JOURNAL OF MATERIALS SCIENCE 32 (1997) 3701–3703

HgO as an internal oxygen source in $Y_1Ba_2Cu_3O_{7-\delta}$

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This paper reports an alternative technique for preparing $Y_1Ba_2Cu_3O_{7-\delta}$ with uniform oxygen stoichiometry which eliminates the need for flowing oxygen during sintering. Our studies show that when HgO is added to the YBaCuO system it provides an abundant source of oxygen during sintering. Mercury diffuses out of the system leaving the crystal structure intact. We have thus been able to obtain a T_c (zero resistivity) of 90 K consistently in HgO doped YBaCuO specimens and sintered in air. An optimum value of HgO leads to a strongly coupled grain material. Resistivity, X-ray fluorescence (XRF), X-ray diffraction (XRD), scanning electron microscopy (SEM) and a.c. susceptibility data are reported.

1. Introduction

$Y_1Ba_2Cu_3O_{7-\delta}$, or YCBO, [1] has the distinction of being the first high T_c oxide superconductor with a T_c above the boiling point of liquid nitrogen. Further, this material can be synthesized in a phase-pure form and is thus superior to the Bi-Sr-Ca-Cu-O [2] and the Tl-Ba-Ca-Cu-O [3] systems which have higher T_c values but are usually obtained in multiphased form. Notwithstanding this advantage the YCBO system suffers from the problem of achieving a perfect oxygen stoichiometry (O_7) throughout the bulk material. Superconducting properties are degraded with increasing oxygen deficiency and the material becomes insulating at $O_{6.4}$ ($\delta = 0.6$). YBCO prepared by the usual ceramic technique and under flowing oxygen has been reported [4, 5] to be deficient in oxygen. The susceptibility studies revealed that T_c well inside the material was far below the T_c (90 K) observed at the surface even when the specimens were sintered under flowing oxygen for prolonged periods. An improved technique was, however, evolved by Conder *et al.* [6] for synthesizing a near stoichiometric YBCO with oxygen close to 7 through optimization of the heating and cooling rates and following an annealing-grinding procedure. These specimens are, however, prepared under 1 bar of oxygen. Microwave sintering [7, 8] has also been used to obtain a completely uniform and oxygen stoichiometric ($\delta = 0$) material.

In this paper, we report an alternative technique of preparing YBCO in atmospheric air with uniform oxygen stoichiometry. It was shown in a recent paper [9] that substitution of Ba by Hg (using HgO in the initial material) leads to a 90 K stoichiometric YBCO even when the specimen is sintered in ambient air. The substitution of Ba by Hg, however, leads to Ba vacancies and T_c decreases systematically as Hg contents are increased. It transpired from these studies [9] that HgO decomposes into Hg metal and O_2 during heating. Hg escapes from the matrix leaving the crystal structure unaltered, as revealed by the XRD data, and the O_2 released provides an excellent ambient for the formation of a stoichiometric YBCO. We therefore decided to use HgO as an additive rather than using it for substitution. This eliminates the problem of Ba vacancies and the consequent decrease of T_c. A consistent value of T_c (90 K) is thus obtained for HgO addition from 0.5 at % to 5 at %. A comparatively lower sintering temperature of 875 °C has been found to be adequate.

2. Experimental procedure

Appropriate quantities of Y_2O_3, $BaCO_3$ and CuO, all of 99.99% purity, were weighed according to the formula unit $Y_1Ba_2Cu_3O_{7-\delta}$, mixed thoroughly and ground in a pestle and mortar. The mixture was calcined in air at 850 °C for 16 h. The calcined mass was crushed, ground and recalcined twice more. HgO was then added to this calcined powder in 0.5, 1, 5, 10 and 20 at % Hg ratio and mixed thoroughly. Rectangular bars of size $45 \times 4 \times 3$ mm and circular pellets of 19 mm diameter were prepared through pressing in the respective dies. These specimens were sintered in air at 875 °C for 16 h, followed by furnace cooling. The usually prescribed precautions were taken in handling toxic HgO.

