

Synthesis and properties of nonstoichiometric samples of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$; $0.04 \leq x \leq 1.00$

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A simple and accurately reproducible route was previously described for the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with intermediate compositions, $0.0 < x < 1.0$, that involves equilibration of appropriate proportions of compounds with $x=0.0$ and $x=1.0$ in sealed tubes. This synthetic procedure has been further explored and products studied by powder diffraction, thermogravimetric analysis, and magnetization measurements. The temperature required for such equilibrations has been studied at three representative compositions, by using sealed H tubes to physically separate the two components. For $0.0 < x < 0.4$, in contrast to earlier suggestions of phase separation, powder x-ray diffraction and the superconducting properties indicate that single-phase orthorhombic materials (on a length scale greater than about 60 Å) are obtained on quenching from temperatures above 350°C. In particular, the superconducting transition temperature varies in a smooth, S-shaped fashion over the $0.04 < x < 0.40$ composition field, the observed variation of the transition width with x is as expected from the variation of dT_c/dx in this range, and there are no indications of multiple superconducting transitions in the dc magnetization data.

I. INTRODUCTION

The properties of $\text{La}_{2-y}(\text{Ba}/\text{Sr})_y\text{CuO}_{4-\delta}$ (Ref. 1), $\text{LnBa}_2\text{Cu}_3\text{O}_{7-x}$ (Ref. 2), and $\text{La}_{3-y}\text{Ba}_{3+y}\text{Cu}_6\text{O}_{14+\delta}$ (Ref. 3) samples are known to depend sensitively on their oxygen contents. However, although the dependence of the stoichiometry x in $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ on temperature and oxygen partial pressure for $T > 450^\circ\text{C}$ has been extensively explored,^{4,5} the dependence of low-temperature properties on x remains less well defined. In part, this reflects that it is generally difficult to prepare homogeneous samples of a desired oxygen content by rapid quenching from higher temperatures. We have, therefore, studied other synthetic approaches and describe here a simple and accurately reproducible route for the synthesis of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ with intermediate compositions $0.0 \leq x \leq 1.0$ at lower temperatures. The method involves equilibration of appropriate proportions of compounds with $x=0.04$ and $x=1.00$ in sealed tubes at $350 < T < 750^\circ\text{C}$. We have investigated the temperature requirement for such equilibrations, and the structural and superconducting properties of nonstoichiometric materials prepared at various temperatures by this technique.

II. EXPERIMENT

A sample of $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ was prepared from appropriate proportions of BaCO_3 , Y_2O_3 (prefired at 1000°C), and CuO as described earlier.⁶ Three methods of synthesizing intermediate compositions were examined. A first series of samples was prepared from $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ by carefully controlled heat treatments *in situ* in a George Associates Faraday magnetometer. Successive values of x were obtained by heating the previously measured sample (*in situ*) up to 350 – 530°C , waiting until the desired weight change was achieved, dropping the temperature to

prevent further weight loss, and removing the evolved oxygen under vacuum.

A second set of samples was prepared by intimate mixing of appropriate proportions of $x=0.04$ and $x=1.00$ materials (the latter prepared by reduction of $\text{YBa}_2\text{Cu}_3\text{O}_{6.96}$ in He at 840°C for 48 h, followed by furnace cooling in He), sealing the mixtures in silica tubes under vacuum, equilibrating at 650 – 670°C for 16 h, and, finally, furnace-cooling. Samples were prepared in sufficient quantities to permit detailed characterization by thermogravimetric analysis (TGA), Meissner-effect (ME) measurements, powder x-ray diffraction (PXD), and a range of other techniques. The sealed-tube synthesis method⁶ has since also been used successfully by other groups (see, e.g., Ref. 7).

In order to further examine the conditions required for equilibration by this method, a third series of samples with targeted compositions close to $x=0.25$ was also prepared by equilibration in H tubes. The appropriate amounts of samples with $x=0.10$ and $x=1.00$ were placed separately into each of the two H-tube arms, the tubes were sealed under vacuum and then heated at temperatures of 150, 250, and 350°C for 66 h. After equilibration under these conditions the contents of the two arms of the H tube were separately analyzed by TGA, PXD, and ME measurements.

