

ON PHASES AND CHARACTERISATION OF QUENCHED $\text{YBa}_2\text{Cu}_3\text{O}_x$

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(Received 8 December 1987)

ABSTRACT

It is shown that quenching of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ melt at different cooling rates yields (besides the known phases of Y_2O_3 , CuO , BaCuO_2 and Y_2BaCuO_5) some unidentified phase(s) other than $\text{YBa}_2\text{Cu}_3\text{O}_x$, $\text{YBa}_4\text{Cu}_2\text{O}_x$ and $\text{YBa}_4\text{Cu}_3\text{O}_x$. Upon reheating the as-quenched samples oxidation and precipitation exotherms are revealed between 250 and 500 °C. The as-quenched and annealed (at 300 and 500 °C) samples do not show superconductivity. This is not achieved unless the sample is heated at temperatures which enable solid-state reactions to occur between the matrix components to form $\text{YBa}_2\text{Cu}_3\text{O}_x$.

INTRODUCTION

In this study we have investigated the reliability of some unconfirmed information which states that a metastable superconductive phase(s) can be obtained by rapid cooling of the $\text{YBa}_2\text{Cu}_3\text{O}_x$ melt. The only available data are those published by McKittrick and coworkers [1,2] who quenched three compositions chosen along the $\text{YBa}_2\text{Cu}_3\text{O}_x$ (i.e. 1:2:3) to BaCuO_2 (i.e. 0:1:1) tie-line under different solidification rates. The melt-drop (about $5 \times 10^2 \text{ K s}^{-1}$) and melt-extraction (about 10^4 – 10^5 K s^{-1}) techniques were applied on presintered pellets melted using an H_2 - O_2 torch flame rich in O_2 . They showed [1] that moderate cooling rates yielded a phase assemblage containing more than one stoichiometric phase. The phases were difficult to identify by X-ray diffraction analysis. The phase assemblage contained [1,2] the 2:1:1 and 0:1:1 phases together with some unidentified phase(s). The latter was the major product of rapid quenching rates and exhibited a prevailing cubic structure for the 1:2:3 initial composition. Such quenched samples became superconductive only after annealing in O_2 at 700 °C for 16 h as a result of the formation of the 1:2:3 compound. However, no measurements were made on samples annealed at lower temperatures and no thermal characterisations were performed on quenched samples.

By employing rapid solidification techniques, which were developed and successfully used in our laboratory for the previous study of the $(\text{Fe,Mn})_2\text{O}_3$ – $(\text{Bi,B})_2\text{O}_3$ system [3,4], we have investigated the low temperature annealing behaviour of quenched samples. This is a continuation of our DTA study of the identification [5] and preparation [6] of the 1:2:3 phase from different raw materials.

EXPERIMENTAL

The 1:2:3 composition was presintered at 900°C in O_2 for 50 h in a similar way to conventional ceramics prepared from the oxide mixture (analysed on the content of cations) [7]. Sample D was melted at 1450°C in a Pt crucible under an O_2 atmosphere for 1 h and was then poured in-between two copper plates forming a specimen about 1 mm thick. A layer of melt was allowed to self-cool, while adhering to the surface of a Pt crucible, which was standing on a metallic support (sample C). For comparison samples A and B were made by pressing pellets from the presintered and powdered 1:2:3 composition, firing them in O_2 for 48 h at 1025 and 1200°C , respectively, and then allowing them to self-cool by removing them quickly from the furnace onto a metallic support.

Differential thermal analysis (DTA) was carried out on powdered samples using a Netzsch DTA unit equipped with a DDK measuring head allowing treatment in dynamic O_2 atmosphere [5] (see Fig. 1). Phase identification was performed on the X-ray diffractometer DRON.1 using Cu $K\alpha$ radiation. The spectral lines of Y ($L\alpha_1$), Ba ($L\alpha_1$) and Cu ($K\alpha_1$) were employed for quantitative analysis using an electron microprobe (EDS) (JEOL JSX-50A). Standards used were $\text{Y}_3\text{Fe}_5\text{O}_{12}$, BaSO_4 and Cu single crystals. A standard four probe technique was used for d.c. resistivity measurements. Contacts were made by silver paste Degussa.