The resistive transition was studied by measuring electrical resistivity as a function of temperature using the usual four probe method in a variable temperature cryostat. A calibrated Si-diode sensor of the type DT-500 (Lake Shore) was used for measuring the specimen temperature. A good thermal contact between the sensor and the specimen was always ensured. The accuracy of the temperature measurement was ± 0.1 K. The diamagnetic transition was studied by measuring the real ($\varkappa'$) part of the a.c. susceptibility between 120 K and 70 K. The crystal structure was determined by obtaining room temperature X-ray diffraction spectra of all the specimens on a Siemens D-500 powder X-ray diffractometer using Cu K_α radiation. Grain morphology was studied using scanning electron microscope (SEM) micrographs on the fractured surfaces of the specimens. To check the presence of Hg in the sintered samples X-ray fluorescence spectra were obtained using a Rigaku 3070 sequential X-ray fluorescence spectrometer equipped with a rhodium target and a window X-ray tube OEG-75. Bulk density of the sintered samples was also measured.

3. Results and discussion

Fig. 1 shows the plots of the normalized resistance versus temperature for all the specimens with different values of Hg (0.5–20 at %) ratio X. The $Y_1Ba_2Cu_3O_{7-\delta}$ specimen without the addition of HgO and air sintered was found to be an insulator and is therefore not plotted in this figure. It is interesting to see that all the specimens with HgO addition become superconducting even though they were sintered in air. All the specimens show quite sharp transitions. Specimens with $X = 0.5$, 1.0 and 5.0 have T_c (zero resistivity) of 90 K, a good value. The transition in specimens with $X = 10$ and 20 is rather broad with T_c values of 85 K. This broad transition is an indication of weak intergrain bonding. The nature of weak intergrain links is clearly seen for these two specimens with $X = 10$ and 20 in the χ'–T plots in Fig. 2.

A sharp transition, on the other hand, is obtained in the specimens with $X = 0.5$, 1.0 and 5.0. The highest diamagnetic transition (91 K) is observed for the specimen with $X = 1.0$ which appears to be an optimum level for HgO addition to this YBCO system for a near perfect oxygen stoichiometry. Specimens with $X = 10$ and 20 are characterized by plateaux in their χ'–T plots, an indication of the presence of weakly coupled grains. The weak intergrain bonding for higher values of X could be due to the increasing density of pores left by the dissociation of HgO and the ultimate evaporation of Hg metal during the air sintering.

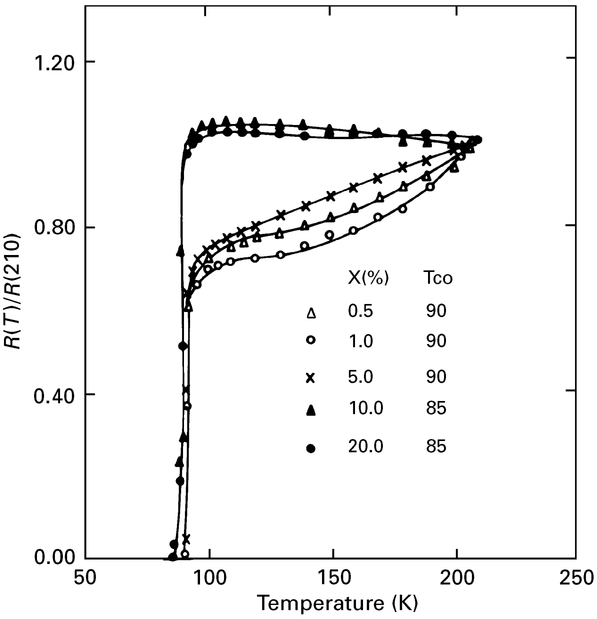

Figure 1 Normalized resistance plotted against temperature for $Y_1Ba_2Cu_3O_{7-\delta}$ $+X$ at % Hg specimens for $X = 0.5$, 1.0, 5.0, 10 and 20, (air sintered at 875 °C for 16 h).

