10^{-4}t$ (J/g⁻¹K⁻¹) was measured in the temperature range $40^\circ\text{C} < t < 400^\circ\text{C}$. The uncertainty of less than 2% is due to special selection of the sample masses.

INTRODUCTION

Barium cuprate is often observed as a parasitic phase during the investigation of high-temperature superconducting materials based on Y–Ba–Cu–O. The first study of this compound was made by Kipka and Muller-Bushbaum [1]; the structure was then reexamined [2]. Some later studies [3] demonstrated the existence of a fairly broad range of oxygen non-stoichiometry: it was suggested that the corresponding oxygen non-stoichiometry index varies from 1.8 to 2.5 [3–8].

Recent X-ray studies [5,7,9] of BaCuO₂ gave somewhat different conclusions from those stated in refs. 1 and 4. For example, it has been shown [7] that the formula Ba_{0.92}Cu_{1.06}O_{2.28} reflects the composition of the monocrystal, and that its structure can be described as a superposition of ordered and disordered Cu–O blocks. Therefore, broad ranges of homogeneity (both anionic and cationic) can exist in the bulk. The cell parameter can vary from 18.27 Å [2] to 18.347 Å [7,9]. An analysis of the influence of oxygen non-stoichiometry on the crystal structure of BaCuO_{2+x} reported in ref. 9 (using iodometry and EMF methods) resulted in the following relation between x and the cell parameter a

$$x(\pm 0.02) = -(153.24 \pm 10.60) + (8.28 \pm 0.58)a \quad (\text{Å})$$

This can be used for estimation of x in quenched samples.

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So far no definite conclusions have been formulated on the limits of the homogeneity ranges in oxygen atmosphere and on the effects of cationic non-stoichiometry. In addition, the suggestions made in ref. 10 on the possible low temperature decomposition of BaCuO_{2+x} , as well as the existence of a copper-oxide-enriched compound, $\text{Ba}_2\text{Cu}_3\text{O}_{5+\gamma}$ on the phase diagram of Ba–Cu–O [8,9,11], led to the present study of this system by means of TG and DSC at temperatures less than 800°C.

SAMPLE PREPARATION

The initial sample of $\text{BaCuO}_{2.075}$ was obtained using ceramic technology with multiple intermediate grinding and annealing in dry oxygen at temperatures under 800°C for 25 h. The samples were quenched to liquid nitrogen temperatures. The oxygen index was determined by iodometry with the uncertainty $x \pm 0.015$. The phase composition was checked by X-ray analysis. Dry oxygen was obtained under pressure of 12 atm, storing it for 7 days over dry KOH. CuO was annealed in dry oxygen for 8 h at 800°C.

The standard reference material for the C_p measurements was synthetic sapphire cylinders, cut from solid ground rods grown by the Vernicul process and obtained from the Union Carbide Corporation.

EXPERIMENTAL

An STA-409 thermoanalyser (Netzsch, Germany) was used, with simultaneous monitoring of the changes in weight and differential temperature (DSC signals) over a wide range of temperature, as well as recording TG at constant temperature. The system was flushed out in a dynamic vacuum (1300°C) and then annealed in oxygen. Before filling with dry oxygen, the system was evacuated to 10^{-3} torr and flushed twice with dry oxygen.

The reproducibility of the base line, the coefficient of sensibility line and the buoyancy correction were checked every 200 working hours. To study the non-stoichiometry, crucibles of Al_2O_3 and MgO, of areas 0.5 and 1 cm^2 , respectively, were used.

Samples weighing less than 60 mg were distributed homogeneously over the bottom of the crucible. To measure the heat capacities, monocrystals of sapphire were used as a reference material.

Five series of experiments were performed with different masses of samples; under the experimental conditions used ($20^\circ\text{C min}^{-1}$, heating in dry oxygen), there is a linear relation between the DSC signal and the sapphire mass over the range 35–90 mg. Beyond this range, the linear dependence no longer holds. To check the calibrating coefficients, CuO of appropriate mass was used, such that the DSC signal at 70°C coincided with the signal of one of the standard samples.

