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TITLE PREPARATION AND CHARACTERIZATION OF ISOTOPIC
OXYGEN-ENRICHED YTTRIUM BARIUM COPPER OXIDE

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PREPARATION AND CHARACTERIZATION OF ISOTOPIC OXYGEN-ENRICHED YTTRIUM BARIUM COPPER OXIDE

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Abstract The preparation of labeled superconducting yttrium barium copper oxides from the labeled metal nitrates is described. The materials were characterized by a variety of physical techniques, and their superconducting properties were measured. Trends are seen in the structural parameters of the materials obtained by the nitrate route and also in isotopically enriched materials prepared via gas-phase exchange. These structural changes are accompanied by changes in superconducting properties. The ^{18}O-enriched yttrium barium copper oxide prepared via the nitrate route has a T_c depressed by 33 K to 59 K, whereas a ^{17}O sample has a T_c between the ^{18}O material and a similarly prepared ^{16}O sample.

Isotopic substitution of high-temperature superconductors has been the subject of intense interest to researchers intrigued with the role of electron-phonon interactions in the mechanism for superconductivity in these materials. By the old wisdom, T_c is generally thought to be a sensitive function of phonon frequency, i.e., the ionic mass, but coulomb correlations can dominate this small effect. If the electron-phonon interaction is significant in the high T_c phases, we still expect that T_c will be similarly influenced by the mass of the ions involved in critical phonon modes. In the yttrium barium copper oxide system, substituting the much heavier lanthanides at the yttrium site has had no significant effect on the superconducting properties.[3] Similarly, isotopic substitution of the barium and copper sites has not led to any observable changes in T_c.[4] Changing the mass of the oxide lattice in $YBa_2Cu_3O_{7-x}$ by partial substitution of ^{18}O for ^{16}O has led to the observation of a small decrease in T_c of <0.5 K upon isotopic oxygen substitution.[5-8] The technique for incorporating ^{18}O into the lattice of the "123" materials in these reports has been gas-phase exchange, which relies on all of the lattice oxide ions being mobile among the different sites on the time scale of the experiment. When we initiated our experiments, we did not expect complete exchange to occur during gas-phase exchange because of the chemical diversity of the sites that the oxide ions occupy. Our hypothesis is that much greater than 6/7 of the oxygen (assuming an oxygen stoichiometry of 7 in the superconducting phase--lack of exchange in one site results in only 6/7 of the oxygen being exchanged) needs to be substituted to verify the presence or lack of a significant isotope effect. The earliest reports of isotopic substitution by gas-phase exchange claimed that from 65-90 at. % ^{18}O had been incorporated into the lattice by using various conditions of time and temperature of annealing under $^{18}O_2$. At only 65 at. % substitution, it is possible that two sites are completely unexchanged, whereas at 90 at. % enrichment, one site may remain completely unexchanged. Because most of the gas-phase exchange experiments reported in the literature used large excesses of >95 at. % ^{18}O dioxygen, one would expect levels of enrichment from gas-phase exchange to be greater than 90 at. %. The estimated levels of gas-phase exchange are approximately 90 at. % and lower, reflecting the fact that the exchanges did not reach equilibrium. To assess the oxygen isotope effect, it was necessary to substitute the lattice with >95 at. % ^{18}O and to perform the substitution in such a manner that there would be no question regarding the homogeneity of isotopic substitution in all sites. At Los Alamos, we have examined the possibility of preparing the "123" phase from a variety of synthetic routes that incorporate the isotopes directly into the lattice upon synthesis. Los Alamos is examining the preparation of thin film superconductors via coevaporation of yttrium, copper, and BaF_2 (Ref. 9), followed by annealing in flowing $^{18}O_2/H_2{}^{18}O$ as a method to incorporate ^{18}O directly into the lattice.[10] We also are examining the synthesis of the "123" phase via oxidation of a

2:1 mixture of the binary alloys BaCu and YCu in $^{18}O_2$ (Ref. 11). Results of these experiments will be published elsewhere. In this paper, we describe our results on materials prepared from labeled metal nitrates and $^{18}O_2$ gas-phase exchange.

Because the "123" phase may be prepared by decomposing mixtures of yttrium, barium, and copper nitrates in an oxygen atmosphere, we synthesized the isotopically enriched metal nitrates using highly ^{18}O-enriched nitric acid. We also prepared samples highly enriched in ^{17}O and ^{16}O for comparison.

