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Oxygen concentration effect on T_c of the Bi-Ca-Sr-Cu-O superconductor

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The T_c of $Bi_2CaSr_2Cu_2O_{8-x}$ can be shifted reversibly over a range of at least 15 K by changing the oxygen concentration. T_c shifts downward for increased oxygen content. This is opposite to the shift seen in $YBa_2Cu_3O_{7-\delta}$ and may be caused by reduction in the Fermi level reducing conductivity in the Bi-O layers. Oxygen concentration is varied by treatment in O_2 at appropriate pressures. The highest $T_c = 78.5$ K of the "80-K" phase is obtained by treating at 600 °C in 10^{-2}-bars oxygen. T_c shifts down to 65.4 K after treatment at 137 bars. The transitions remain sharp, with no evidence of significant structural change by x-ray powder diffraction. The original T_c is restored upon retreatment in O_2 at low partial pressure. The 110-K phase showed a much smaller shift ($\Delta T_c \sim 4$ K) after treatment in O_2 at 134 bars.

Variable oxygen stoichiometry is known to be important to the electrical conductivity of many metallic oxides[1,2] and to high-temperature superconductivity in the cuprates.[2] For example, stoichiometric La_2CuO_4, an insulator, is rendered conducting, and in fact superconducting,[3] by treatment in high-pressure oxygen (3 kbar). The T_c of $La_{2-x}Sr_xCuO_{4-y}$ increases by O_2 treatment and decreases on treatment under vacuum.[4] $YBa_2Cu_3O_{7-\delta}$ is rapidly and reversibly oxidized and reduced in the temperature range 400–800 °C,[5] and slow cooling in oxygen is necessary to produce a good superconductor[5,6] with high oxygen content ($\delta \leq 0.1$), a large Meissner effect, and $T_c \approx 92$ K. In contrast, Bi-Ca-Sr-Cu-O had previously been found to be relatively insensitive to oxygen treatment. After synthesis, it can be either slow cooled[7,8] or quenched[9] in air or O_2 with satisfactory results, though rapid quenching has been reported[10] to raise T_c. We find that, by treatment in O_2 at appropriate pressures between 10^{-2} and 10^2 bars, the oxygen content and the T_c of Bi-Ca-Sr-Cu-O can be varied.

Experiments were carried out on two materials. Bi-Ca-Sr-Cu-O I displayed a single superconducting transition at about 80 K, while Bi-Ca-Sr-Cu-O II contained two phases with transitions at ~80 and ~110 K. Both materials were prepared by solid-state reaction of Bi_2O_3(99.999% pure)+$CaCO_3$(99% pure)+$SrCO_3$(99% pure+1%$BaCO_3$)+CuO (99.999% pure) in gold-lined alumina boats. Bi-Ca-Sr-Cu-O I had a starting stochiometry of $Bi_{2.15}Ca_{1.17}Sr_{1.68}Cu_2O_{8+\delta}$ and was fired at 850 °C in 100 ml/min flowing oxygen for 1 h and furnace cooled (~9 °C/min to 400 °C, and then slower to room temperature). Bi-Ca-Sr-Cu-O II had a starting stochiometry of $BiCa_3SrCu_4O_{8+\delta}$ and was fired in air at 800 °C for 24 h, then at 870 °C for 100 h, followed by furnace cooling. All pellets were reground and mixed thoroughly to ensure sample uniformity, pressed into tablets, and then broken into pieces which were subjected to different high-pressure treatments.

Samples of Bi-Ca-Sr-Cu-O I were annealed in oxygen gas at various pressures, temperatures, and times using a commercial high-pressure oxygen furnace.[11] The sample treated in 10^{-2}-bar O_2 had the highest T_c, so it was chosen as the reference sample. Meissner diamagnetism (χ_m) measurements were made on a SHE superconducting quantum interference device (SQUID) magnetometer while cooling in a known constant field in the range 5–8 Oe. To minimize the uncertainties arising from variation of the demagnetizing factor with sample orientation, the samples were shaped as flakes, and the largest dimension was oriented along the field direction. For all samples, T_c was taken as the point where the χ_m curve crosses -5×10^{-5} emu/g (the smallest value which could be measured reliably).