TABLE 1
Non-stoichiometry of BaCuO_{2+x}

Sam- ple	Atmosphere	t ($\pm 1^\circ\text{C}$)	Time of annealing (min)	Time of of equi- librium (min)	Change of mass (mg)	$\delta = 2 + x$ (± 0.02)	Phase composi- tion
1	Dry O_2 , 1 atm	908	400	300	-0.51	2.00	BaCuO_{2+x}
2	Dry O_2 , 1 atm	808	800	500	-0.31	2.03	BaCuO_{2+x}
3	Dry O_2 , 1 atm	710	1000	200	-0.03	2.07	BaCuO_{2+x}
4	Dry O_2 , 1 atm	616	6760	3000	0.24	2.11	BaCuO_{2+x}
5	$\text{O}_2 + (\text{CO}_2 + \text{H}_2\text{O})$, 1 atm	710	3000	200	-0.03	2.07	BaCuO_{2+x}
6	$\text{O}_2 + (\text{CO}_2 + \text{H}_2\text{O})$, 1 atm	616	15700	-	1.95	2.36	BaCuO_{2+x} BaCO_3 Ba(OH)_2 $\text{Ba}_2\text{Cu}_3\text{O}_y$

The phase composition of the samples after TG testing was determined by X-ray diffraction (Guinier camera, FR-552, Cu $K\alpha_1$ with Ge as an internal standard) and by thermogram analysis.

RESULTS

The experimental results for the oxygen index δ in BaCuO_δ obtained by isothermal annealing in dry oxygen are summarized in Table 1. Figures 1

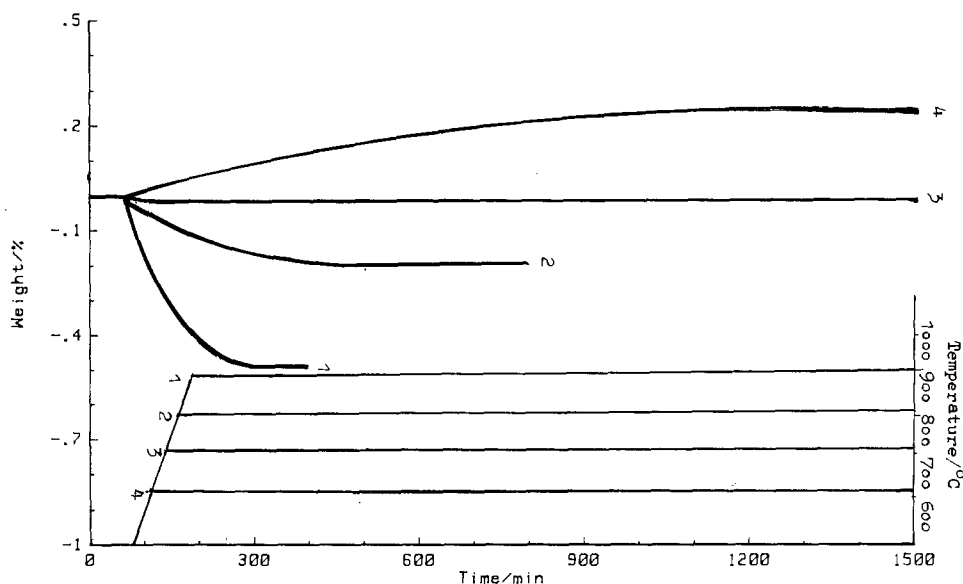


Fig. 1. Change of mass for samples 1-4 vs. time and temperature in dry oxygen.

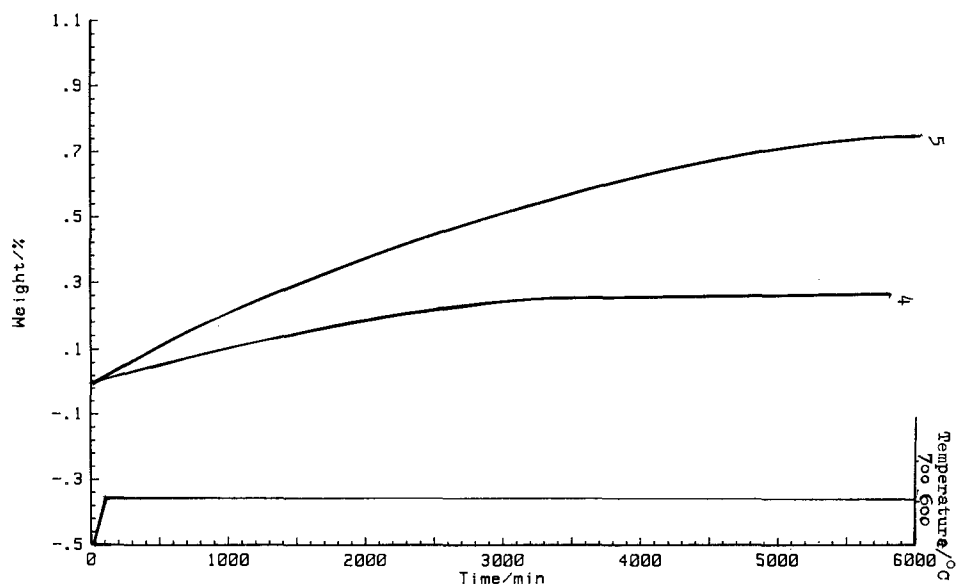


Fig. 2. Change of mass for samples 4 and 5 at 616°C: sample 4 in dry O_2 ; sample 5 in $O_2 + (CO_2 + H_2O)$.