All "123" samples and the yttrium powder used as a starting material were handled under purified argon in a glove box or on a Schlenk[12] line using standard Schlenk techniques to avoid contamination with ^{16}O atmospheric constituents. Isotopically enriched nitric acid was prepared by reacting $^{15}N^{18}O$ with $H_2{}^{18}O$ in the presence of a slight excess of $^{18}O_2$ (Ref. 13). The $H^{15}N^{18}O_3$ prepared was isolated and purified by vacuum distillation. Similarly, ^{17}O-enriched nitric acid was prepared from $N^{16}O$, ^{17}O-enriched water, and ^{17}O-enriched oxygen. The isotopic composition of the $HN^{18}O_3$ (in atomic %) was ^{16}O-4%, ^{17}O-0.4%, and ^{18}O-95.6%. The $HN^{17}O_3$ used was ^{16}O-26.8%, ^{17}O-40.5%, and ^{18}O-32.7%.

Samples of isotopically enriched $YBa_2Cu_3{}^*O_{7-x}$ (asterisk denotes isotopic enrichment of ^{16}O, ^{17}O, or ^{18}O) were prepared by dissolving yttrium and copper metal and $BaC^{16}O_3$ in an excess of 50%

HN^*O_3. All samples were prepared in an identical fashion. In a typical preparation, 177.2 mg yttrium powder, (99.999%, Alfa), 389.4 mg copper wire (99.999%, Aldrich), and 759.1 mg $BaCO_3$ (99.999%, Aldrich) are dissolved under a counterflow of argon in 5 cm^3 of cold (0°C) HN^*O_3. Vigorous evolution of H_2 and N^*O_x occurs during the addition of the metals. Carbon dioxide effervesces rapidly during addition of the $BaCO_3$, and BaN^*O_3 precipitates. A transfer arm and receiver are attached to the reaction flask and are flushed with argon. The suspension is frozen (LN_2), and the apparatus is evacuated. Excess HN^*O_3 and $H_2{}^*O$ are removed from the metal nitrates by vacuum distillation at room temperature which yields a light-blue powder of the hydrated, mixed metal nitrates. The HN^*O_3 recovered from the ^{18}O synthesis contained 94.2 at. % ^{18}O, 1.3 at. % ^{17}O, and 4.5 at. % ^{16}O. The isotopic content of the nitric acid may be slightly degraded because of isotopic exchange with $C^{16}O_2$ from the $BaCO_3$. We consider 94 at. % to be the lower limit of ^{18}O incorporation into the subsequently formed ^{18}O-enriched "123" compound, which has been confirmed to be 95-96 at. % ^{18}O by laser ionization mass spectroscopy (Lawrence Livermore National Laboratory) for a sample of ^{18}O-labeled yttrium barium copper oxide. The mixture of hydrated mixed metal nitrates is then pyrolyzed under flowing argon at 450° to 500°C for 2 hours to yield a gray-black material. The reaction flask is transferred into the glove box, and the residue is scraped into a mortar and ground with a pestle to a fine dark-gray powder. The powder is then pressed to a loose pellet (intentionally porous to facilitate oxygen diffusion). The pellet is placed in a boat (platinum or quartz), isolated in a quartz tube, and removed from the drybox. The apparatus is placed into a clamshell furnace, attached to a vacuum line, and evacuated.

After backfilling the vessel with the appropriate isotopically enriched oxygen, a constant flow of <1 cm^3 $^*O_2$/min at 580 torr (atmospheric pressure in Los Alamos) is established. The reaction vessel is isolated from the atmosphere by two cold traps (-78°C) and a bubbler in series. The initial heating cycle is as follows: the temperature is ramped from 30° to 200°C in 5 min and held for 5 min, is ramped to 650° in 30 min and held at this temperature for 1 hour. N^*O_x evolution begins at approximately 350°C and appears to be complete after 1 hour at 650°C. The temperature is then raised over a period of 30 min to 960°C, held for 4 hours, then cooled under a constant flow of $^*O_2$ to 100°C over a period of 200 min. The apparatus is isolated from the atmosphere, and the sample is returned to the glove box, where the sample is reground and pelletized, and the heating process under $^*O_2$ is repeated with the 1-hour hold time at 650°C eliminated. Two samples each of the ^{16}O- and ^{17}O-enriched "123" and three samples of the ^{18}O-enriched "123" superconductors were prepared with this annealing procedure. In addition, some ^{18}O samples were annealed a third time at 700°C for 1.5 hour, cooled at 2°/min to 500°C, held at this temperature for 30 min, and then cooled to room temperature in 100 min. Samples were examined by x-ray diffraction (XRD), transmission electron microscopy (TEM), electron microprobe, scanning electron microscopy (SEM), and chemical analysis; in addition, the superconducting properties of the samples were measured.

