An ¹⁷O NMR Study on Oxygen Exchange in YBa₂Cu₃O_{7-x}

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Received December 20, 1989; in revised form January 31, 1990

This study evaluated the effect of reaction conditions on the extent and uniformity of ¹⁷O-labeled YBa₂Cu₃O_{7-x}. It was shown by ¹⁷O NMR spectroscopy and high-resolution SIMS that statistical ¹⁷O-enrichment is achieved at high temperatures by synthesis from oxides under an ¹⁷O₂ atmosphere, or by direct ¹⁷O₂ exchange of preformed YBa₂Cu₃O_{7-x}. Nonuniform enrichment can be achieved at low temperatures and with the use of short reaction times. An ¹⁷O₂ circulator is described which proved useful for handling, purifying, and recovering the labeled oxygen. © 1990 Academic Press, Inc.

Introduction

YBa₂Cu₃O_{7-x} has two very distinctive properties. Most importantly, it is the first superconductor with T_c greater than the boiling point of nitrogen (1). Chemically this material is interesting because its oxygen content can be varied over the range 0 < x < 1 while preserving the perovskite structure (2). These two distinctive properties are interdependent insofar as T_c varies from 92 K with $x \approx 0$, to 60 K for $x \approx 0.4$, to 30 K for $x \approx 0.7$ (3). The normal state resistivity of the material is also very sensitive to the value of x (4).

At least some of the oxygen sites in YBa₂ Cu₃O_{7-x} are directly involved in the superconducting pathway, while other oxygen sites appear to play a more indirect if not spectator role (5). Consequently, there is great interest in the development of ¹⁷O NMR spectroscopy as an atomic level probe of the magnetic character of the various oxygen sites, both as a function of stoi-

chiometry and temperature. Practical ¹⁷O NMR spectroscopy requires enrichment since the natural abundance of the isotope is only 0.037%, and recent ¹⁷O NMR studies have exploited the oxygen lability of $YBa_2Cu_3O_{7-x}$ to prepare isotopically enriched samples (6, 7). Similar techniques have been employed to prepare ¹⁸O-enriched samples for study of the isotope effect on T_c (8). The reliability of these procedures has been debated with regard to the uniformity of the enrichment (9), and as a result newer procedures were developed; in these procedures Y, Ba, and Cu metals in a 1:2:3 ratio were burned in ${}^{18}O_2$ gas (10-12). Questions of uniform isotope enrichment hinge on the fact that there are four crystallographically different oxygen sites in the x = 0 compound, each of which can be expected to be differently labile.

In this report we describe experiments designed to test the uniformity of isotopic enrichment of $YBa_2Cu_3O_{7-x}$. The progress of this enrichment is evaluated by ¹⁷O NMR



PRESSURE

GAUGE

Â

GAS BULB CHECK VALVE

SOLENOID

PUMP

PISTON

(Fe CORE)

PUMP CONTROLLER

spectroscopy. We have recently shown that this technique, as applied to magnetically oriented crystallites of $YBa_2Cu_3O_{7-x}$, can resolve 19 of the 20 possible NMR transitions for the four crystallographically independent oxygen sites (13). Our ¹⁷O NMR results reported herein show that uniform isotopic enrichment is easily achieved. We also show that under very mild conditions selective enrichment is also possible.

Results

Preparation of $1^{7}O$ -labeled YBa₂Cu₃O_{7-x}. Our initial attempts to prepare ¹⁷O-labeled YBa₂Cu₃O_{7-x} focused on synthesis from individual metal oxides under a static ¹⁷O₂ atmosphere. We reasoned that this method of synthesis would probably guarantee ¹⁷O labeling at each of the four oxygen sites. Xray powder diffraction analysis showed, however, that samples produced in this way were heavily contaminated with Y_2Ba CuO_5 and $BaCuO_2$. The reason that these phases form in the static atmosphere is not obvious, although we propose that flowing gas may serve to drive off volatile impurities, like CO₂ and H₂O. In any case, these problems induced us to design an apparatus which would simulate flowing gas conditions without wasting precious ${}^{17}O_2$.