Oxygen contents given subsequently were determined for each sample by TGA in a 5 vol% H_2 –95 vol% He atmosphere using a Dupont 1090/951 thermal analyzer. The value of x is determined from the weight loss on complete conversion to yttrium and barium oxides and copper metal at 1000°C . Meissner-effect data were obtained using a George Associates Faraday magnetometer in a magnetic field of 50 G, or using a Princeton Applied Research vibrating sample magnetometer in a field of 10 G.

Powder x-ray-diffraction data were measured on an automated Siemens D500 diffractometer using $\text{Cu } K\alpha$ radia-

tion. Samples were loaded into 2-mm-deep aluminum sample trays or spread over a thin layer of silicon grease on a quartz crystal, depending on sample quantity. Diffraction profiles were scanned in ω - 2θ mode over the range $2.0^\circ \leq 2\theta \leq 92.0^\circ$ in steps of 0.02° , with count times of 2 s at each point. Incident-beam divergence slits of 1° were used for this full data range. No particular precautions were taken to minimize preferred orientation effects, which in some cases were noticeable in the measured PXD profiles. Rietveld analyses were performed on the powder x-ray-diffraction data from all samples in order to establish or quantify phase purity and to obtain accurate lattice constants.

The full-matrix least-squares Rietveld refinements⁸ were achieved using a locally modified version of the DBW3.2 code of Wiles and Young.⁹ The background was treated by linear interpolation between a set of estimated points that were updated periodically. The peak shapes were described by the pseudo-Voigt-function. Scattering factors for the species Y^{3+} , Ba^{2+} , Cu^{2+} , and O^{1-} were used. Space groups $Pmmm$ [No. 47 (Ref. 10)] or $P4/mmm$ [No. 123 (Ref. 10)] were assumed for the orthorhombic and tetragonal phases, respectively. Complete structure analyses for selected materials were also achieved based on powder neutron-diffraction data collected at ambient temperature and below.^{6,11}

III. RESULTS AND DISCUSSION

The samples in both arms of the H tubes examined after treatment for 66 h at 150°C and at 250°C were identical to the starting materials. For the H tube treated at 350°C for 66 h, however, the TGA (Fig. 1) and ME data (Fig. 2) for materials from both sides are closely similar, demonstrating that complete equilibration with respect to oxygen content had occurred. Thus, the data shown in Fig. 1

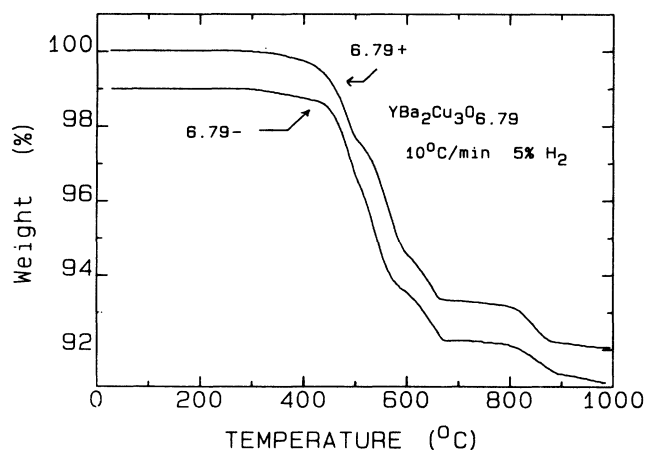


FIG. 1. Thermogravimetric analysis scans (Dupont 1090/951 TGA, 5 vol% H_2 -95 vol% He , $10^\circ\text{C min}^{-1}$) of samples with initial compositions of $x=0.10$ (labeled 6.79-, lower; offset along the weight axis to permit comparison) and $x=1.00$ (labeled 6.79+ upper) after separate equilibration in the two arms of a sealed H tube for 66 h at 350°C .