Examination of the powder XRD results indicates that the materials prepared by the nitrate route often contain small amounts of $Y_2BaCu^*O_5$ ("211") and some Cu^*O. This result is confirmed by SEM/electron microprobe examination. TEM found no observable differences in morphology of the various isotopically enriched materials. No significant differences were found between the nitrate-derived or typical oxide/carbonate-derived ^{16}O-enriched materials, so it appears that the mode of synthesis does not influence the properties of the materials. Elemental analyses were performed to obtain the bulk composition (atomic emission spectroscopy). Analyses of single grains were determined by electron microprobe using both energy- and wavelength-dispersive spectrometers. Results of these determinations are shown in Table 1. There appears to be a trend in the stoichiometry of individual grains in samples containing the heavier isotopes prepared by the nitrate route. As the mass of the

TABLE 1 Analyses[a] of Isotopic Samples Prepared via the Nitrate Route

Isotope	Y	Ba	Cu
^{16}O	1.07 (1.08)	2.0	3.17 (3.01)
^{16}O	1.07 (1.07)	2.0	3.11 (3.03)
^{16}O[b]	- (1.04)	2.0	- (2.96)
^{17}O	0.98 (1.05)	2.0	3.14 (2.88)
^{17}O	1.07 (1.11)	2.0	3.08 (2.90)
^{18}O	0.97 (1.04)	2.0	2.82 (2.85)
^{18}O	- (1.03)	2.0	- (2.85)
^{18}O	1.02 (1.04)	2.0	3.05 (2.82)

[a] Bulk stoichiometry determined by atomic emission spectroscopy. Electron microprobe data from examination of 10-12 grains of the "123" phase are indicated in parentheses. All values normalized to Ba=2.

[b] Sample prepared via the carbonate/oxide route.

oxygen isotope increases, the amount of copper in single grains of "123" decreases, and the amount of Cu^*O inclusions found in the bulk increase. These inclusions are not taken up into the lattice of the copper-deficient superconducting phase even upon extended firing in $^{18}O_2$. This suggests that a chemical isotope effect may occur during the decomposition of the nitrates that controls the copper stoichiometry of the resulting superconducting phase. One such ^{18}O-enriched sample, which was "deficient" in copper in the grains ($YBa_2Cu_{2.85}O_{7-x}$) but had a large number of

$Cu^{*}O$ inclusions and a bulk stoichiometry of $YBa_2Cu_3{}^{*}O_{7-x}$, was fired in $^{16}O_2$. Subsequently, XRD and microprobe examination indicated that the "excess" CuO inclusions had been taken up into the lattice. Thus, there appears to be a subtle balance in the phase composition of the yttrium barium copper oxide system, which is dependent upon the oxygen isotope present in the lattice.

Examination of unit cell parameters obtained from high-resolution XRD indicates additional trends among the isotopically labeled material obtained via the nitrate route (Table 2). As the mass of the oxygen isotope substituted into the lattice increases, the a and b parameters increase significantly, and the c parameter decreases substantially. The unit cell volume remains fairly constant and at values consistent with complete oxygenation. These trends are not consistent with the trends observed in increasingly oxygen deficient ^{16}O samples, where the c

TABLE 2 XRD Data for Nitrate-Derived Y Ba Cu Oxides

Sample	a(Å)	b(Å)	c(Å)	vol(Å^3)	T_c
^{16}O	3.8189	3.8867	11.680(1)	173.37	93.5
^{17}O	3.8247	3.8885	11.674(2)	173.62	78
^{18}O	3.8304	3.8897	11.669(3)	173.86	59

Standard deviations for the a and b parameters are 0.0005 Å.