The quartz/Pyrex apparatus shown in Fig. 1 allows for the closed system circulation of ${}^{17}O_2$ gas, which is pumped with a water-cooled solenoid piston. The pump has the capability of adjustable flow rates. The circulating gas is continuously scrubbed, at room temperature, with P_4O_{10} (for H₂O) and Ascarite, a CO₂-absorbing reagent containing NaOH, and the ${}^{17}O_2$ is then reheated before contact with the sample. At the end of an experiment the ${}^{17}O_2$ is recovered into a storage bulb by condensing it with liquid nitrogen. The pressure in the apparatus was monitored with a vacuum/pressure gauge; in our experiments the pressure varied from 0.8 atm (at 100°C) to 1 atm (at 970°C).

Sample A (Table I) was prepared from a pellet of Y₂O₃, BaO₂, and Cu₂O in the aforementioned circulator at 970°C. After two such preparations we observed that part of the dessicant which was originally a freeflowing powder, had become a viscous liquid, indicating that it had partially X-ray powder hydrolyzed. diffraction demonstrated that all YBa₂Cu₃O_{7-x} samples were highly pure (Fig. 2). Magnetic susceptibility measurements on magnetically aligned polycrystals (see below) showed that the samples have sharp diamagnetic transitions (Fig. 2, inset).

¹⁷O NMR characterization. The ¹⁷O-NMR spectrum of Sample A was obtained at 11.7 T, using a spin echo pulse sequence on magnetically aligned crystallites embedded in Duro-TM epoxy resin (6). The spec-

TABLE 1 Sample Preparation Summary

Samples	Precursors	Reaction duration
A	Cu ₂ O, BaO ₂ , Y ₂ O ₃	36 hr at 970°C and 24 hr at 490°C
B	YBa ₂ Cu ₃ O _{7-x}	168 hr at 400°C
С	YBa ₂ Cu ₃ O _{7-x}	24 hr at 400°C
D	$YBa_2Cu_3O_{7-x}$	4 hr at 400°C



VAC. PUMP

P205

SAMPLE CHAMBER

(QUARTZ)



FIG. 2. X-ray powder patterns for Sample A (see Table I). Inset: Magnetic susceptibility data on polycrystals of Sample A in an epoxy matrix.

tra were referenced with respect to water at 0 ppm, positive values corresponding to high-frequency shifts (IUPAC δ scale). The absorptions at ~ 2700 , ~ 1800 , and ~ 900 ppm downfield from H₂O were assigned to the chain (O4), the plane (O2, O3), and the column (O1) oxygens, respectively (Fig. 3) and are due to $\frac{1}{2}$, $-\frac{1}{2}$ transitions (13). The carrier frequency was set between the O1 and O2, O3 resonances. The chemical shifts are in agreement with those obtained in previous studies by ourselves and Takigawa et al., in which the samples were prepared differently (6, 7). Synthesis of $YBa_2Cu_3O_{7-x}$ from its oxide precursors under flowing ¹⁷O₂ gas ensures a high probability of homogeneous ¹⁷O atom distribution among the four oxygen sites.

Selective ¹⁷O enrichment. The availability of statistically enriched (as determined from integrated intensities of spectra recorded on resonance) YBa₂Cu₃O_{7-x} encouraged us to attempt selective ¹⁷O-labeling. Samples B-D, derived from a single batch of YBa₂Cu₃O_{7-x}, $x \sim 0$, were exposed to flowing ${}^{17}O_2$ at 400°C for 7 days, 1 day and 4 hr, respectively.

In recording the ¹⁷O NMR spectra of these three samples, the spectrometer frequency was first centered on the O1 resonance, to compare the (O2, O3)/(O1) intensity ratio, and then on the O4 resonance, to compare the (O2, O3)/(O4) intensity ratio. Since Sample *D* was only exposed to ¹⁷O₂ for 4 hr, the level of enrichment is low, and the signal-to-noise ratio of its NMR spectrum was not as good as those of the other samples.