RESULTS

X-ray diffraction analysis of the rapidly quenched sample D showed no traces of a glassy state (the typical diffraction background and DTA detectable glass-transformation region were missing) (see Fig. 1). This is in accordance with refs. 1 and 2. By comparing the diffraction pattern with the standard patterns of the 1:2:3, 2:1:1, 0:1:1, 1:0:1 and single oxide phases we could clearly identify only Y_2O_3 in D and Y_2O_3 and 0:1:1 in C. Sample D exhibited less identifiable lines than C. In addition, some unidentified patterns were found in samples D and C. The respective d values are listed in Table 1 and are compared with those reported by McKittrick et al. [1] for the rapidly quenched sample of the 1:2:3 composition. The 1:3:4 composi-

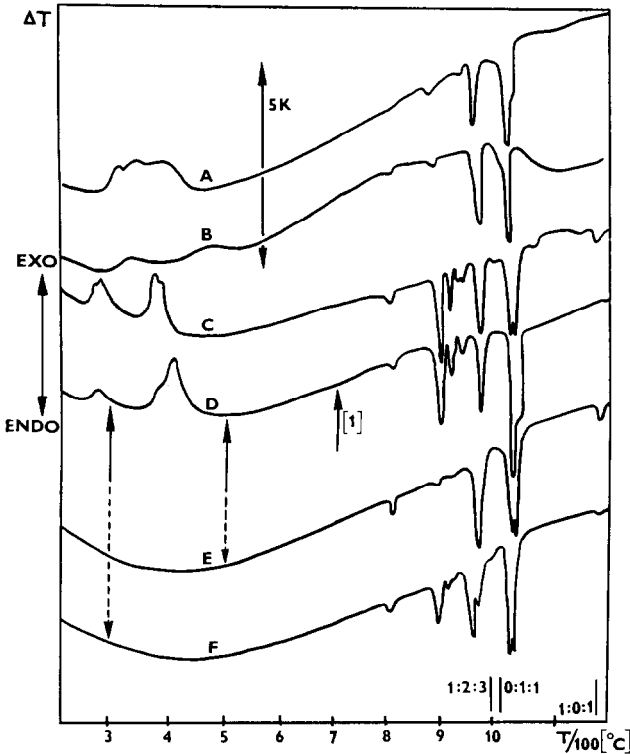


Fig. 1. DTA curves of $\text{YBa}_2\text{Cu}_3\text{O}_x$ prepared using different high-temperature treatments: A, fired at 1025°C , 48 h, self-quenched; B, fired at 1200°C , 48 h, self-quenched; C, melted at 1450°C , 1 h, self-quenched; D, melted at 1450°C , 1 h, splat-quenched; E, sample D, annealed at 500°C , 150 h; F, sample D, annealed at 300°C , 150 h; [1], annealing temperature reported in ref. 1. Temperature calibration by ICTA/NBS temperature standards with Al_2O_3 as the reference specimen; powdered sample, weight 100 mg; dynamic O_2 atmosphere; heating rate, 5 K min^{-1} ; sensitivity $0.1\text{ mV per } 25\text{ cm}$ using a Pt-Pt(10% Rh) thermocouple.

tion [1] is also included owing to the possibility of a deficiency of Y_2O_3 in the initial melts. In addition, the d values of other phases which could possibly be formed [8], i.e. 1:4:2 and 1:4:3 (recently established to exist within the temperature range $1025\text{--}1175^\circ\text{C}$) were included. It should be noted that the 1:4:3 phase is present in the phase diagram of the pseudobinary cut 1:0:1 to 0:1:1 [9] and that the 1:4:2 phase has a cubic structure similar to that reported by McKittrick et al. [1]. The conventionally fired samples A and B contained the 2:1:1 phase, the latter also exhibiting some traces of CuO .

The annealing temperatures for the thermal treatment of the as-quenched sample D were chosen as 300 and 500°C in accordance with the exothermic peaks displayed on the DTA curves (see Fig. 1). Such a relatively low temperature thermal treatment for 150 h revealed only minor changes in the

