INSTITUTE OF PHYSICS PUBLISHING SUPERCONDUCTOR SCIENCE AND TECHNOLOGY
Supercond. Sci. Technol. **17** (2004) 685–688 PII: S0953-2048(04)69790-9

$YBa_2Cu_3O_7$ synthesis using microwave heating

Angelo Agostino[1,2], **Paola Benzi**[1,2], **Mario Castiglioni**[1], **Nicoletta Rizzi**[1] and **Paolo Volpe**[1,2]

[1] Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino, C. so Massimo d'Azeglio, 48 10125 Torino, Italy
[2] Istituto Nazionale di Fisica della Materia, Villa Brignole, corso Perrone 24, 16152 Genova, Italy

E-mail: paola.benzi@unito.it

Received 30 September 2003
Published 16 March 2004
Online at stacks.iop.org/SUST/17/685 (DOI: 10.1088/0953-2048/17/4/021)

Abstract

The superconducting material $YBa_2Cu_3O_{7-x}$ was prepared by microwave heating of an oxide mixture (Y_2O_3, BaO, CuO). The time required for the synthesis is reduced to about 3.5 h compared to 1–2 days if conventional heating is used. If during the microwave heating the boat containing the starting powders is surrounded by SiC, the Y_2BaCuO_5 insulating phase does not appear.

1. Introduction

$YBa_2Cu_3O_{7-x}$ (Y-123) is one of the most studied high critical temperature superconductive materials. Many papers have been published on the Y–Ba–Cu–O system in which Y, Ba or Cu are replaced by rare earth elements to obtain physical property modifications, such as higher critical temperature and critical current density.

The synthesis of these materials can be obtained by the solid state reaction technique, which requires long heating cycles [1–7]. The heating–cooling cycle, if a conventional oven is used, may be as long as 70 h [7, 5]. On the other hand, microwave heating has been suggested as a means of reducing the time of preparation, the energy consumption [8–10] and as a sintering tool [11, 12]. In our laboratory we are studying the possibility to substitute the conventional oven with a microwave oven for the synthesis of YBCO and the Y–Ba–Cu–O system doped with rare earth elements. In this paper we report on the evolution of the Y, Ba, and Cu oxides mixture to the superconducting cuprate $YBa_2Cu_3O_{7-x}$ via microwave heating.

2. Experimental details

The reacting oxide mixtures were obtained by thermal treatment of a stoichiometric mixture of $Ba(NO_3)_2$, Y_2O_3 and CuO (Fluka) in an electric furnace at 650 °C. 5.0 g of the powdered mixture obtained by treatment in an electric oven were pressed at about 1 GPa, and a piece (10 mm × 5 mm × 2 mm) of the resulting pellet was placed in an alumina boat which was introduced into a silica tube placed in a domestic (Candy), multi-mode, 600 W microwave oven operating at 2.45 GHz; the silica tube was supported by a refractory brick. The oven was modified to allow a stream of oxygen to flow through the silica tube containing the sample. The oxygen flow was adjusted to about 100 ml min^{-1}. The oven was equipped with a CEAM Pt–Rh–Pt thermocouple for temperature measurements. The samples were heated for periods of 30 min. After each heating step, the sample was allowed to cool for about 20 min, and an aliquot was taken for x-ray analysis. The total heating time was 4.5 h. In some cases the alumina boat containing the sample was surrounded by powdered SiC, which readily absorbs microwave energy, causing a rapid increase of the sample temperature. A powder x-ray diffractometer (Siemens D5000, Bragg–Brentano geometry and Göbel mirror, Cu Kα radiation) was used to follow the reaction between the oxides. The critical temperature for the superconducting transition (T_c) was determined by both resistivity and magnetic susceptibility using a home-made four-probe voltmeter and a LakeShore 7000 susceptometer, respectively. The apparent densities of some samples after microwave treatment were measured using a Berman balance. Samples were also investigated with a scanning electron microscope (SEM) (Oxford Instruments).

3. Results and discussion

$Ba(NO_3)_2$ melts at 592 °C, incorporating Y_2O_3 and CuO, and then decomposes to BaO at higher temperature. After

0953-2048/04/040685+04$30.00

Table 1. The composition of the reacting mixture as a function of heating time under oxygen flow. The values represent the crystal phase percentages in the mixture (211 = Y_2BaCuO_5 123 = $YBa_2Cu_3O_{7-x}$) (nd = not detected).