The χ_m curves of Bi-Ca-Sr-Cu-O I samples annealed at 600 °C for 1 h in O_2 at pressures of 10^{-2}, 10^{-1}, 1, 8, and 137 bars are given in Fig. 1. With increased treatment pressure and oxygen content, T_c shifts progressively to lower temperature. The sharpness of the transitions is nearly maintained for pressures up to 8 bars; the transition of the sample treated at 137 bars is slightly

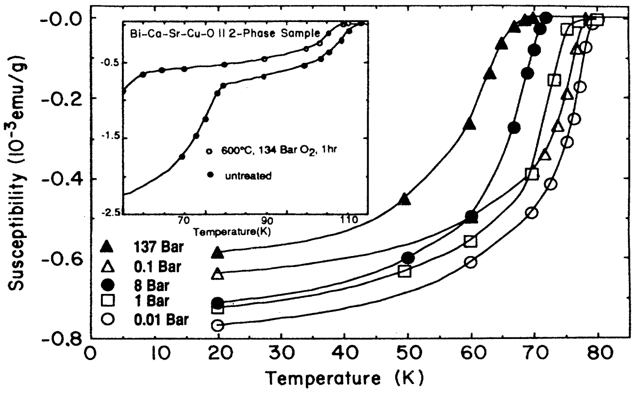

FIG. 1. Shift of T_c vs O_2 pressure during anneal at 600 °C. The χ_m curves of Bi-Ca-Sr-Cu-O I samples annealed for 1 h at 600 °C in oxygen at various pressures show that treatment at higher-pressure shifts T_c to lower temperature; the transition remains sharp. Inset: χ_m curves of Bi-Ca-Sr-Cu-O II, before and after treatment in 134 bars O_2 at 600 °C for 1 h. The shift of T_c of the 110-K phase is only ~4 K, while the T_c shift of the 80-K phase is much larger.

broadened. It is clear that the optimal O_2 treatment pressure is 10^{-2} bar or less at 600 °C.

To determine the sensitivity to cooling rate, a sample was cooled slowly (5 °C/min) after high-pressure treatment while another sample was cooled at 30 °C/min. Both samples showed the same T_c and χ_m. Therefore, all samples were cooled at 30 °C/min unless otherwise stated. The T_c of an untreated sample, which had been cooled from 850 °C in 1-bar O_2 after synthesis, is several degrees higher than that of a sample annealed at 600 °C in 1 bar. This indicates that the cooling rate of the untreated sample (~9 °C/min from 850 to 400 °C) was too rapid for equilibrium to be reached near 600 °C. Rapid cooling prevents significant oxygen pickup because of insufficient time for oxygen to diffuse into the sample. This may explain the observations of increase in T_c by rapid quench from ~850 °C (Ref. 10).

Increasing the high-pressure treatment time or temperature had little effect on the T_c shift, indicating that equilibrium oxygen content had been reached. Samples were treated at 600 °C in high-pressure O_2 (133–143 bars) for 1, 4, and 8 h; the T_c's were reduced to 65.4, 68.7, and 65.5 K, respectively. χ_m at 20 K was somewhat reduced, but there was no systematic change in T_c with increasing annealing time. The shifted transitions of the treated samples remained sharp, indicating that the treatment time was sufficient. If the time had been inadequate, the oxygen content near the surface and in the interior would have differed, resulting in a broadened transition. Figure 2(a) shows χ_m curves of samples treated at 600, 700, and 800 °C for 1 h. The T_c's were all in the range of 63–67 K. Increasing the treatment temperature from 600 to 700 °C resulted in ~25% reduction of χ_m at 20 K, and treatment at 800 °C caused about a 75% reduction. Consistent with this, Ginley *et al.*[12] found a total loss of superconductivity after annealing single crystals of Bi-Ca-Sr-Cu-O at 850 °C in 10^2 bars O_2 for 12 h.