Figure 4 shows the ¹⁷O NMR spectra of the three samples when the spectrometer frequency was centered on the O1 resonance. As can be seen from these spectra, the (O2, O3)/(O1) intensity ratio decreases on going from Samples *B* to *D*. Figure 5 shows the ¹⁷O NMR spectra of Samples *C* and *D* when the spectrometer frequency was on the O4 resonance. These results show that the (O2, O3)/(O4) ratio of Sample *C* is greater than that of Sample *D*; Sample *B* has a similar (O2, O3)/(O4) ratio as Sam(02, 03)



Frequency shift (ppm from H₂O)

FIG. 3. ¹⁷O NMR spectrum for Sample A (spectrometer frequency was offset between the resonant frequencies of the chain and the plane oxygens. Inset: Structure of YBa₂Cu₃O_{7-x}, showing the labeling scheme for chain (O4), column (O1), and plane (O2, O3) oxygens.

ple C (spectrum not shown). The comparison of CuO₂ plane/nonplane oxygen intensity ratios strongly suggests that ¹⁷O atoms in Sample D are not distributed between sites in the same way as those in Samples B or C: ¹⁷O has replaced the column and chain sites more than plane positions, in Sample D. We thus conclude that ¹⁷O atoms first exchange into nonplane sites. However, as the enrichment proceeds, site exchange occurs between the nonplane and plane positions. We did not investigate anneal times shorter than 4 hr since such poorly labeled samples would require extremely long data acquisition times. We did anneal YBa₂Cu₃O_{7-x} in ¹⁷O₂ gas at 300°C for 24 hr, and the ¹⁷O NMR spectrum of that sample (data not shown) again had a very poor S/N ratio, but showed a weak signal, due to the plane oxygens (O2, O3).

Our observation of ¹⁷O labeling of the plane (O2, O3), column (O1), and chain (O4) sites at low anneal temperatures is consistent with a recent Raman study on ¹⁸O selective enrichment of $YBa_2Cu_3O_{7-x}$ (14).

¹⁶ $O: {}^{17}O: {}^{18}O$ ratios for enriched samples. Using high-resolution secondary ion mass spectrometry (SIMS), we examined the ¹⁶ $O: {}^{17}O: {}^{18}O$ isotope ratio of Samples A and B. This technique is capable of distinguishing ${}^{17}O$ from ${}^{1}H{}^{16}O$, $\Delta M \approx 0.005$ amu. The intensity vs time plots obtained from this analysis are shown in Fig. 6. The ¹⁶ $O: {}^{17}O: {}^{18}O$ ratio and the ${}^{17}O$ level in both of these samples were virtually the same. This implies that ${}^{17}O$ -labeling of YBa₂ Cu₃O_{7-x} at 400°C for 1 week produces the same results as ${}^{17}O$ -labeling done at 970°C for 36 hr.

Conclusions

The primary result of this study is that the four oxygen sites in YBa₂Cu₃O_{7-x} can be statistically enriched. Our arguments rest on the fact that the ¹⁷O NMR and SIMS data are unaffected by the method of synthesis, be it synthesis from oxides under ¹⁷O₂ or gas exchange of preformed YBa₂ Cu₃O_{7-x}. The study permits more confident interpretation of recently published ¹⁷O NMR spectra (13), at least with regard to relative peak intensities. Under very mild conditions we could effect selective enrichment into nonplane sites: this selectivity was, however, achieved at the cost of a rather low net enrichment.

Experimental Section

Chemicals. ${}^{17}O_2$ gas was prepared by electrolysis of $H_2{}^{17}O$ by Dr. J. Fitzpatrick,



Frequency shift (ppm from H₂O)

FIG. 4. ¹⁷O NMR spectra for Samples B (left), C (middle), and D (right); the spectrometer frequency was centered on the column oxygen signal at \approx 900 ppm. These spectra show the effect of oxygen exchange times (168, 24, and 4 hr, respectively) on the relative intensity of the column oxygen signal.

at the Los Alamos National Laboratory. Its isotopic composition was 23.2% (¹⁶O), 47.2% (¹⁷O), and 29.6% (¹⁸O); this gas was used throughout this study. The following

chemicals were used as purchased: BaO_2 (99.99%, Anderson Physics, Urbana, IL), Y_2O_3 (99.99%, Aldrich, Milwaukee, WI), Cu_2O (99.95%, Alfa, Danvers, MA), As-



FIG. 5. ¹⁷O NMR spectra for Samples C (left) and D (right) (the spectrometer frequency was centered on the chain oxygen signal at \approx 2700 ppm). These spectra show the effect of oxygen exchange times (24 and 4 hr, respectively) on the relative intensity of the chain oxygen signal.