Pattern	Time (min)	Y_2O_3[a]	CuO	$BaCuO_2$	$Y_2Cu_2O_5$	211	123	Temp. (°C)
1[b]	0	10	1	89	nd	nd	nd	
2	60	13	1	83	3	nd	nd	504
3	90	nd	nd	91	9	nd	nd	645
4	120	nd	nd	47	27	2	24	676
5	150	nd	nd	19	nd	8	73	760
6	180	nd	nd	11	nd	35	54 (T + O)[c]	812
7	210	nd	nd	nd	nd	nd	100 (T + O)[c]	855
8	240	nd	nd	nd	nd	nd	100 (O)[c]	910
9	270	nd	2	nd	nd	20	78 (T + O)[c]	950
10	300	nd	nd	nd	nd	41	59 (T + O)[c]	975

[a] As stated before, the percentage of Y_2O_3 is underestimated because of the formation of a vitreous phase [11].

[b] Starting mixture of oxides just after the decomposition of the Ba nitrate at 650 °C.

[c] T and O indicate tetragonal and orthogonal phase, respectively.

Table 2. The composition of the reacting mixture versus heating time under oxygen flow (alumina boat surrounded by SiC). The values represent the crystal phase percentages in the mixture (211 = Y_2BaCuO_5, 123 = $YBa_2Cu_3O_{7-x}$) (nd = not detected).

Pattern	Time (min)	Y_2O_3[a]	CuO	$BaCuO_2$	$Y_2Cu_2O_5$	211	123	Temp. (°C)
1	0[b]	10	1	89	nd	nd	nd	
2	60	6	6	78	10	nd	nd	655
3	120	8	2	74	16	nd	nd	785
4	180	nd	1	77	11	nd	11 (O)[c]	895
5	210	nd	nd	nd	nd	nd	100 (O)[c]	925

[a] See note in table 1.

[b] Starting mixture of oxides just after the decomposition of the nitrates at 650 °C.

[c] O indicates orthogonal phase.

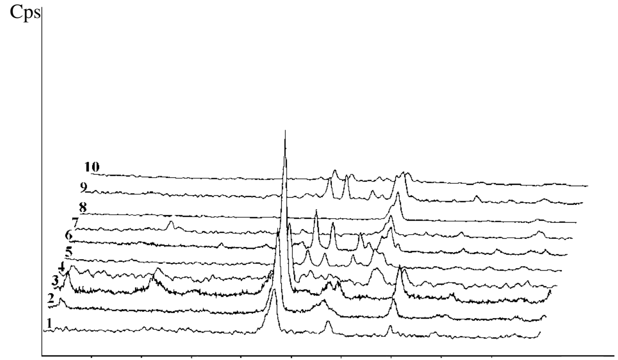

Figure 1. X-ray powder diffraction patterns of samples before microwave treatment and after different actual heating times in the microwave oven.

0.5 h heating in a conventional oven at 650 °C the mixture contains Y_2O_3, traces of CuO and $BaCuO_2$ (first row of tables 1 and 2). In figure 1 the x-ray powder diffraction patterns of samples before the microwave treatment and after different actual heating times in the microwave oven are reported.

It can be seen in which way the sample composition smoothly changes during the reaction. The ratio of the relative amounts of the phases present was determined at least semi-quantitatively by using the ratio of the intensities of non-overlapped, intense reflections from each compound. This is possible because the x-ray powder diffraction patterns are additive, and the presence of one component does not affect the powder pattern of the other components [13]. The Y_2O_3 content is heavily underestimated because of the formation of a vitreous phase [14]. The results of such integration are reported in table 1.

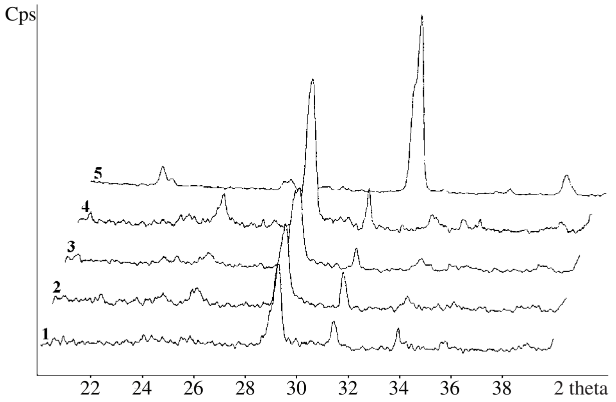

Figure 2. X-ray powder diffraction patterns of samples before microwave treatment and after different actual heating times in the microwave oven, for samples surrounded by SiC.