The lowering of T_c by treatment in high-pressure oxygen is reversible, as shown in Fig. 2(b). Two samples, which had been treated in high-pressure O_2 (118–137 bars), were retreated at 10^{-1} bar at 600 °C for 1 h. The T_c's of the retreated samples and another sample which was only treated in 10^{-1} bar were within 1–2 K. The χ_m (20 K) values were nearly restored to that of the untreated sample.

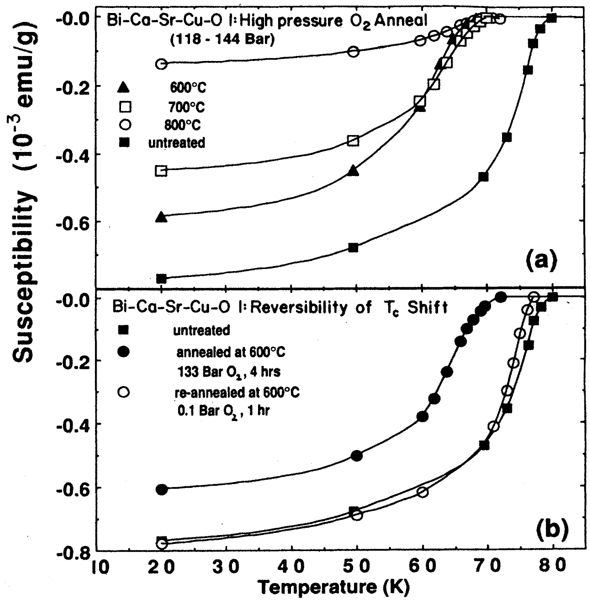

FIG. 2. (a) Effect of varying the temperature of high-pressure O_2 treatment: χ_m curves of Bi-Ca-Sr-Cu-O I samples annealed for 1 h at 600, 700, and 800 °C in high-pressure oxygen (137, 144, and 118 bars, respectively). The shifts in T_c are nearly the same, although treatment at higher temperature reduces the magnitude of the low-temperature susceptibility. (b) Reversibility of T_c shift upon reannealing in O_2 at low pressure (~10^{-1} bar): The χ_m curve of sample Bi-Ca-Sr-Cu-O I (○), annealed at 600 °C in 133-bars O_2 for 1 h and then reannealed at 600 °C in 10^{-1} bar, is shown along with the curve of the same sample (●) before reannealing. The T_c and susceptibility both have been nearly restored to the previous levels, indicated by the curve of the unannealed sample. We conclude that the shift of T_c caused by treatment in high-pressure O_2 is reversible.

X-ray powder diffraction was performed on the untreated, treated, and the retreated Bi-Ca-Sr-Cu-O I samples. The patterns were examined for the superconducting phase and for impurity phases and compared to the published structures.[8,9,13] All samples tested had a majority of the superconducting phase, along with impurities $CaCuO_2$, CuO, and SrO and an unidentified peak at $2\theta = 33.8°$. In the treated samples and retreated samples, the lines due to CuO and SrO decreased in intensity below the background level, while the peaks due to $CaCuO_2$ and the peak at $2\theta = 33.8°$ decreased but were still detectable, probably due to further reaction taking place during treatment. No new phases were observed after high-pressure treatment, and the lattice parameters a and c were unchanged to within ±1.5% and ±0.3%. No x-ray line splitting was observed in Bi-Ca-Sr-Cu-O treated in high- and low-pressure O_2. From our estimated resolution, we rule out any orthorhombic distortion greater than 0.4%.