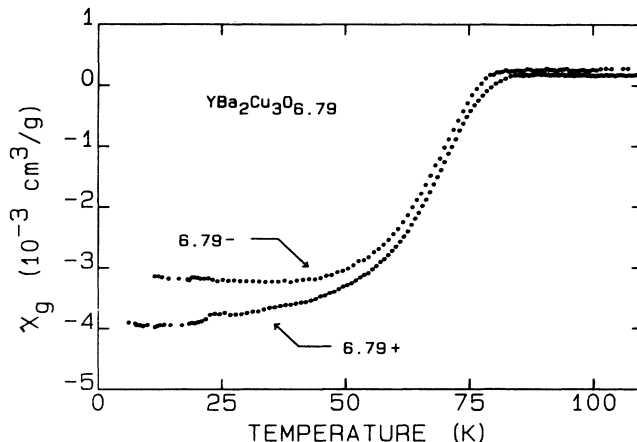


FIG. 2. Meissner-effect data for the same two samples of Fig. 1 (Princeton Applied Research vibrating sample magnetometer, applied field 10 G).

give identical oxygen contents of 6.79 (the estimated precision of the compositions, x determined by TGA is ± 0.03). The ME data plotted in Fig. 2 show nearly identical onset temperatures for superconductivity and similar diamagnetic susceptibilities. The computed volume fractions are approximately 25% (for the sample which started with a composition of $x=0.10$, labeled 6.79-) and 32% (for the sample which was originally $x=1.00$, labeled 6.79+). Importantly, there is no evidence for two separate superconducting transitions at $T_c \sim 90$ K and $T_c \sim 60$ K. The results of the Rietveld analyses of the PXD data for the two materials showed the presence only of orthorhombic phases with optimized lattice constants of $a=3.8258(4)$ Å, $b=3.8881(4)$ Å, and $c=11.706(2)$ Å [6.79+], and $a=3.8252(4)$ Å, $b=3.8873(4)$ Å, and $c=11.700(1)$ Å [6.79-]. Typical observed, calculated, and difference PXD profiles (data for the 6.79- sample) are shown in Fig. 3.

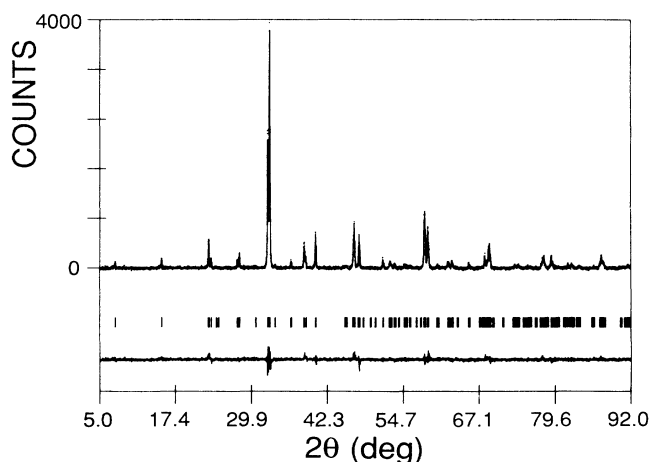


FIG. 3. Final observed (points), calculated (continuous line connecting computed data points), and difference (lower, same scale) powder x-ray-diffraction profiles for $YBa_2Cu_3O_{6.79}$ (6.79- sample).

These experiments indicate that a temperature of 350°C is sufficient for synthesis of the $x=0.21$ composition by this sealed-tube equilibration technique. This method provides an accurately reproducible, convenient route to nonstoichiometric materials with intermediate compositions $0.04 \leq x \leq 1.00$. The same method is also applicable to single-crystal samples and to sintered pellets, although, for kinetic reasons, considerably longer equilibration times are required.