parameter and unit cell volume are observed to increase substantially upon removal of oxygen.[14-15] We have compared the nitrate-derived samples with gas-phase-exchanged samples that were prepared by repeated extended firing of ^{16}O-enriched "123" in $^{18}O_2$. As the exchange proceeds and presumably as the amount of ^{18}O in the lattice increases, the a and b parameters increase, whereas the c parameter and unit cell volume remain at constant values indicative of complete oxygenation (Table 3). The increase in the a and b parameters, observed in the gas-phase-exchanged samples, is substantially less than the increase observed in the nitrate-derived materials. The above experiments indicate that incorporation of ^{18}O into the lattice by either

TABLE 3 XRD Data for $^{18}O_2$ Gas-Phase-Exchanged Samples

Sample	a(Å)	b(Å)	c(Å)	vol(Å^3)	T_c
$^{16}O^a$	3.8177	3.8860	11.679(1)	173.26	93
$^{18}O^b$	3.8226	3.8879	11.679(1)	173.56	92.1
$^{18}O^c$	3.8238	3.8891	11.678(2)	173.66	90.4
$^{18}O^d$	3.8221	3.8879	11.674(2)	173.48	92.7

[a] Starting material.
[b] Two exchange cycles at 950°C, total time of 53 hours.
[c] Sample b, with two more cycles at 950°C, total time 111 hours.
[d] Sample c exchanged with $^{16}O_2$, 950°C, 10 hours.

gas-phase exchange or preparation from the labeled nitrates subtly alters the structure. At this time, we do not know why there is such a large difference in the structural behavior of the ^{18}O-enriched gas-phase-exchanged samples and the nitrate-derived samples. We are attempting to prepare large samples of enriched materials for powder neutron diffraction studies of these phenomena.

The resistivity of the isotopically enriched nitrate-derived materials is shown in Figure 1. No corrections have been made for porosity. The onsets determined from magnetic susceptibility and ac resistivity measurements for the ^{18}O-, ^{17}O-, and ^{16}O-enriched materials (given as resistive midpoint and the 10-90% width in parentheses) are 59(5.5) K, 77(10) K, and 93.0(1.5) K, respectively. All samples examined had metallic normal state resistivity signatures, indicative of adequate oxygenation. The ^{17}O sample had an oxygen stoichiometry of 7.3 ± 0.4 with a combination of Rutherford back scattering and oxygen isotopic analysis. These observations indicate that the isotopically labeled materials are adequately oxygenated, consistent with the XRD data discussed above.

Gas-phase exchange of ^{16}O into the ^{18}O- and ^{17}O-enriched samples (4 hours at 960°C in flowing $^{16}O_2$ followed by a slow cool to room temperature) resulted in increased T_c's. The T_c of the ^{18}O nitrate-derived sample increased from 59 to 76 K (width of 7 K), whereas the T_c of the ^{17}O sample

