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Thermodynamic stability of 34 compounds of the system Y–Ba–Cu–O

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Abstract

Using the method of thermodynamic simulation the thermal decomposition of 34 previously described (Moiseev et al., Thermochim. Acta 198 (1992) 267) compounds is described in Ar and O_2. They can be classified into metastable ($Y:Ba:Cu_O = 2:8:6_{17}$, $2:4:6_{13}$, $2:1:3_7$, $2:4:2_9$, $2:6:4_{13}$, $2:10:4_{17}$, $2:0:2_5$, $0:3:5_8$, $0:2:1_3$, $2:12:6_{21}$, $2:6:5_{15}$, $2:10:6_{19}$, $2:8:4_{15}$, $2:4:7_{14}$, $2:2:4_9$, $2:3:5_{11}$, $1:2:3_7$, $6:16:10_{35}$) and stable ($Y:Ba:Cu_O = 1:2:3_6$, $2:4:7_{15}$, $4:1:5_{12}$, $0:2:3_5$, $2:0:1_4$, $0:3:1_4$, $2:1:1_5$, $2:6:2_{11}$, $1:0:1_2$, $2:2:0_5$, $4:3:0_9$, $2:4:0_7$, $0:1:1_2$, $2:4:8_{15}$).

INTRODUCTION

With the help of the method of thermodynamnic simulation (TDS) [1,2] the thermal decomposition of 34 compounds was studied, their properties being given in ref. 3, at a total pressure of 10^5 Pa in Ar and O_2 at 100–2000 K in steps of 100 K.

The aim of this work is to estimate the stability of superconducting and concomitant compounds, and the sequence, composition and ratio of the decomposition products.

STABLE COMPOUNDS (Table 1)

The thermodynamic stability (TS) was considered in terms of the extent to which the initial formula composition of the compound was retained over a definite temperature range and also the appearance of the intermediate or final decomposition products of other initial compounds.

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TABLE 1

Temperture range of stability of compounds in the Y–Ba–Cu–O system

No.	Compound	Stability range (K)		Recommended T_{melt}
		Ar	O_2	
1	$YBa_2Cu_3O_6$	100–1446	900–1200	1446 [a] 1300 [b,c]
2	$Y_2Ba_4Cu_7O_{15}$	100–900	100–900	900 [c,d]
3	$Y_4BaCu_5O_{12}$	100–1342	100–1342	1342 [d]
4	$Ba_2Cu_3O_5$	100–1014	100–1014	1014 [d]
5	Y_2CuO_4	100–1840	100–1840	1840 [d]
6	Ba_3CuO_4	100–1315	100–1315	1315 [d]
7	Y_2BaO_4	100–1610	100–1610	1610 [d]
8	Y_2BaCuO_5	100–700	700	800 [a,c]
9	$Y_2Ba_6Cu_2O_{11}$	100–800	100–800	900 [c,d]
10	$YCuO_2$	100–1560	– [e]	1560 [a]
11	$Y_2Ba_2O_5$	100–200	– [e]	300 [a,c]
12	$Y_4Ba_3O_9$	100–1300	– [e]	1400 [a,c]
13	$Y_2Ba_4O_7$	100–700	– [e]	800 [a,c]
14	$BaCuO_2$	200–400	– [e]	500 [a,c]
15	$Y_2Ba_4Cu_8O_{15}$	200–600	– [e]	700 [a,c]

[a] In Ar. [b] In O_2. [c] Decomposition temperature T_{decomp} (K). [d] In Ar and O_2. [e] Not stable.