Meissner-effect data for various samples prepared by sealed-tube equilibration at 650–670°C (VSM Data) are shown in Fig. 4. These data are similar to those reported for samples prepared *in situ* in the Faraday balance.⁶ Between $x=0.04$ and $x=0.40$, the computed superconducting volume fraction is 38–55%, but the fraction decreases rapidly at higher x values. The midpoint temperature of the superconducting transition is plotted versus oxygen content in Fig. 5, where the previous Faraday balance data obtained in a field of 50 G on a series of samples prepared *in situ*⁶ are also included. The two data sets are consistent, and reveal the presence of two T_c plateaus at ~ 90 K for $0 \leq x \leq 0.1$ and ~ 50 K for $0.30 \leq x \leq 0.45$. The results for samples equilibrated at lower temperatures lie on the same S-shaped curve. For example, the midpoint T_c 's of the two samples (6.79+ and 6.79–) prepared by equilibration at 350°C, equal at $T_c=67$ K, lie almost exactly on the smooth curve drawn in Fig. 5. Also included (Figs. 4 and 5) are data for a sample with $x=0.26$ (TGA analysis) that was prepared by annealing an appropriate mixture of the $x=0.10$ and $x=1.00$ materials at 650°C for 24 h, 750°C for 48 h, and then at 336°C for 18 days. The midpoint T_c (54 K) again lies close to the curve in Fig. 5. The transition width for this material is narrow, implying that no phase separation has occurred.

From the data in Fig. 4 and Ref. 6, a measure of the superconducting transition width ΔT_c (defined as the difference in temperature at which a sample attains 10%

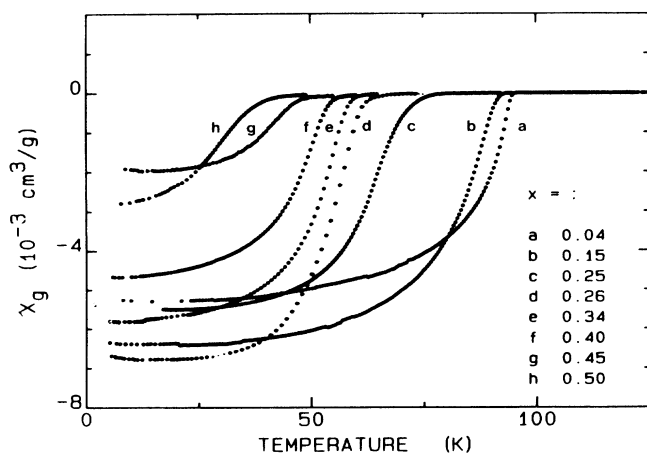


FIG. 4. Meissner-effect data for several samples prepared by the sealed-tube equilibration route (Princeton Applied Research vibrating sample magnetometer, applied field 10 G). The oxygen contents x determined by TGA are indicated for each data set.

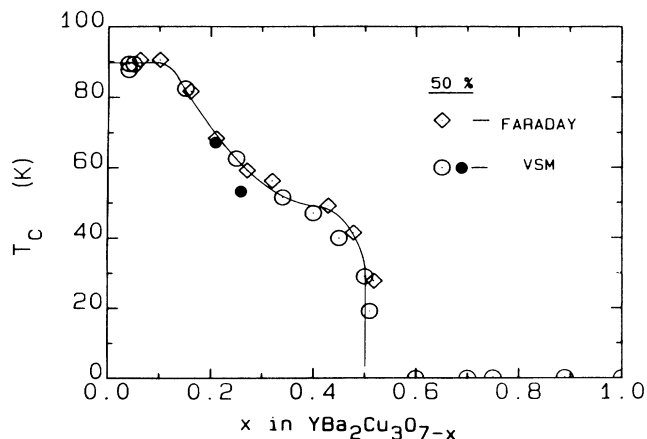


FIG. 5. The superconducting transition temperature T_c vs oxygen content x as determined by Meissner-effect measurements [\diamond , Faraday magnetometer data (Ref. 6); \odot and \bullet , vibrating sample magnetometer (VSM) data]. Data from samples produced both by sealed tube equilibrations at 650–670°C (\odot) and at $\leq 350^\circ\text{C}$ (\bullet), and by *in situ* control of the oxygen content in the Faraday balance are plotted (Ref. 6). The samples with $x > 0.6$ are tetragonal materials quenched from $\sim 650^\circ\text{C}$.