For the experiments with SiC, the x-ray powder diffraction patterns of samples before microwave treatment and after different actual heating times in the microwave oven are reported in figure 2, and the results of the integration in table 2.

The first rows of tables 1 and 2 indicate that CuO reacts very easily with BaO according to equation (1), which already starts during the decomposition of barium nitrate at 650 °C. Apparently only when all the BaO has been consumed does Y_2O_3 start to react with CuO according to equation (2). The

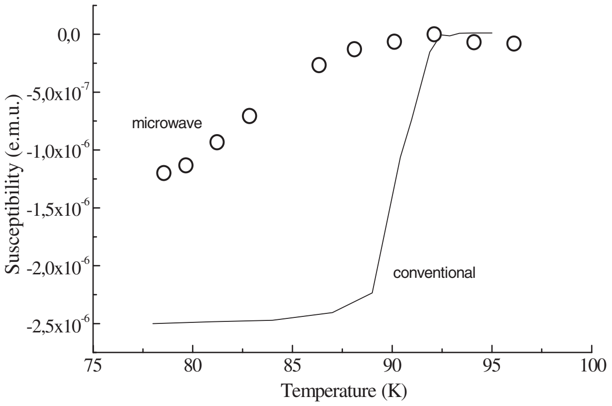

Figure 3. The change of magnetic susceptibility as a function of temperature for a YBCO sample prepared as in table 1 and with a conventional oven. Note: the curve of the YBCO sample obtained with microwave heating has been multiplied by a factor 10^{-2}.

reaction of Y_2O_3 with $BaCuO_2$ [15, 16] to yield the insulating phase Y_2BaCuO_5 (Y-211 phase), equation (3), only starts after prolonged microwave treatment.

$$BaO + CuO \rightarrow BaCuO_2 \tag{1}$$

$$Y_2O_3 + 2CuO \rightarrow Y_2Cu_2O_5 \tag{2}$$

$$BaCuO_2 + Y_2O_3 \rightarrow Y_2BaCuO_5. \tag{3}$$

As the main components of the mixture become $BaCuO_2$ and $Y_2Cu_2O_5$, they begin to react together, as in equation (4), yielding the semiconducting tetragonal Y-123 phase after about 120 min of dielectric heating. After 150 min the tetragonal phase disappears, yielding the orthorhombic superconducting Y-123 phase, through equation (5) [17].

$$4BaCuO_2 + Y_2Cu_2O_5 \rightarrow 2YBa_2Cu_3O_{6.5} \tag{4}$$

$$4YBa_2Cu_3O_{6.5} + (2 - x)O_2 \rightarrow 4YBa_2Cu_3O_{7-x}. \tag{5}$$

The results reported in table 2 indicate that the extra heating effect due to the SiC does not cause a substantial increase in the rate of formation of the Y-123 phase. It should be noted, however, that the Y-123 phase which appears after about 180 min, when SiC is used, is only the orthorhombic one, and that it is not contaminated either by tetragonal Y-123 or by the intermediate Y-211, (Y_2BaCuO_5).

This finding indicates that the reaction temperature in the presence of an SiC bath is higher. In fact, the rapid formation of Y-123 free from Y-211 was observed when the reactants are rapidly reacted in a preheated conventional furnace [18] at about 920 °C or when, for example, citrate gel is used as an intermediate [19].

In both sets of experiments reported in tables 1 and 2 no macroscopic melting of the reaction mixture was observed.

It is worth noting that, while an appreciable contamination of Al_2O_3 crucibles was observed when the reaction is performed in a conventional oven [20], the alumina boat used for the reaction under microwaves did not show any kind of contamination after repeated 5 h treatments under microwaves, both with and without SiC.

The data reported in table 1 are in good agreement with the results of Flor and co-workers on the reactions between the intermediates oxides [15, 16].

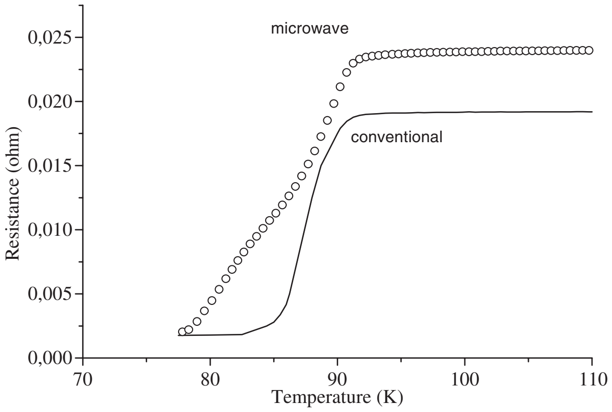

Figure 4. The change of resistance as a function of temperature for a YBCO sample prepared as in table 1 and with a conventional oven.