The samples were weighed before and after treatment to estimate the changes in oxygen content. All samples lost weight during their first treatment except those annealed at 800 °C. This may indicate that the material had not been completely reacted, or that volatiles picked up during storage were driven off. Assuming that this irreversible weight loss is the same for all samples, we estimated the uptake of oxygen from the difference in weight loss between samples. In support of this procedure, weight loss was observed to be correlated with treatment pressure; samples treated at lower pressure had greater weight loss and higher T_c (see Fig. 3). For comparison among samples, weight differences were taken with respect the sample treated in 10^{-2}-bar O_2 which had the highest T_c and the most weight loss after treatment. Despite the substantial scatter, samples which were treated at 133–148 bars at 600 °C, had about +0.7% weight difference with respect to the 10^{-2}-bar treated sample. This corresponds to ~0.4 oxygen per formula unit of $Bi_2(Ca+Sr)_3Cu_2O_{8+\delta}$.

Preliminary measurements were made on two single

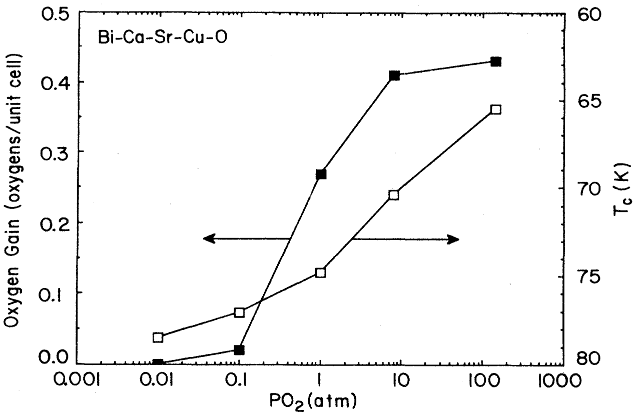

FIG. 3. Plot of $\log_{10}P(O_2)$ vs oxygen gain and vs T_c. With increasing pressure, T_c falls to ~65 K at 130-bars O_2 while the oxygen content increases by ~0.4 atoms/formula unit (note inverted temperature scale). We find that over the pressure range of $1-10^2$ bars, $T_c \approx 75$ K-4.4 $[\log_{10}P(O_2)]$.

crystals of Bi-Ca-Sr-Cu-O with initial $T_c=89$ K and large χ_m. One was treated at 600 °C at 132 bars for 2 h, and the other at 700 °C at 144 bars for 1 h. The T_c's were lowered to 80 and 84.5 K, respectively. The transitions remained sharp. The shift in T_c is comparable to that found in Bi-Ca-Sr-Cu-O I polycrystalline samples.

Two pieces of Bi-Ca-Sr-Cu-O II were subjected to different high-pressure O_2 treatments. One sample was treated at 600 °C for 1 h in 134 bars of O_2, while the other sample was treated at 800 °C for 2 h at 138 bars (see inset of Fig. 1). The shift in T_c of the low-temperature phase is difficult to determine because of the differing magnitudes of χ_m but appears to be ~20 K, reasonably consistent with the results for Bi-Ca-Sr-Cu-O I. In contrast, the shift is much smaller in the 110-K phase; we estimate $\Delta T_c \sim 4$ K.

We have found that increased oxygen content in the 80-K phase Bi-Ca-Sr-Cu-O depresses T_c by as much as 15 K, in contrast to $YBa_2Cu_3O_{7-\delta}$ and $La_{2-x}Sr_xCuO_{4-y}$, in which adding oxygen raises T_c. We also note that, in contrast to $YBa_2Cu_3O_{7-\delta}$ where only the Cu ions may take on several valencies, in Bi-Ca-Sr-Cu-O the Bi ions as well as the Cu ions are multivalent. Additional oxygen ions introduced by treatment in high-pressure O_2 may be located in the Bi-O layers, raising the oxidation state of the Bi ions. Further studies are now underway to confirm the location of the added oxygen.