and 50% of its maximum diamagnetic susceptibility) is plotted against oxygen content x in Fig. 6. For these samples, ΔT_c reaches a maximum near $x=0.2$. This composition is close to that at which the bulk T_c is varying most rapidly with oxygen content (Fig. 5), suggesting that the maximum in ΔT_c is due to a small variation, Δx , in x within the sample. For such a case, the relationship

$$\Delta T_c = \Delta T_c^0 + \frac{dT_c}{dx} \Delta x, \quad (1)$$

where ΔT_c^0 is a minimum transition width, would be obtained. Inserting in Eq. (1) the ΔT_c data of Fig. 6 and the dT_c/dx values from Fig. 7, a good fit (indicated by the filled circles in Fig. 6) is indeed obtained. The corre-

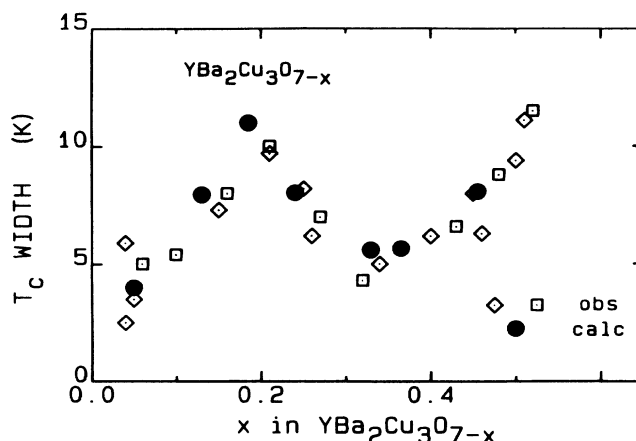


FIG. 6. A measure of the superconducting transition width plotted against oxygen content for various samples (\diamond, \square , see text). The filled circles represent values calculated on the basis of Eq. (1), assuming $\Delta T_c^0=4$ K, $\Delta x=0.027$.

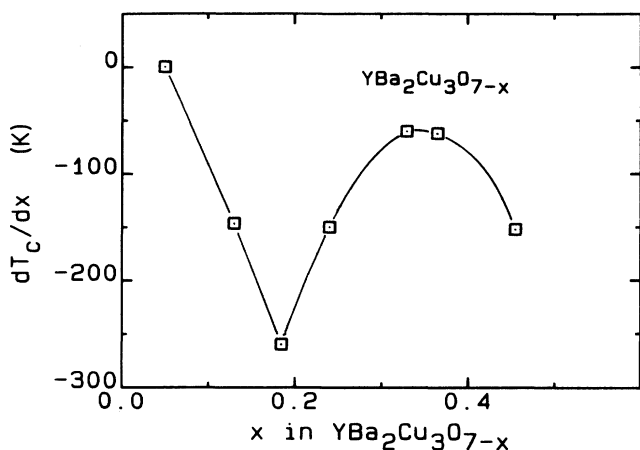


FIG. 7. Differential change in superconducting transition midpoint temperature with oxygen content. Data derived from data displayed in Fig. 5. The solid curve is a guide to the eye.

sponding fitting parameters are $\Delta T_c^0 \approx 4(1)$ K and $\Delta x = 0.027(5)$. Meissner-effect data from other groups for quenched samples¹²⁻¹⁵ show ΔT_c variations similar to that in Fig. 6 and Ref. 6. Thus, for materials with $0.04 \leq x \leq 0.4$ quenched from $T \geq 350^\circ\text{C}$, the superconducting behavior can be interpreted in terms of a homogeneous superconducting state, with an oxygen inhomogeneity of $\Delta x \sim 0.03$. The data show no evidence for phase separation into oxygen-rich $x \approx 0.0$, $T_c \sim 90$ K and oxygen-poor $x \approx 0.33$, $T_c \approx 50$ K materials. If such phase separation were to occur on a length scale greater than approximately twice the maximum coherence length of 20–30 Å,¹⁶ evidence for two distinct T_c 's in these compositions would be observed, and Eq. (1) would not be expected to hold. By analogy with other oxygen-deficient perovskites such as BaBiO_{3-x},¹⁷ however, oxygen-vacancy ordering might be anticipated to occur under certain conditions, and some evidence for local vacancy order in the YBa₂Cu₃O_{7-x} system at various compositions has been reported¹⁸⁻²⁰ based on electron diffraction data.