If the microwave heating is continued over 4 h, the metastable [17] superconducting YBCO phase starts to decompose to the more stable phases: the non-superconducting Y_2BaCuO_5, CuO and $BaCu_2O_3$. The latter is hardly detectable by x-ray diffraction because it melts at the decomposition temperature and is present as a glassy material in the final analysed sample [21].

The oxygen content of the superconducting orthorhombic Y-123 phase was determined by iodometric titration [22] and was found to be 6.89 ± 0.02. The oxygen content can also be calculated from the change of the *c* unit cell parameter as determined from the x-ray diffraction spectra. Unit cell parameters were refined by a least squares method using four reflections obtained on the XRD patterns.

The values obtained for the sample prepared without an SiC bath were 3.82, 3.89 and 11.67 Å; for sample prepared with an SiC bath they were 3.83, 3.88 and 11.69 Å.

Using this method, the oxygen stoichiometry for the orthorhombic Y-123 phase was found to be 6.94 ± 0.02 for pattern 8 of table 1 and 6.85 ± 0.02 for the Y-123 prepared using the SiC bath, pattern 5 of table 2, respectively [23].

The ideal density of the orthorhombic YBCO phase is 6.38. The apparent densities of samples prepared by microwave heating with and without SiC were measured. The density of samples prepared with the microwave alone is about 72.1% of the ideal, while that of samples prepared with both microwave and SiC is about 89.0%. The above results should be compared with the densities of samples prepared in the traditional method after 20 h annealing, which are about 87.5% of the ideal [24].

The YBCO samples obtained by microwave heating both with and without the SiC bath show good superconducting properties. Figures 3 and 4 show the change of magnetic susceptibility and of resistance versus temperature respectively for a YBCO sample prepared as in table 1.

In the same figures the analogous curves of a typical YBCO sample obtained with conventional heating, as described in [5], are also shown for comparison.

The broad ΔT_c of the curves related to the microwave-sinterized sample is attributable to an insufficient grain coupling.

The different critical temperatures observed in figures 3 and 4 are due to the different kind of measurement: in

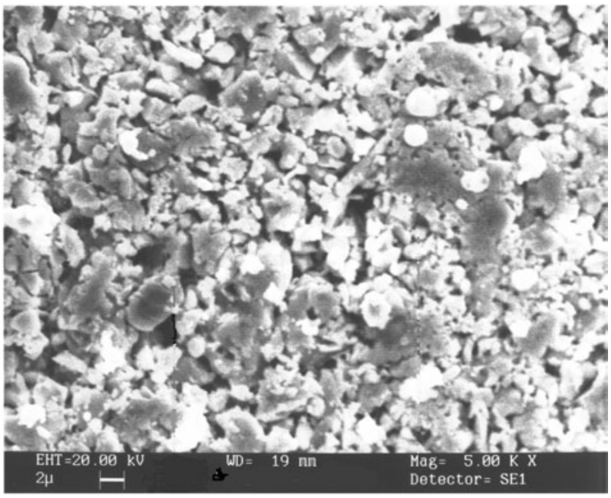

Figure 5. An SEM image of a YBCO sample prepared as in table 1.

Table 3. The characteristics of YBCO samples obtained with microwave and conventional sintering.

	Sintering method	
	Conventional	Microwave
T_c (K)	93	91
ΔT_c (K)	4–5	10
d (g cm^{-3})	6, 38	5, 68
Annealing time (h)	24	4
Grains size (μm)	∼10	>2

fact resistivity is a one-dimensional measurement while susceptibility is a volumetric measurement [25].

In some cases in the R/T_c curves a shoulder between 77 and 86 K is observed. This fact probably derives from non-uniform sample microwave heating [26]. This leads to an inhomogeneous sample with the possible intergrowth of different phases with lower T_c.

An SEM picture of a YBCO sample prepared as in table 1 (figure 5) shows that most of the grains have a considerably smaller size with respect to that observed in YBCO samples obtained with a conventional oven [5]. Moreover, figure 5 shows the presence of voids in the microstructure, leading to a low density material.