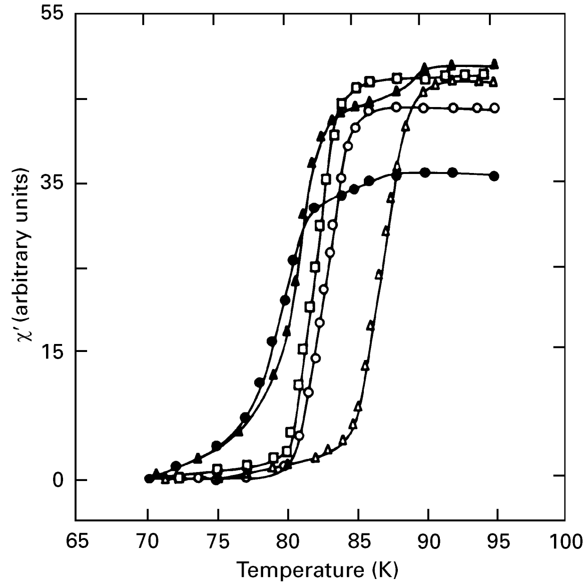

Figure 2 The real part of the a.c. susceptibility plotted against temperature for $Y_1Ba_2Cu_3O_{7-\delta}$ $+X$ at % Hg specimen for $X = 0.5$ (○), 1.0 (△), 5.0 (□), 10 (▲) and 20 (●), (air sintered at 875 °C for 16 h).

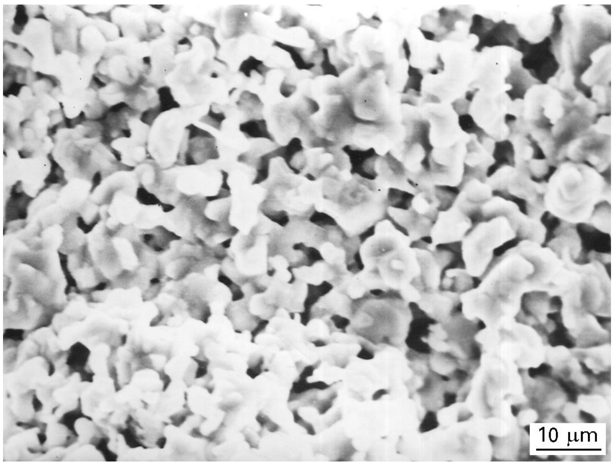

Figure 3 A typical SEM photograph taken on the fractured surface of the specimen with $X = 20$.

A typical SEM micrograph taken on the specimen with $X = 20$ shows a very uniform density of pores throughout the entire specimen, as shown in Fig. 3. The bulk density measurements confirm this. The density of the pure YBCO samples ($X = 0$) is $3.4\ \mathrm{g\,cm^{-3}}$, which is rather low because of the low sintering temperature, 875 °C. The density decreases significantly with HgO addition. The density decreases by 10.9% for $X = 5.0$ and by 16.2% for $X = 20$.

The XRD spectra for three representative specimens with $X = 0.5$, 5.0 and 20 are reproduced in Fig. 4. No changes in crystal structure or lattice parameters were observed with increasing X. There is no shift in the peak positions with increasing X values. No reflections corresponding to pure Hg or known Hg-compounds are seen in the XRD spectra. This indicates that mercury is not incorporated in the system nor does it influence the crystal structure.

Since XRD cannot detect Hg concentration below 2–3% we checked two representative specimens with