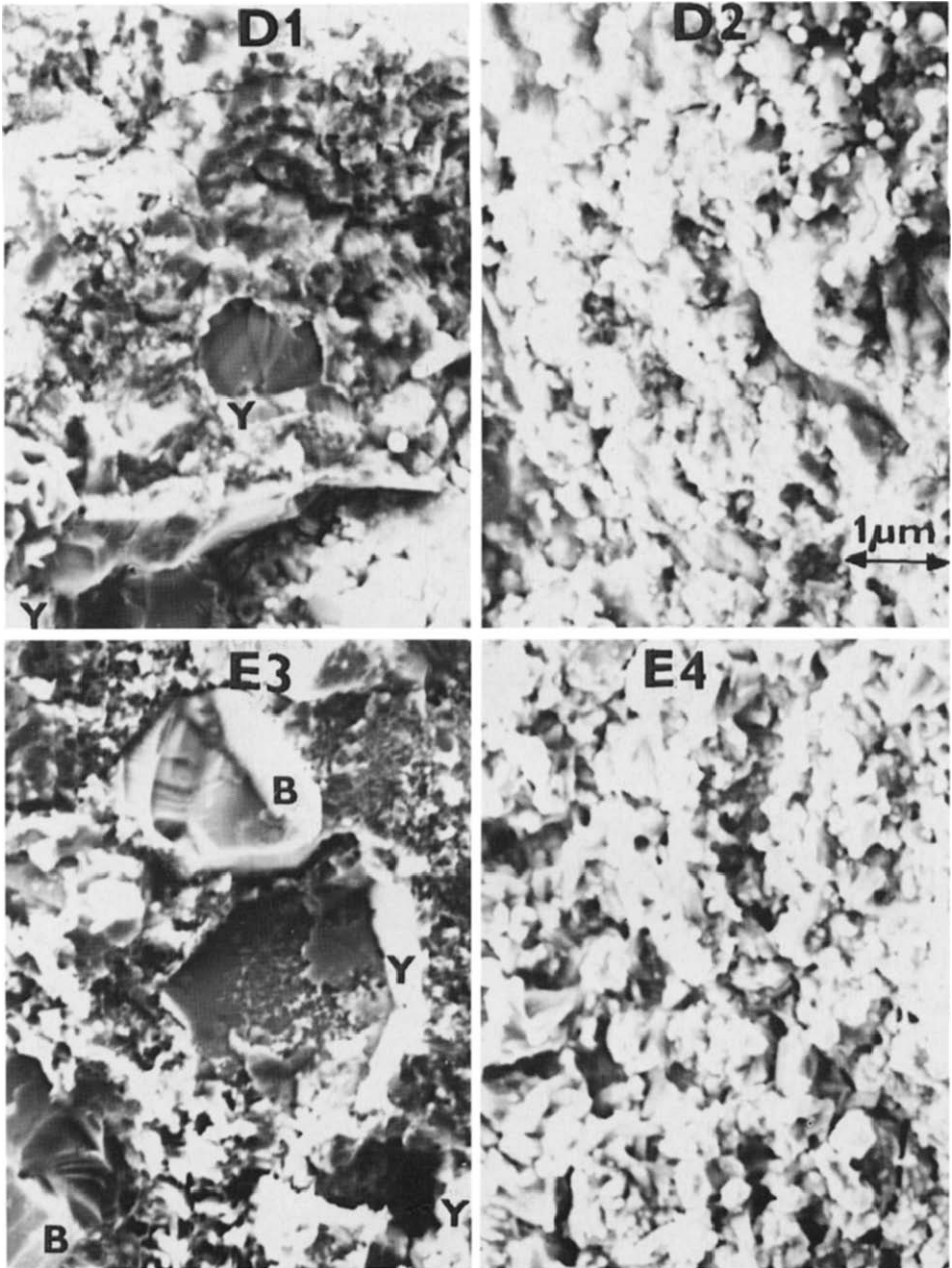


Fig. 2. Scanning electron micrographs of the fracture surface: D, splat-quenched sample D with clearly visible Y_2O_3 (Y) crystallites (D1) and morphology of the average matrix (D2); E, sample D annealed at 500°C showing crystallites of Y_2O_3 (Y) and BaCuO_2 (B) in (E3) and morphology of the average matrix (E4).