FIG. 6. SIMS ion intensity vs sputter time profiles of Samples A (left) and B (right).

carite II (Thomas Scientific, Swedesboro, NJ).

Apparatus. The schematic diagram of the ${}^{17}O_2$ gas circulator is shown in Fig. 1. It consists of four detachable parts: the solenoid driven piston pump, the ${}^{17}O_2$ gas bulb, the quartz sample chamber, and a right-angled connector which connects the gas bulb to the sample chamber. The four parts are interconnected by greased (Dow Corning, Midland, MI) ground-glass ball-joints.

The piston of the pump is a glass tube packed with iron powder. The pump controller consists of a Signetics NE 555 integrated circuit timer which has a variable pulse rate, adjusted by a potentiometer. The timer drives a Magnecraft solid-state relay which in turn switches the 117-V AC line to the solenoid coil. The solenoid coil (number 20 formvar insulated copper wire) is wound on a nylon bobbin with a center hole. Gas pressure inside the apparatus, as indicated by the vacuum/pressure gauge (H. O. Trerice Co., Detroit, MI), is 0.8 atm at 100°C and 1 atm at a sample temperature of 970° C.

Instrumentation. Powder X-ray diffraction patterns were recorded using a Rigaku Geigerflex D/max-B diffractometer. Magnetic susceptibility measurements were carried out using a SQUID magnetometer (SHE Corporation, San Diego, CA). A MnF₂ standard (National Bureau of Standards, Washington, DC) was used to measure the actual applied field. No demagnetizing corrections were used. ¹⁷O NMR measurements were performed on a 500 MHz (11.7 T) spectrometer using a "homebuilt" probe (13). ${}^{16}\text{O}$: ${}^{17}\text{O}$: ${}^{18}\text{O}$ ratios were obtained using a CAMECA secondary ion mass spectrometer (SIMS) by Dr. C. Hitzman (Charles Evans and Associates, Redwood City, CA). Syntheses were done using a prelinearized two-zone horizontal furnace (Marshall, Scott Valley, CA).

Preparation of Sample A. A mixture of

4.768 g of Y_2O_3 , BaO₂, and Cu₂O in the metal atom ratio of 1:2:3 was ground using an agate mortar and pestle under an N₂ atmosphere, then pressed into five pellets, each 8 mm in diameter and 2 mm thick. The pellets were oriented in a platinum boat so as to minimize their contact with the Pt surface. The apparatus was evacuated for 4 h with the sample chamber set at 100°C. At the end of the evacuation time, ${}^{17}O_2$ was released from the storage bulb and the pump was started at a flow rate of 5 cm³/s. The sample was heated at 970°C for 24 hr. A small amount of green material, probably Y_2BaCuO_5 and $Ba_3Y_2PtCu_2O_{10}$ (15) was scraped from where the pellets had contacted the boat. The pellets were then ground, repelleted, and subjected to a second heat treatment at 970°C for 12 hr followed by annealing at 490°C for 24 hr. Throughout this and the other syntheses the heating rate was always 100°C/hr and the cooling rate was 50°C/hr.

Preparation of Samples B–D. A mother batch of unenriched YBa₂Cu₃O_{7-x}, $x \sim 0$, was prepared using a standard procedure (6). The batch was divided into three portions. The first portion was annealed in a flowing ¹⁷O₂ gas at 400°C for 168 hr (Sample B). The second and third portions were annealed at the same temperature but for 24 hr (Sample C) and 4 hr (Sample D), respectively.

Acknowledgments

This research was supported by the National Science Foundation through Grants NSF DMR 86-12860 and 88-14789. We thank Dr. Lenore Koczon for preliminary studies, Dr. John Fitzpatrick (Los Alamos National Laboratories) for providing ${}^{17}O_2$ gas, and Professor Kenneth Suslick and his research group for help with the design of the circulator pump.

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