$Y_4BaCu_5O_{12}$, $Ba_2Cu_3O_5$, Y_2CuO_4, Ba_3CuO_4, Y_2BaO_4 are stable until T_{melt} in inert (Ar) and oxygen atmospheres. For the remaining compounds, the stability in Ar is greater than in O_2. For some compounds the temperature range of phase existence narrows in O_2 ($YBa_2Cu_3O_6$, Y_2BaCuO_5); for others the presence of O_2 leads to total decomposition ($YCuO_2$, $Y_2Ba_2O_5$, $Y_4Ba_3O_9$, $Y_2Ba_4O_7$, $BaCuO_2$, $Y_2Ba_4Cu_8O_{15}$). $Y_2Ba_4Cu_7O_{15}$, Y_2BaCuO_5 and $Y_2Ba_6Cu_2O_{11}$ decompose at $T < T_{melt}$ according to ref. 3.

Among superconducting compounds ($YBa_2Cu_3O_7$ ("123" phase) with $T_c = 92$ K, $Y_2Ba_4Cu_7O_{15}$ ("247" phase) with $T_c = 14$–68 K [4] or 95 K [5], and $YBa_2Cu_4O_8$ ("124" phase) with $T_c = 80$ K [6]), only the "247" phase is thermodynamically stable.

METASTABLE COMPOUNDS (Table 2)

In both Ar and O_2, there is a wide temperature range (100–1400 K) for which the mixture of decomposition products has a constant ratio. For the ranges 100–(600–800) K, except for the initial $Y_2Cu_2O_5$, $Ba_3Cu_5O_8$ and $Y_2Ba_{12}Cu_6O_{21}$ (in Ar), the "247" phase is present in the mixture of decomposition products, which once more proves its TS.

In Ar at 100–(600–800) K, except for the initial "124" phase $Y_2Cu_2O_5$, $Ba_3Cu_5O_8$ and Ba_2CuO_3, in the mixture of decomposition products

$YBa_2Cu_3O_6$ is present; in O_2, except for the initial "124" phase $Y_2BaCu_3O_7$, $Y_2Ba_2Cu_4O_9$ and binary cuprates, BaO_2 is present.

Analysis of the region preceding the formation of the melt phase shows that binary oxides $YBa_2Cu_3O_6$ and $Y_4BaCu_5O_{12}$ are the most stable among thermodynamically stable phases.

When the decomposition products of ternary metastable oxides melt, the temperatures are close to 1600 K.

Consequently, in future investigations of the Y–Ba–Cu–O system, there is no need to take into account the compounds given in Table 2.

SUPERCONDUCTING COMPOUNDS

"123" Phase

In Ar as a result of decomposition, at 100–500 K Y_2BaCuO_5, $Y_2Ba_6Cu_2O_{11}$, BaO_2 and the "247" phase coexist in the mole ratio 1.488:1:2.48:11.41; at 600 K the same phases coexist in the ratio 4.11:5.68:1:43.31; at 700 K Y_2BaCuO_5, $Y_2Ba_6Cu_2O_{11}$ and the "247" phase coexist in the ratio 1:1.5:11. In the range 800–1300 K only $YBa_2Cu_3O_6$ exists (the sum of the impurities in this is $\leq 2 \times 10^{-5}$ mol.%). At 1400–1500 K Y_2CuO_4(cr), Y_2BaO_4(cr) and $Ba_2Cu_3O_5$(l) coexist in the ratio 1.5:1:4.5. Above 1610 K a homogeneous melt forms.

In O_2 at 100–700 K Y_2CuO_4, BaO_2 and the "247" phase coexist in the ratio 12:1.5:1. In the range 900–1200 K only $YBa_2Cu_3O_6$ exists (the sum of the impurities $\leq 1 \times 10^{-4}$ mol.%). At $T \geq 1300$ K, the composition and concentration of every phase is identical to that found in an Ar environment.

At 100–700(800) K the "247" phase exists in the decomposition products: the maximum concentration in Ar is 97.41 mol.% (600 K) and in O_2 is 88.2 mol.% (800 K). In the range 800(900)–1300(1200) K only $YBa_2Cu_3O_6$ exists.