and 2 show the changes in sample mass (in %) with time and temperature. To estimate δ we used

$$\delta = 2.075 + \left(\frac{\Delta m_\theta - \Delta m_{BC}}{m} \right) \left(\frac{M_{BaCuO_{2.075}}}{M_{O_2}} \right)$$

where Δm_θ is the mass change of the sample by time θ , m is initial mass of sample, Δm_{BC} is the buoyancy correction by time θ , and M is the molecular mass.

Table 2 shows the heat capacities of $BaCuO_{2.075}$ as well as the heat capacities of CuO used as a reference material. To obtain the dependence

TABLE 2

Heat capacity of $BaCuO_{2.075}$ at 70°C and $C_p(t)$ for $40 < t < 400^\circ C$

Sapphire mass (mg)	References CuO mass (mg)	$C_p(CuO)$ ($J K^{-1} g^{-1}$)		Deviation from ref. 12 (%)	$C_p(BaCuO_{2.075})^a$ ($J K^{-1} g^{-1}$)
		Ref. 12	Measured at 70°C		
35.00	84.23	0.133	0.132	0.7	0.4217, 0.4210 0.4210
60.93			0.132	0.7	0.4100, 0.4095 0.4010
87.38			0.135	1.5	0.4215, 0.4098 0.4155

^a With $40 < t < 400^\circ C$, $C_p(BaCuO_{2.075}) \pm 2\% = 0.405 + 1.5 \times 10^{-4} t$ $J K^{-1} g^{-1}$.

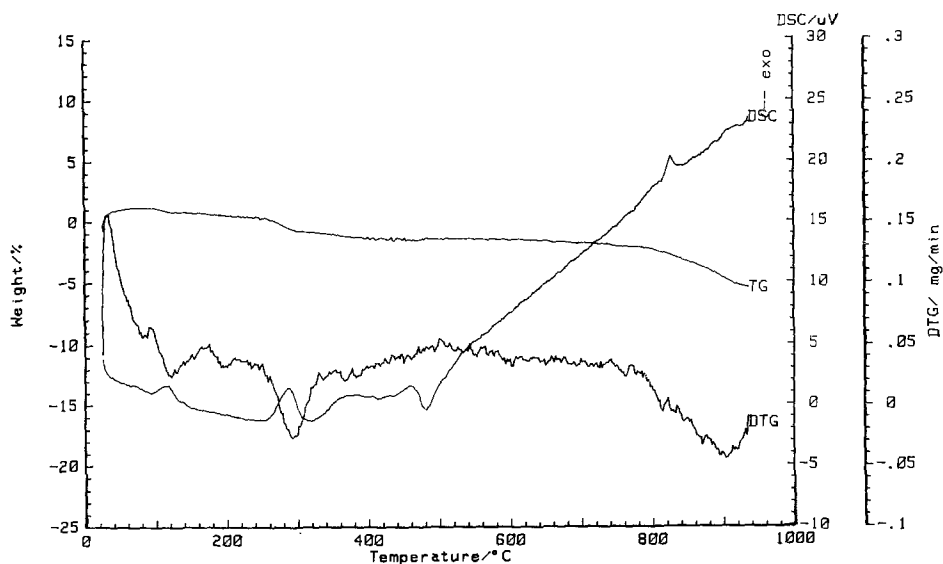


Fig. 3. Thermogram of sample 5 after annealing at 616°C in O_2 + a small admixture of $CO_2 + H_2O$.

of $C_p(BaCuO_{2.075})$ on t , we have analysed the results of 9 series of measurements for C_p (3 sample masses and 3 sapphire masses). Uncertainties have been estimated as deviations from mean values.