TABLE 1

Estimate of unidentified phases present under different thermal treatment

d values (nm) (± 0.002)	As-quenched samples		Heat-treated sample D		Compared phases	
	1:2:3	1:2:3	1:3:4	1:4:2 [8]	1:4:3 [9]	
	$C (10^2 \text{ K s}^{-1})$	$D (10^3 \text{ K s}^{-1})$	$[1] (10^4 \text{ K s}^{-1})$	$E (500^\circ \text{C})$	$F (300^\circ \text{C})$	Tetrag. Cubic
0.157			m			
0.166	w	w	w			w w
0.168		m		w	m	m m
0.170	w					
0.189	w	w	m			
0.204			m	w		w m
0.218			m			m m
0.234						
0.247			s			m m
0.276	s			w		
0.287					w	s s
0.290		s		s	s	m m
0.312						
0.324						s s
0.366	m	w		m	w	

Intensity of diffraction lines: w, weak; m, medium; s, strong; vs, very strong.

identifiable compounds. Certain lines of unknown phases listed in Table 1 increased slightly. The Y_2O_3 lines did not change. Some extra lines were found in sample E (annealed at $500^\circ C$) corresponding to the 0:1:1 phase accompanied by very uncertain traces for CuO.

When analysing the as-quenched sample D by EDS we found crystallites of Y_2O_3 (see Fig. 2). The major matrix had an average composition of about 1:14:12, which is formally close to the compound 0:1:1. However, the 0:1:1 compound was not identified by X-ray diffraction. The matrix composition was comparable with the eutectic 0:2:3 composition lying on the tie-line of Y_2O_3 to 1:2:3. This may probably appear when Y_2O_3 segregates from the 1:2:3 initial melts. Sample F (annealed at $300^\circ C$) showed a matrix compositional change from 1:14:12 (D) to about 1:5:4, whereas that of E (annealed at $500^\circ C$) gave an estimate of about 2:9:5 for the matrix, containing newly developed 0:1:1 as well as the crystallites of Y_2O_3 (Fig. 2). The apparent compositional coincidence of the above composition with that of the 1:4:2 phase supports the inclusion of the corresponding d values in Table 1. The morphology of matrix D did not change during annealing at $500^\circ C$ (see Fig. 2; D2 and E4).

DTA runs (Fig. 1) showed almost the same high temperature changes. The as-quenched samples C and D and sample F (annealed at $300^\circ C$) displayed some reactions between 870 and $950^\circ C$ which were missing in the ordinary sintered samples A ($1025^\circ C$) and B ($1200^\circ C$) and in sample E

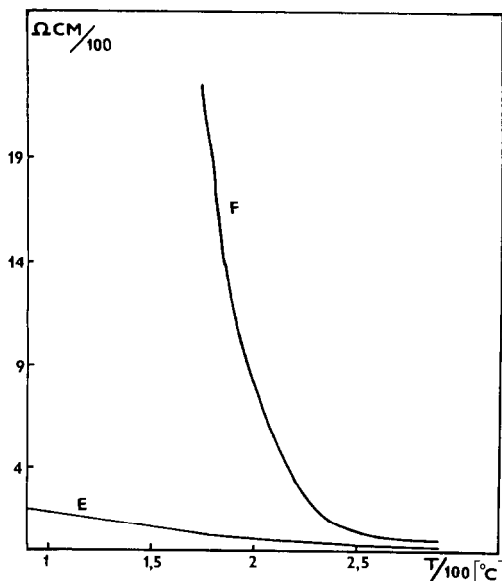


Fig. 3. d.c. resistivity curves of $YBa_2Cu_3O_x$ prepared by rapid quenching of melt followed by specimen annealing at $300^\circ C$ (F) and $500^\circ C$ (E). The current density was about $2 \times 10^{-5} A cm^{-2}$.

annealed at 500 °C. It follows that during heating the samples reach a comparable state if a high enough temperature is reached which allows solid-state reactions to occur.

The as-quenched samples displayed a very high electrical resistivity at room temperature. After annealing, the thermal dependence revealed exponential (F) and linear (E) characteristics (see Fig. 3).