In table 3 the characteristics of YBCO samples obtained both with microwave and conventional sintering are collected.

The results obtained indicate that the superconducting properties of YBCO samples obtained with microwave heating are lower with respect to those of YBCO samples obtained with conventional heating; therefore the samples are not suitable for practical applications.

4. Conclusions

The results obtained indicate that at least in the case of simple microwave heating, the same intermediate compounds are formed in the same sequence as in conventional furnace heating.

YBCO samples can be obtained with a very sharp reduction in reaction time and, when the microwave treatment is performed in a reaction boat surrounded by SiC, the absence of the 211 phase and the formation of the 123 orthorhombic superconducting phase alone are observed. At the present stage of our research, they do not exhibit sufficient superconducting properties for practical applications. Nevertheless we think that the synthesis of Y–B–C–O systems with microwave heating can show promise. Further studies both on the synthesis of YBCO films on different substrates and on the Y–Ba–Cu–O system doped with rare earth elements are at present in progress, and the preliminary results are encouraging.

Acknowledgments

This work was supported by MURST (40%). The authors are indebted to Professor G Chiari (Dip. di Scienze Mineralogiche e Petrologiche, Univ. di Torino) for access to the x-ray diffractometer.

References

[1] Tan W S and Wu X S 2001 *J. Supercond.* **14** 525
[2] Chihiro T, Shigeto T and Akihiko N 2002 *Physica* C **378–381** 344
[3] Adigüzel H I and Izgi T 2002 *J. Supercond.* **15** 549
[4] Bradea I, Popa S, Aldica G, Mihalache V and Crisan A 2002 *J. Supercond.* **15** 237
[5] Agostino A, Benzi P, Rizzi N and Volpe P 2002 *Supercond. Sci. Technol.* **15** 902
[6] Harada T and Yoshida K 2003 *Physica* C **391** 1
[7] Sleight A W 1991 *Phys. Today* **6** 24
[8] Baghurst D R, Chippindale A M and Mingos D M P 1988 *Nature* **332** 311
[9] Manfredotti C, Castiglioni M, Polesello P, Rizzi N and Volpe P 1996 *Mater. Res. Soc. Symp. Proc.* **430** 145
[10] Rowley A T, Wroe R, Vàzquez-Navarro D, Lo W and Cardwell D A 1997 *J. Mater. Sci.* **32** 4541
[11] Cherradi A, Martinel S, Desgardin G, Provost J and Raveau B 1997 *Supercond. Sci. Technol.* **10** 475
[12] Dawery A H, Binner J G P and Cross T E 1996 *Mater. Res. Soc. Symp. Proc.* **430** 169
[13] Vanderah T (ed) 1995 *Chemistry of Superconductor Materials* (Park Ridge, NJ: Noyes Publishers) p 450
[14] Coppa N V 1992 *J. Mater. Res.* **7** 2017
[15] Flor G, Scavini M, Anselmi Tamburini U and Spinolo G 1990 *Solid State Ion.* **43** 77
[16] Anselmi Tamburini U, Ghigna P, Spinolo G and Flor G 1991 *J. Phys. Chem. Solids* **52** 715
[17] Sleight A W 1995 *Acc. Chem. Res.* **28** 103
[18] Guha J P 1988 *J. Am. Ceram. Soc.* **71** C273
[19] Thomson W J, Wang H, Parkman D B, Li D X, Strasik M, Luhman T S, Han H and Aksay I A 1989 *J. Am. Ceram. Soc.* **72** 1977
[20] Scheel H J 1994 *MRS Bull.* (September) 26
[21] Chu P Y and Buchanan R C 1993 *J. Mater. Res.* **8** 2134
[22] Chen W M, Lam C C, Li L Y, Geng J F, Wu F M, Hung K C and Jin X 1996 *J. Supercond.* **9** 551
[23] Chiari G and Rizzi N 2003 private communication
[24] Manfredotti C, Fizzotti F, Vittone E, Polesello P, Rizzi N, Cantelli V, Bruno P, Volpe P, Castiglioni M, Benzi P, Pallavidino P, Chiari G and Borghi A 1994 *Nuovo Cimento* D **16** 1729
[25] Goldfarb R B, Lelental M and Thompson C A 1991 *Office of Naval Research Workshop on Magnetic Susceptibility of Superconductors and Other Spin Systems (Berkeley Springs, WV, May 1991)*
[26] Kato M, Sakakibara K and Koike Y 1997 *Japan. J. Appl. Phys.* **36** L1291