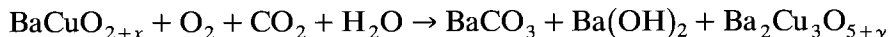
DISCUSSION

We have shown that the homogeneous range of barium cuprate is small (no more than 5.5 mol.% of oxygen) and that its boundaries are not strongly dependent on temperature. The rate of approaching equilibrium is high and depends on both the temperature and the difference in masses at equilibrium and for the initial samples. We have noted that the interaction between small amounts of $CO_2 + H_2O$ and $BaCuO_{2+x}$ begins at lower temperatures (700°C). Eleven days annealing at 616°C results in a relatively large increase of mass (sample 5) and an effective oxygen index of 2.36. The thermogram of sample 5, shown in Fig. 3, indicates the presence of $Ba(OH)_2 \cdot 8H_2O$ and $BaCO_3$. This is demonstrated by the characteristic loss of the $Ba(OH)_2 \cdot 8H_2O$ water molecules at 250°C and by the heat effect of the $\alpha \rightarrow \beta$ transition at 808°C of $BaCO_3$.

X-ray analysis indicated the presence of the following phases in the system: $BaCuO_{2+x}$, $BaCO_3$ and $Ba_2Cu_3O_{5+\gamma}$. We have also determined the cell parameters: $BaCuO_{2+x}$, $a = 18.2962 \text{ \AA}$ (over 56 lines); $Ba_2Cu_3O_{5+\gamma}$, $a = 7.362$ (1) \AA , $b = 4.251$ (1) \AA , $c = 11.375$ (2) \AA (over 10 lines); $BaCO_3$, $a = 5.313$ (3) \AA , $b = 8.902$ (2) \AA , $c = 6.432$ (3) \AA (over 9 lines).

We confirm the results of Tompson et al. [11], namely that $\text{Ba}_2\text{Cu}_3\text{O}_{5+\gamma}$ has an incommensurate modulated structure with *c*-centred orthorhombic average unit cell for which $a = b\sqrt{3}$.

To summarize, we suggest that the phases determined are products of the process



We doubt the conclusions presented in several publications that BaCuO_{2+x} possesses a broad range of non-stoichiometry (≈ 25 mol.%) or that BaCuO_2 degradation is possible in O_2 atmosphere ($p_{\text{O}_2} = 1$ atm and $t > 600^\circ\text{C}$) [13]. In our opinion, the experimental discrepancies in these studies are probably related to the use of oxygen containing admixtures of CO_2 and H_2O . According to the process mentioned above, this could result in misleading conclusions.

REFERENCES

- 1 R. Kipka and Hk. Muller-Buschbaum, Z. Naturforsch., 32b (1977) 121.
- 2 W. Gutau and Hk. Muller-Buschbaum, J. Less-Common Met., 152 (1989) L11.
- 3 Ju.Ja. Skolis, S.F. Pashin and M.L. Kovba, Superconductivity: Phys. Chem. Eng., 3 (1990) 2792.
- 4 M. Arjomand and D.J. Machin, J. Chem. Soc. Dalton Trans., (1975) 1061.
- 5 M.T. Weller and D.R. Lines, J. Solid State Chem., 82 (1989) 21.
- 6 U. Straub, D. Krug, Ch. Ziegler, D. Schmeiser and F. Gopel, Mater. Res. Bull., 24 (1989) 681.
- 7 E.F. Paulus, G. Mische, H. Fuess, I. Jehia and U. Löchner, J. Solid State Chem., 90 (1991) 17.
- 8 N.F. Zakharchuk, V.S. Kravchenko, V.E. Fedorov, A.A. Karamzin, A.I. Romanenko, A.N. Trusniokova, N.G. Koronova and O.G. Potapova, Study of charge position of copper and oxygen by using the method of V-I-metry in solid state, Preprint 89-17, Novosibirsk, Academy of Science of the USSR, Siberian Branch, Institute of Inorganic Chemistry, 1989, 66 pages.
- 9 S.F. Pashin, Ph. D. Thesis, Moscow State University, 1991.
- 10 S.F. Pashin, E.L. Antipov, L.M. Kovba and Yu.Ya. Skolis, Superconductivity: Phys. Chem. Eng., 2 (1989) 102.
- 11 J.G. Tompson, J.D. Fitzgerald, R.L. Vithers, P.Y. Barlao and Y.S. Anderson, Mater. Res. Bull., 24 (1989) N4, 505.
- 12 JANAF thermochemical tables, 2nd edn., NSRDS-NBS37, Washington DC, 1971.
- 13 G.V. Basuev and V.V. Anzigna, Superconductivity: Phys. Chem. Eng., 3 (1990) 1264.