A survey of experiments [7] shows that in nitrogen the "123" phase at 763–883 K loses O_2 in an "ortho⟶tetra" transformation, with formation (in this temperature range) of $YBa_2Cu_3O_6$; in O_2 the same process takes place at 873–1253 K. At 200°C, heating the "123" phase for 700–900 h in air leads to stratification, with formation of "ortho" and "tetra" modifications of the "123" phase [8–10]. TDS results [7] (the "123" phase is a regular solution of $YBa_2Cu_3O_6 + YBa_2Cu_3O_7$; in the system only Y_2BaCuO_5, $BaCuO_2$, $Y_2Cu_2O_5$ and oxides were considered) agree with refs. 8–10. However, increasing the number of compounds in the system and presentation of the "123" phase as a compound $YBa_2Cu_3O_7$ leads (in Ar and O_2, as was shown above) to different results at low T.

In ref. 11 different ideas on the decomposition of the "123" phase are given, presenting it as a solid solution of a quasibinary system with cation

TABLE 2

Decomposition of metastable compounds

No.	Initial composition	Ar		O_2		T of transition into melt (K)
		100–(600–800) K	Before total melting	100–(600–700) K	Before total melting	
1	$Y_2Ba_8Cu_6O_{17}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	"123"-O_6 Ba_3CuO_4 Y_2BaO_4	BaO_2 $Y_2Ba_6Cu_2O_{11}$ "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	1610
2	$Y_2Ba_4Cu_6O_{13}$	Y_2BaCuO_5 "123"-O_6 $Y_2Ba_6Cu_2O_{11}$ "247"	123-O_6 Y_2BaO_4 Y_2CuO_4 $Ba_2Cu_3O_5$	BaO_2 Y_2BaCuO_5 "247"	As in Ar	1610
3	$YBa_2Cu_4O_8$ [a]	CuO "247"	CuO Cu_2O $Y_4BaCu_5O_{12}$ $Ba_2Cu_3O_5$	As in Ar	As in Ar	1500
4	$YBa_2Cu_3O_7$ [a]	Y_2BaCuO_5 $Y_2Ba_6Cu_2O_{11}$ BaO_2 "247"	Y_2CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	Y_2CuO_4 BaO_2 "247"	As in Ar	1610
5	$Y_2BaCu_3O_7$	123-O_6 Y_2CuO_4 "247"	123-O_6 Y_2CuO_4 $Y_4BaCu_5O_{12}$ $Ba_2Cu_3O_5$	Y_2CuO_4 "247" $Y_4BaCu_5O_{12}$	Y_2CuO_4 $Y_4BaCu_5O_{12}$ $Ba_2Cu_3O_5$	1610
6	$Y_2Ba_4Cu_2O_9$	Y_2BaCuO_5 "123"-O_6 $Y_2Ba_6Cu_2O_{11}$ "247"	123-O_6 Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 $Y_2Ba_6Cu_2O_{11}$ "247" Y_2BaCuO_5	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	1610
7	$Y_2Ba_6Cu_4O_{13}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	"123"-O_6 Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 "247" $Y_2Ba_6Cu_2O_{11}$	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	1610
8	$Y_2Ba_{10}Cu_4O_{17}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	"123"-O_6 Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 "123"-O_6 Ba_3CuO_4 "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	1610