Several band-structure calculations[14,15] of $Bi_2CaSr_2Cu_2O_8$ indicate that Bi-O bands above the Fermi level dip down to form pockets resulting in metallic conduction in the Bi-O layers. It has been suggested[15] that these conducting layers enhance the coupling between superconducting CuO_2 layers. In contrast, the Bi-O layers in $Bi_2Sr_2CuO_6$ give rise to bands which do not cross the Fermi level, or only cross in a very small region, and this may explain the much lower T_c (Ref. 15). Then, we may reason that in $Bi_2CaSr_2Cu_2O_8$ the added oxygen ions lower the Fermi level, reducing the metallic conductivity of the Bi-O layers, thereby depressing T_c. However, the band calculations should be used with caution, since they were done on idealized structures without incommensurate modulation which is known to be present.

The shift of T_c in the 110-K phase is much smaller, indicating either that this phase takes up less oxygen under the same conditions, or that the added oxygen is less effective in suppressing T_c. If band-structure calculations show that the Bi-O bands dip down farther below the Fermi level in this phase, the metallic character of the Bi-O layers would be less sensitive to a shift of the Fermi level caused by addition of oxygen, and this would explain the smaller shift in T_c.

Specific conclusions about the optimum processing conditions for the 80-K superconductor $Bi_2CaSr_2Cu_2O_8$ can be drawn from our experiments. To achieve the highest T_c, the O_2 partial pressure should be reduced to a low value (≤ 0.01 bar) while the sample is slowly cooled through the 600 °C range after synthesis. Treatment for 1 h at 600 °C is sufficient for T_c to reach its optimal value.

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[1] J. Smit and H. P. J. Wijn, *Ferrites* (Wiley, New York, 1959), pp. 229–236; F. S. Galasso, *Structure, Properties and Preparation of Perovskite-Type Compounds* (Pergamon, New York, 1969), pp. 63–70.

[2] J. M. Tarascon *et al.*, in *Proceedings of the Symposium on High Temperature Superconductors,* edited by D. U. Gubser and M. Schluter (Materials Research Society, Pittsburgh, 1987), Vol. EA-11, pp. 65–67.

[3] J. E. Schirber, B. Morosin, D. S. Ginley, W. Fu, E. L. Venturini, and J. F. Kwak, Physica C **152**, 121 (1988).

[4] J. M. Tarascon *et al.*, Science, **235**, 1373 (1987).

[5] D. E. Morris *et al.*, in Ref. 2, pp. 209–213.

[6] Y. K. Huang *et al.*, in Ref. 2, pp. 137–139; K. Nakamura *et al.*, *ibid.* pp. 239–242; Y. Kubo *et al.*, *ibid.* p. 267.

[7] H. Maeda, Y. Tanaka, M. Fukutomi, and T. Asano, Jpn. J. Appl. Phys. Lett. **27**, L209 (1988).

[8] J. M. Tarascon *et al.*, Phys. Rev. B **37**, 9382 (1988); J. B. Torrance *et al.*, Solid State Commun. **66**, 703 (1988); H. W. Zandbergen *et al.*, Nature (London) **332**, 620 (1988); M. A. Subramanian *et al.*, Science **239**, 1015 (1988).

[9] T. M. Shaw *et al.*, Phys. Rev. B **37**, 9856 (1988).

[10] J. L. Tallon *et al.*, Nature (London) **333**, 153 (1988); M. B. Maple *et al.*, Physica B&C (to be published); D. P. Almond *et al.*, Supercond. Sci. Tech. **1**, 123 (1988); Y. K. Huang *et al.*, J. Crystal Growth (to be published).

[11] Morris Research, 1862 Euclid Ave., Berkeley, CA 94709.

[12] D. S. Ginley *et al.* (upublished).

[13] R. M. Hazen *et al.*, Phys. Rev. Lett. **60**, 1174 (1988).

[14] M. S. Hybertsen and L. F. Mattheiss, Phys. Rev. Lett. **60**, 1661 (1988); H. Krakauer and W. E. Pickett, *ibid.* **60**, 1665 (1988); S. Massidda, J. Yu, and A. J. Freeman, Physica C **152**, 251 (1988); F. Herman, R. V. Kasowski, and W. Y. Hsu, Phys. Rev. B **38**, 204 (1988).

[15] P. A. Sterne and C. S. Wang, J Phys. C (to be published).