

## On the Thermodynamic Stability of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ Superconducting Phase

Nata I. Matskevich,\* Fedor A. Kuznetsov, Tatiana L. Popova, Valentin A. Titov, Valentin S. Kravchenko, Valentina P. Shaburova and Olga G. Potapova

*Institute of Inorganic Chemistry, Siberian Branch of the Russian Academy of Sciences, 630090 Novosibirsk, Russian Federation. Fax: +7 383 235 5960*

Experimental data on the thermodynamic properties of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and related phases has been obtained.

The problem of the thermodynamic stability of the 1-2-3 phase in the Y-Ba-Cu-O system has been considered in a number of recent publications. It appears that, in the high temperature region, the phase is thermodynamically stable. However, the authors of a paper<sup>1</sup> based on results obtained by a solution calorimetry method stated that at room temperature the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  phase is less stable than a mixture of two phases with the same nominal composition:  $\text{Y}_2\text{Cu}_2\text{O}_5 + \text{BaCuO}_2$ . In contrast to previous papers this conclusion was reported by Morss *et al.*<sup>2</sup> who also employed solution calorimetry methods to study the stability of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  at room temperature.

This communication presents additional experimental information on the thermodynamic properties of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and related phases so as to clarify the stability of the 1-2-3 phase.

The solution calorimetry method described elsewhere was used. The reproducibility of the calorimeter was 0.03%. All experiments were performed at 323 K. At lower temperatures the rate of dissolution of  $\text{Y}_2\text{O}_3$  is too small, which ultimately

leads to measurements of low precision. The general procedure for the calorimetric experiments is described in ref. 3.

The substances employed in the calorimetric experiments were:  $\text{CuO}$ ,  $\text{Y}_2\text{O}_3$  and  $\text{BaCO}_3$  of high purity.  $\text{BaCuO}_2$  was synthesized in air by sintering of  $\text{CuO}$  and  $\text{BaCO}_3$ . Samples of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  were prepared from  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and  $\text{CuO}$ . The prepared orthorhombic phase  $\text{YBa}_2\text{Cu}_3\text{O}_{6.9}$  had  $T_c = 92$  K.

All phases employed were characterized by X-ray powder diffraction methods and chemical method analysis. The X-ray powder diffraction method was performed using known standards and allowed the purity level to be fixed at 2–4%. The results of chemical analysis for  $\text{BaCuO}_2$  were: Ba 58.8% and Cu 26.4%, and for  $\text{YBa}_2\text{Cu}_3\text{O}_{6.5}$ : Y 13.3%, Ba 40.7% and Cu 28.9%. Phase analysis performed by a differential solution method indicated the purity of the compound to be about 1%. So, according to the analytical results, all the samples used in the calorimetric study were found to be of a single phase. The oxygen content was determined by measuring the crystal lattice parameter volumes. According to the analytical results

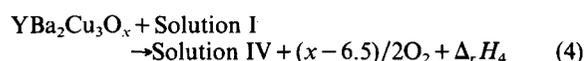
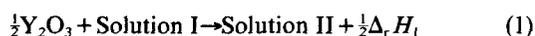
obtained from all samples, it was possible to compare the heat of dissolution of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  ( $x=6.4-6.9$ ) with the heats of dissolution of the mixtures (i) and (ii).



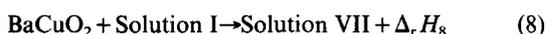
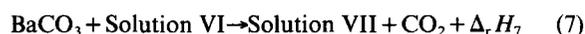
and



Solutions of 6 mol  $\text{dm}^{-3}$  HCl were used as solvents in all the runs. The mass of substance ( $m$ ) used in each experiment was:  $m(\text{Y}_2\text{O}_3)=0.06$  g;  $m(\text{CuO})=0.1$  g;  $m(\text{BaCO}_3)=0.2$  g;  $m(\text{BaCuO}_2)=0.2$  g and  $m(\text{YBa}_2\text{Cu}_3\text{O}_x)=0.3$  g. The volume of the calorimeter was 200 ml. The dissolution processes studied were reactions (1)–(5).



To independently obtain the enthalpy of formation of barium cuprate the enthalpy of reactions (6)–(8) was measured.

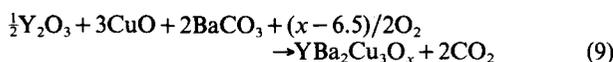


That solutions obtained by dissolution of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  phase (varying  $x$ ) and by dissolution of mixtures (1) and (2) were identical was proved by measuring the electronic spectra of the solution in the region  $10^4-3 \times 10^4 \text{ cm}^{-1}$ . It was shown that in experiments conducted in air the spectra of the solutions became identical 10–15 min after dissolution had finished for any composition of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  phase.