DISCUSSION

On quenching the 1:2:3 melt, the decreasing temperature yields crystallisation when the cooling rate is too low to stop the nucleation–growth process. Quenching at about 10^2 K s^{-1} (C) allows the formation of the 0:1:1 phase below 1025 °C, where cooling is probably not effective enough, but did not produce phases stable at higher temperatures such as 2:1:1 and possibly also 1:4:3 [8]. A greater quenching rate (D) and the possible retainment of this rate even at low temperatures (by good contact with the heat absorbing Cu plates) prevented crystallisation yielding Y_2O_3 only (possibly not completely dissolved in the melt at 1450 °C or, more likely, crystallised already during the manual time delay caused by pouring the melt in-between the plates). The resulting shift in the melt composition to lower contents of Y_2O_3 possibly prevented the formation of the 2:1:1 phase [4]. On reheating the as-quenched samples, (Fig. 1), the first exothermic process at about 250 °C is probably oxidation of Cu_2O to CuO . Annealing at a temperature just above this process (300 °C) did not reveal any changes in the crystallised phases. The second exothermic effect (Fig. 1) is probably associated with crystalline phase formation, e.g. that of the 0:1:1 phase, since the sample annealed at 500 °C clearly showed the lines of the 0:1:1 phase. In contrast to the reported annealing experiments at still higher temperatures (e.g. 700 °C [1]) the 1:2:3 phase was not detected. It probably develops at higher temperatures which allow the reaction of Y_2O_3 with the Ba–Cu-rich matrix (in a similar way to conventional sintering from oxide mixtures). This is in accordance with the increasing content of Y_2O_3 in the matrix detected by EDS in the samples D, F and E. We should note that the similar EDS analysis reported in ref. 1 revealed a non-uniform composition across the transverse section of the sample which was in the region of 2:9:15 and 4:1:3 for the edges and centres of the as-quenched flakes. This is probably a result of an uneven quenching process caused by a very effective, but short lasting, contact with the rotating wheel, followed probably by self-cooling of the sample after disconnecting the cooling contact at lower temperatures. Our side contacts were maintained during the whole course of quenching and possibly provided a better homogeneity of temperatures even at low temperatures, which allowed low temperature crystallisations to be achieved. Similarly, we can assume that the method of melting used in this

study provided more homogeneous flux than that of spot melting by torch flame. A disadvantage of melting in a crucible is the possible contamination of the sample by the crucible material. However, we did not detect any dissolved Pt during the melting of our samples.

From Table 1 it appears that the unidentified phases bear no clear resemblance to those characterised by McKittrick et al. [1], or to those found by us when studying the relevant phase diagram [9]. In addition, we did not prove the presence of the well-known phases 2:1:1 and 1:2:3 or the existence of the orthorhombic 2:1:3 phase [10], which probably does not exist as a compound at all. Unidentified phases, developed in the rapidly cooled melts of 1:2:3, did not show any evidence of superconductivity. The positive trend of electrical resistivity, for the samples annealed at 300 and 500 °C, may be attributed to the development of phase(s) close to the composition of a desired superconductive phase (possibly 1:4:2, but probably the initial stoichiometry of the 1:2:3 phase, which is re-formed at temperatures above 700 °C [1]).

CONCLUSIONS

When cooling melts of the 1:2:3 composition the first crystals to appear are those of Y_2O_3 . These are later accompanied by the 4:3:0 and 1:2:0 phases [9]. When avoiding high-temperature crystallisation of the melt by effective cooling (applied at an early stage of quenching) the 2:1:1 (with some CuO) and 0:1:1 phases can precipitate depending on the loss or gain of Y_2O_3 with respect to the initial 1:2:3 composition, respectively. Although the 1:2:3 phase is stable from room temperature up to 1000 °C [5] it is not formed below 700 °C [1]. As-quenched samples do not reveal superconductivity although they contain some unidentified phases showing the metallic characteristic of a dependence of electric resistivity on temperature. The variability of the matrix composition does not exclude the possibility of developing a suitable composition to provide a phase exhibiting superconductivity by changing preparation conditions (quenching versus reheating versus composition) systematically. So far, however, superconductivity has been achieved, by the formation of the 1:2:3 phase through the ordinary reactions taking place in the solid state above 700 °C (similar to conventional oxide sintering). The solidification of melts produces samples with high density and may possibly lead to modifications of the structure (e.g. by multiplication of layers of $O-Cu^{3+}-O$ [11], which are assumed to be responsible for superconductivity at increased critical temperatures). In this light, we can suppose that the addition of glass-forming oxides [11] may suppress undesired crystallisation, which is unavoidable at lower temperatures for the pure melts of 1:2:3, and may ease glass formation even at moderate cooling rates. It is important to determine whether such dilutions

would destroy superconductivity. Yan et al. [12] showed that the addition of SiO₂ (up to 50 mol%) does not substantially change the critical temperatures measured for sintered samples containing the 1:2:3 phase. The increase in melt viscosity achieved and the consequent possibility of glass formation upon suitable quenching can possibly produce both the practicable formation of phases different from those normally available according to the equilibrium relations in the relevant phase diagram [9] and the workability of samples for fabricating the desired forms (e.g. filaments) [11]. This is the subject of further study.

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