9	$Y_2Cu_2O_5$	Y_2CuO_4 CuO (1200 K)	Cu_2O Y_2CuO_4	Y_2CuO_4 CuO (1400 K)	As in Ar	1560
10	$Ba_3Cu_5O_8$	CuO $Ba_2Cu_3O_5$ (1400 K)	Cu_2O $Ba_2Cu_3O_5$	As in Ar	As in Ar	1515
11	Ba_2CuO_3	Ba_3CuO_4 $Ba_2Cu_3O_5$	Ba_3CuO_4 $Ba_2Cu_3O_5$	BaO_2 $Ba_2Cu_3O_5$	As in Ar	1315
12	$Y_2Ba_{12}Cu_6O_{21}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 "123"-O_6 Ba_3CuO_4 "247"	As in Ar	1610
13	$Y_2Ba_6Cu_6O_{15}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 $Y_2Ba_6Cu_2O_{11}$ "247"	As in Ar	1610
14	$Y_2Ba_{10}Cu_6O_{19}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	As in Ar	1610
15	$Y_2Ba_8Cu_4O_{15}$	"123"-O_6 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 $Y_2Ba_6Cu_2O_{11}$ Ba_3CuO_4 "247"	As in Ar	1610
16	$Y_2Ba_4Cu_7O_{14}$	"123"-O_6 $Y_2Ba_4Cu_8O_{15}$ "247"	Y_2CuO_4 "123"-O_6 $Y_4BaCu_5O_{12}$ $Ba_2Cu_3O_5$	BaO_2 "247" CuO $Y_4BaCu_5O_{12}$	Y_2CuO_4 $Ba_2Cu_3O_5$	–[b]
17	$Y_2Ba_2Cu_4O_9$	"123"-O_6 Y_2CuO_4 $Y_4BaCu_5O_{12}$ "247"	123-O_6 Y_2CuO_4 $Y_4BaCu_5O_{12}$	Y_2CuO_4 "247"	Y_2BaO_4 $Y_4BaCu_5O_{12}$ $Ba_2Cu_3O_5$	1700
18	$Y_2Ba_3Cu_5O_{11}$	"123"-O_6 Y_2BaCuO_5 Y_2CuO_4 "247"	"123"-O_6 Y_2CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 Y_2CuO_4 "247"	Y_2CuO_4 Y_2CuO_4 $Ba_2Cu_3O_4$	1500
19	$Y_6Ba_{16}Cu_{10}O_{35}$	Y_2BaCuO_5 "123"-O_6 $Y_2Ba_6Cu_2O_{11}$ "247"	Ba_3CuO_4 Y_2BaO_4 $Ba_2Cu_3O_5$	BaO_2 $Y_2Ba_6Cu_2O_{11}$ "247"	As in Ar	1610

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[a] Superconducting. [b] T_{trans} in melt is 1700 K. At 400–800 K in O_2 only the "247" phase is present.

composition “123” ($YBa_2Cu_3O_{6+z}$) and phase diagram “$Z-T$ (K)”. In particular, for $Z=1$, decomposition according to ref. 11 may lead to the appearance of the “247” phase. The conclusion about the thermodynamic instability of the “123” phase reached in ref. 11, is proved by us.

“124” Phase

At 100–600 K in Ar, as a result of $YBa_2Cu_4O_8$ decomposition CuO and the “247” phase coexist in equimolar ratio; at 700 K, a mixture of the phases CuO, “247”, $Y_4BaCu_5O_{12}$ and $Ba_2Cu_3O_5$ in the ratio 14.9:13.7:1:3.5 coexist. In the range 800–1300 K, the ratio $CuO:Y_4BaCu_5O_{12}:Ba_2Cu_3O_5$ is kept equal to 1:2:7; above 1014 K $Ba_2Cu_3O_5$ melts. At 1400 K CuO(cr), Cu_2O(cr) and $Y_4BaCu_5O_{12}$(l), $Ba_2Cu_3O_5$(l) coexist in the ratio 1.43:6.86:24. At $T \geq 1500$ K the melt is formed.

In O_2 the behaviour of the “124” phase is almost identical to that described above. The range of CuO and “247” phase coexistence (100–700 K) increases a little.

On the basis of refs. 4–6, 12 and 13, one can draw the following conclusions.

By varying P, T and P_{O_2} from “123” phase and CuO it is possible to synthesize the “124” and “247” phases.

Thermogravimetry shows the “124” phase to be more stable than the “123” phase.

The pressure in the system considerably influences the conditions of synthesis (decomposition) of the phases “123”, “124” and “247”.

In attempts at thermodynamic interpretation of the results for the system, simple oxides were taken into account in addition to the group of superconducting phases Y_2BaCuO_5 and $BaCuO_2$.

The conditions at which the experiments are performed do not guarantee that the system will reach equilibrium.