The more oxygen deficient side of the phase field is complicated by the presence of the orthorhombic-tetragonal phase transition. A tentative phase diagram for the system has the orthorhombic-tetragonal transition occurring at successively lower temperatures as x tends to 1.0. At $x = 1.00$, the structure is accurately tetragonal below 950°C . Data on quenched samples show that the tetragonal phase can be maintained at low temperatures for $x \geq 0.6-0.7$. Rietveld analysis of powder x-ray-diffraction data for a sample with $x = 0.51$ quenched from 650°C , demonstrated two-phase behavior for x close to 0.5.⁶ Compounds with $x = 0.59$ (prepared by direct reduction at 840°C followed by quenching) and $x = 0.60$ (prepared by sealed-tube equilibration of a mixture of $x = 0.04$ and $x = 1.00$ materials at 640°C for 24 h) are tetragonal within the precision of the x-ray data. The ME data show no detectable superconductivity in these samples at least down to 4.2 K (Fig. 5).

For compositions corresponding to $x > 0.4$, equilibrium is apparently less easily achieved and compositions pre-

pared by different techniques or from different starting points are not equivalent. Lower temperature synthesis ($360 \leq T \leq 520^\circ\text{C}$) by the zirconium gettering route suggest that a pure orthorhombic phase occurs at $x = 0.7$.²¹ In contrast, a sealed-tube equilibration of appropriate proportions of $x = 0.1$ and 1.0 materials at 365°C for 40 h gave a sample with, on an average $x = 0.65$ by TGA, but which PXD showed to be a biphasic mixture of orthorhombic and tetragonal components. The Rietveld refinements gave relative scale factors indicating a fractional orthorhombic content of 0.7(1) and lattice constants $a = 3.860(1)$ Å, $c = 11.824(3)$ Å, and $a = 3.836(1)$ Å, $b = 3.879(1)$ Å, $c = 11.740(5)$ Å for the tetragonal and orthorhombic phases, respectively. Meissner-effect data on this sample showed a superconducting transition with an onset $T_c = 60$ K and a midpoint $T_c = 50$ K. The changes observed in the cell constants and T_c relative to the starting materials, indicate that partial oxygen exchange occurred. The lattice constants compare with values of $a = 3.859$ Å, $c = 11.832$ Å for an $x = 1.00$ material,⁶ and $a = 3.833$ Å, $b = 3.884$ Å, $c = 11.711$ Å for $x = 0.34$.⁶ In order to obtain further information concerning the equilibrium phase at $x = 0.65$, a tetragonal, nonsuperconducting sample was prepared by quenching from 650°C . This sample was separated into two parts which were then separately annealed at 365 and 450°C for 66 and 97 h, respectively. No evidence for phase separation was obtained, ME measurements showing no indication of superconductivity down to 4.2 K. The data for the $x = 0.65$ composition thus indicate that equilibrium is not achieved at 365°C and consequently no conclusion can be drawn as to whether the tetragonal phase or the phase separated mixture is the thermodynamically stable arrangement in this region of the phase diagram.

IV. CONCLUSION

In the YBa₂Cu₃O_{7-x} system for $0.0 < x < 0.4$, powder x-ray diffraction and the superconducting properties indicate that single-phase orthorhombic materials (on a length scale greater than about 60 Å) are obtained on quenching from temperatures above 350°C . For such single-phase materials, the superconducting temperature varies in a smooth fashion over the $0.04 \leq x \leq 0.40$ composition field and the observed variation of the transition width with x is as expected from the variation of dT_c/dx in this range. Powder x-ray diffraction and Meissner-effect data for more oxygen-deficient samples, $x > 0.5$, indicate that under sealed tube conditions at temperature above 600°C , homogeneous single-phase tetragonal samples are obtained. However, below 400°C there are significant kinetic barriers to the formation of homogeneous materials from mixtures of orthorhombic and tetragonal components and/or to phase separation from the tetragonal phase.

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