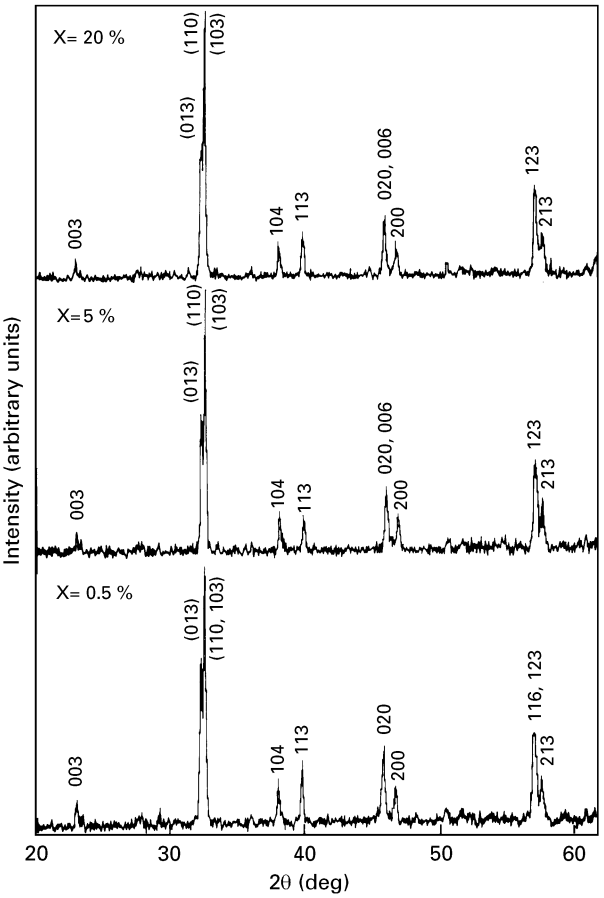

Figure 4 XRD spectra of $Y_1Ba_2Cu_3O_{7-\delta}$ $+X$ at % Hg specimens with $X = 0.5$, 5.0 and 20, (air sintered at 875 °C for 16 h).

X = 5 and 20 by the X-ray fluorescence technique. The measurements were carried out under vacuum by using the concentration of a primary coarse slit (foil spacing 0.45 mm, length 100 mm) and a secondary Soller slit (foil spacing 0.15 mm, length 100 mm), a flat LiF (200) crystal and NaI(Tl) scintillation counter. The two samples were irradiated with X-rays generated at 40 kV/30 mA rating. The Hg L_{α_I} peak occurring at 35.89° (2θ) was chosen for the analysis. Since this peak tends to overlap with the Rh $K_{\alpha_{II}}$ peak (2θ = 35.54°), a Zr (140 μm thick) filter was used to supress the Rh $K_{\alpha_{II}}$ peak. No Hg peak at 2θ = 35.89° was observed thereby confirming the absence of Hg even in the specimen with highest HgO addition ($X = 20$).

The absence of Hg in these specimens is as expected. As discussed in detail in our earlier publication [10] HgO decomposes at 476 °C [11] into Hg atoms and O_2 molecules in the ratio 2:1. The partial pressure of the two components will also be in the same ratio. The total equilibrium pressure over HgO at 430 °C is stated [12] to be 0.65 atm. This will give a partial pressure of oxygen of 0.22 atm. which is approximately equal to the partial pressure of oxygen in atmospheric air. As the temperature increases, the partial pressure of oxygen increases exponentially making an abundant source of oxygen available during the sintering reaction. This high oxygen ambient can raise the oxidation state of Cu in this system close to the optimum value (+2.2) conducive to a high T_c value [13] and also moves the oxygen stoichiometry close to 7. The fact that all the specimens show a sharp superconducting transition indicates that sufficient oxygen was available during the cool down after sintering. Our experimental data show a consistent value of $T_c = 90$ K for X values betwen 0.5 and 5.0. For higher HgO additions the transition width increases as shown by the resistive as well as by the diamagnetic transition. This could perhaps be attributed to the voids caused by the Hg evaporation from the bulk material. The susceptibility data show that the sharpest T_c is obtained at $X = 1.0$ for specimens sintered at 875 °C. A sintering temperature of 875 °C seems to be adequate for the formation of a 90 K superconducting phase in this system with HgO addition.

4. Conclusions

We have found an internal oxygen source for $Y_1Ba_2Cu_3O_{7-\delta}$ which appears to solve the problem of a surface barrier to external oxygen diffusion. The addition of HgO leads to a uniform oxygen stoichiometry within the bulk material during sintering. Mercury is not found to be incorporated in the system nor does it alter the crystal structure.

Acknowledgements

The authors thank S.U.M. Rao, D.K. Suri and D.P. Singh for their help in obtaining SEM, XRD and XRF data respectively. They also thank Prof. E.S.R. Gopal, B.B. Sharma, S.V. Sharma and I.P. Jain for useful discussions. One of us (AP) would like to thank UGC for the award of a Junior Research Fellowship.

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Received 25 March 1996
and accepted 11 February 1997