In ref. 14 at $P_{O_2}=1$ atm, the behaviour of the “124” phase is described by the equilbrium

$$YBa_2Cu_3O_{6+z} + CuO + (1-z)/2\,O_2 \rightleftharpoons YBa_2Cu_4O_8 \qquad (1)$$

below 1118 K the reaction being shifted to the right; at $T > 1118$ K the “124” phase decomposes. In ref. 14 the possibility of decomposition with formation of “247” and CuO phases is assumed.

“247” Phase

In Ar at 100–800 K, CuO (100–500 K), $Ba_2Cu_3O_5$ (above 200 K), $Y_4BaCu_5O_{12}$ (above 600 K) and $YBa_2Cu_3O_6$ (700 K and higher) exist together with impurities. Their respective proportions at 800 K are 6.5×10^{-5}, 10.9, 3.5 and 10.4 mol.%. At 900–1100 K phases form as a result of the decomposition given by

$$7Y_2Ba_4Cu_7O_{15} \rightarrow 6YBa_2Cu_3O_6 + 2Y_4BaCu_5O_{12} + 7Ba_2Cu_3O_5 + 5O_2 \qquad (2)$$

In the range 1200–1400 K $YBa_2Cu_3O_6$(cr), Y_2CuO_4(cr) and $Ba_2Cu_3O_5$(l) coexist. Above 1700 K the only condensed phase is the melt.

In O_2, the initial phase exists at 100–800 K, together with a small amount ($\leqslant 1 \times 10^{-5}$ mol.%) of impurities Y_2CuO_4 and BaO_2. At 900–1100 K the phase mixture exists according to eqn. (2); at 1200–1500 K, Y_2CuO_4(cr) and $Ba_2Cu_3O_5$(l) exist in the ratio 1:2. Above 1700 K the melt is formed.

Analysis of literature data shows that no direct experimental measurements of the "247" phase stability in Ar and O_2 under equilibrium conditions have been made. In ref. 4, at $P_{O_2} = 7$–8 bar and with T decreasing from 1000 to 700 K in the system "123"–CuO, the sequence of phase appearance is "123" → "123" and "247" → "247" → "124". According to authors of ref. 4, this testifies to the higher stability of the "124" phase than the "247" phase.

Thus, our data agree with the conclusions in ref. 11 about the thermodynamic instability of the "123" phase. After analysis of known experimental data, the question of thermodynamic stability of the "124" and "247" phases remains open. In ref. 11 it is supposed that the "124" phase is the only thermodynamically stable compound from the considered group of superconductors. According to our results only the "247" phase is thermodynamically stable.

DISCUSSION

In our opinion, the thermodynamic stability of a compound can be estimated mainly by way of TDS of the compound's behaviour at definite T, P and gas environment composition, necessarily taking into account the thermodynamic functions of all (in the limit) compounds from the elements of the system. Judgement of the thermodynamic stability of a compound, based only on experiment will very often be indefinite because there is no guarantee that the system has ever reached equilibrium state. In this case, the experimentally observed stability should be discussed at definite system composition and exposure time.

The use of non-equilibrium experimental data for the description of phase stability is a permissible pseudothermodynamic method; it has some application and is useful for practical specialists in the field of so-called kinetic phase diagrams [15]. However, data thus obtained cannot be considered thermodynamically pure and do not provide the principal answer concerning the stability/metastability of phases, owing to the geometric hindrance of the formation and/or decomposition processes [16].

Because the known experimental data about the phase composition of the system Y–Ba–Cu–O, i.e. the time intervals of the existence of the various phases cannot be considered as obtained under equilibrium conditions, TDS of this system was conducted with a limited number of compounds and so in the sytem Y–Ba–Cu–O only a pseudothermodynamic analysis has been carried out as far as we know. It is worth mentioning that this work is the first attempt to apply TDS simulation for estimation of the stability of compounds in the Y–Ba–Cu–O system.

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