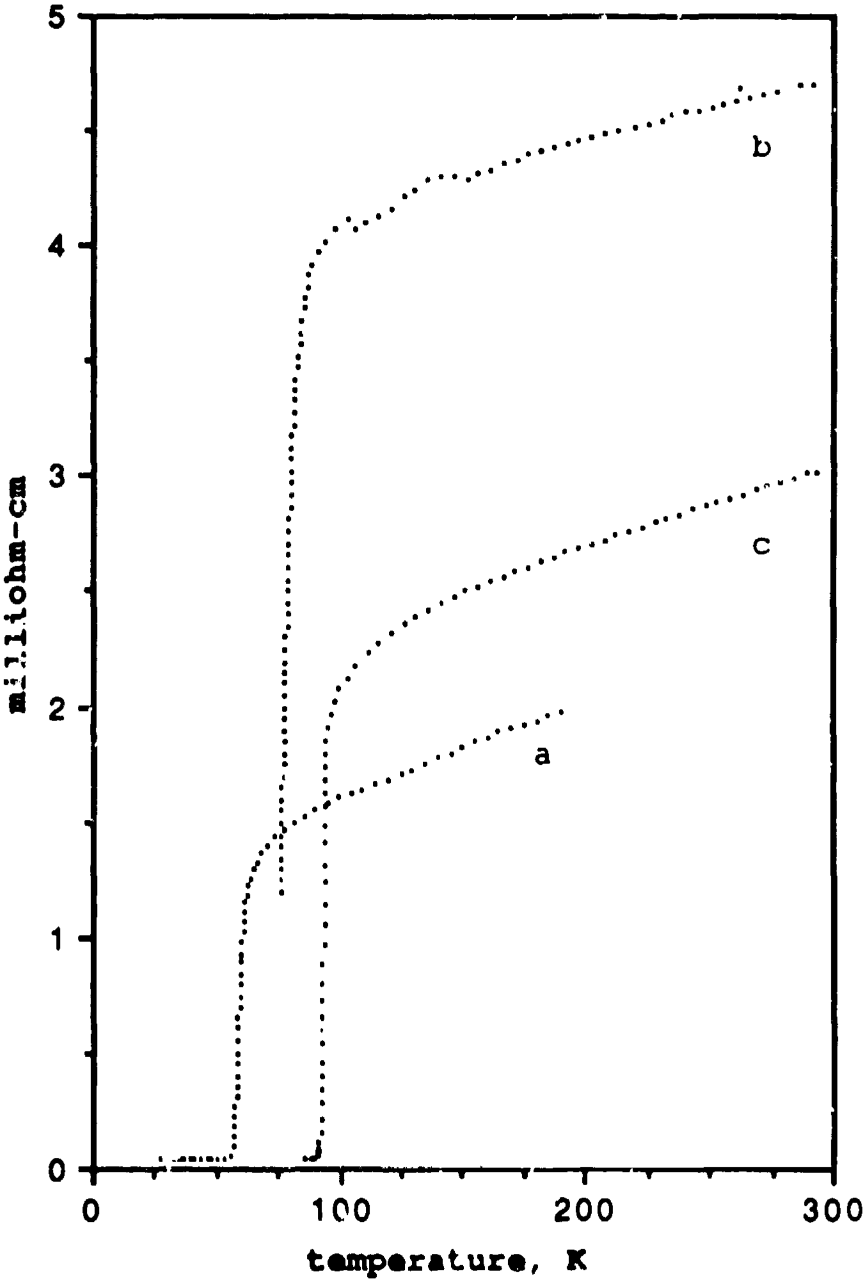

FIGURE 1. Resistivity versus temperature for isotopically enriched superconductors: (a) ^{18}O, (b) ^{17}O, (c) ^{16}O. ^{18}O- and ^{17}O-enriched samples mesured in a N_2 cryostat, hence the temperature range is limited to above 77 K. Porosity of the samples (by SEM) falls in the order b>c>a.

increased from 77 to 90.5 K (width of 1.7 K). The ^{17}O-enriched sample, even after exchange with $^{16}O_2$, has a T_c lying between the ^{18}O- and ^{16}O-enriched materials, which suggests that the depression in T_c is related to the mass of the oxygen isotope. The shifts that we observe in the nitrate-derived materials are surprisingly larger than the shifts observed in samples prepared by gas-phase exchange. Because we also observe surprisingly large differences in the structural parameters of the isotopically labeled nitrate-derived samples, the question is not how the heavier isotopes decrease T_c, but rather, how do the heavier isotopes effect the structure of the superconducting phase? Since there is no precedent for the preparation of highly enriched perovskites in the literature, we have little guidance as to what to expect structurally with high levels of isotopic enrichment. However, it is surprising to us that there is any structural perturbation upon enrichment with the heavier isotopes. Another point that we are addressing is the difference in gas-phase exchanged samples relative to the nitrate-derived samples. Currently, we are carefully characterizing a number of gas-phase-exchanged samples to determine the influence of copper deficiency and degree of exchange upon the structural and superconducting properties of these materials. Early indications are that copper deficiency in ^{16}O yttrium barium copper oxide (stoichiometry measured in individual grains by electron microprobe analysis) does not measurably effect T_c and that there is only a slight perturbation of the a lattice parameter. Gas-phase exchange of ^{18}O into copper deficient ^{16}O samples is not observed to effect T_c to any greater extent than exchange into stoichiometric "123" samples. At this time, it appears that copper deficiency in the nitrate-derived samples does not explain the structural differences or the changes in T_c we observe in materials prepared by the nitrate route. Clearly, the unusual physical properties of the isotopically enriched nitrate-derived yttrium barium copper oxide superconductors is a manifestation of the unusual chemistry of this system.

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