It should be noted that in the experiments we used different sequences of dissolving phases, not only those described in reactions (1)–(3) and (6)–(8). This was done to avoid systematic errors. It was found that, within the accuracy of measurements, the total amount of liberated heat was independent of dissolution sequence. Selected sets of thermochemical reactions permit us to obtain values of enthalpy of formation of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{BaCuO}_2$  phases with very limited use of literature reference data. The set also permits us to make a cross check of the figures obtained.

The enthalpies of reactions (1)–(8) were of the order:  $\Delta_r H_1 = -390 \text{ kJ mol}^{-1}$ ;  $\Delta_r H_4 = -850 \text{ kJ mol}^{-1}$ ;  $\Delta_r H_2 = \Delta_r H_6 = -55 \text{ kJ mol}^{-1}$ ;  $\Delta_r H_5 = \Delta_r H_8 = -270 \text{ kJ mol}^{-1}$  and  $\Delta_r H_3 = \Delta_r H_7 = -12 \text{ kJ mol}^{-1}$ .

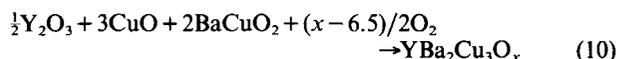
The measured enthalpies of dissolution were used for the calculation of enthalpy of reaction (9) for different oxygen content in the 1-2-3 phase ( $T=323 \text{ K}$ ).



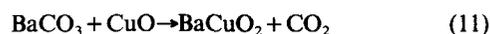
$$\Delta_r H \quad (x=6.9) = +417 \pm 5 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.5) =$$

$$+460 \pm 3 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.7) = +440 \pm 5 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.4) = +462 \pm 3 \text{ kJ mol}^{-1} \text{ and } \Delta_r H \quad (x=6.6) = +457 \pm 3 \text{ kJ mol}^{-1}.$$

For reaction (10) enthalpies were calculated as follows:



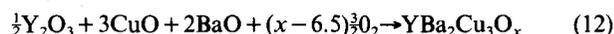
$$\Delta_r H \quad (x=6.9) = +13 \pm 4 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.5) = +56 \pm 3 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.7) = +36 \pm 5 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.4) = +59 \pm 3 \text{ kJ mol}^{-1} \text{ and } \Delta_r H \quad (x=6.6) = +53 \pm 3 \text{ kJ mol}^{-1}.$$



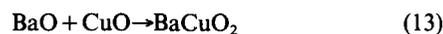
For reaction (11) enthalpy was calculated as follows:  $\Delta_r H$  (323 K) =  $201 \pm 5 \text{ kJ mol}^{-1}$ .

We can see that data obtained from different thermodynamic cycles are in good agreement, thus indicating the absence of essential systematic errors in the measurements.

Literature data for the heat of reaction of  $\text{BaO} + \text{CO}_2 \rightarrow \text{BaCO}_3$  and data on heat capacities of different substances<sup>4</sup> were used to calculate the enthalpy of formation of  $\text{YBa}_2\text{Cu}_3\text{O}_x$  and  $\text{BaCuO}_2$  from individual oxides at standard temperature (298.15 K).



$$\text{For reaction (12): } \Delta_r H \quad (x=6.9) = -122 \pm 5 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.5) = -79 \pm 3 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.7) = -99 \pm 5 \text{ kJ mol}^{-1}; \quad \Delta_r H \quad (x=6.4) = -77 \pm 3 \text{ kJ mol}^{-1} \text{ and } \Delta_r H \quad (x=6.6) = -82 \pm 3 \text{ kJ mol}^{-1}.$$



For reaction (13),  $\Delta_r H = -66 \pm 5 \text{ kJ mol}^{-1}$ .

The data obtained in the present work using the entropy of the  $\text{YBa}_2\text{Cu}_3\text{O}_x$  phase<sup>5</sup> and the entropy of  $\text{BaCuO}_2$ <sup>5</sup> allow us to conclude that at room and lower temperature the 1:2:3 phase is thermodynamically less favourable than the mixture  $\frac{1}{2}\text{Y}_2\text{O}_3 + \text{CuO} + 2\text{BaCuO}_2$ .

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Received: Moscow, 20th April 1992

Cambridge, 8th June 1992; Com. 2/02077G