Processing, Structure, and High-Temperature Superconductivity

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The superconducting behavior in oxygen defect perovskite oxides is found to depend on the amount and order of oxygen in the structure. In the case of $Y_1Ba_2Cu_3O_{9-y}$, the highest and sharpest transitions are related to ordering of one-dimensional Cu-O ribbons in the structure which are in turn coupled to a network of adjacent 2-dimensional Cu-O sheets. The isostructural rare earth derivatives of $Y_1Ba_2Cu_3O_{9-y}$ are found to display similar behavior.

Since the initial discovery by Bednorz and Muller (1) of higher temperature superconductivity, new breakthroughs and advances in this field have continued at a furious pace (2). Within the span of a few months, the superconducting transition temperature (Tc) of 35 K in the layered perovskite $La_{2-x}Ba_xCuO_{4-y}$ jumped to near 100 K in the distorted cubic perovskite $Y_1Ba_2Cu_3O_{9-y}$. Quite early it was recognized that the superconducting properties of $Y_1Ba_2Cu_3O_{9-y}$ depended on the processing conditions (3,4). This can be understood by considering the idealized structure of $Y_1Ba_2Cu_3O_{9-y}$ which is shown in Figure 1. This structure involves an ordering of Ba-Y-Ba in triplets (5) and in principle, can accommodate nine oxygens. Experimentally (4,6,7), however, this value has been determined to be approximately seven. How the oxygens distribute themselves in the structure turns out to be very dependent on processing conditions and is the key to achieving the highest and sharpest superconducting transitions.

Numerous X-ray and neutron diffraction studies (1,8) have determined that the Y plane is vacant, accounting for one oxygen vacancy. The Cu basal plane at the end of the unit cell accounts for the other vacancy which is split between them. It is the ordering of oxygen in these basal planes that appears to be a critical structural feature for high Tc(9). This ordering gives rise to 1-dimensional CuO_2 ribbons along the b-axis. These 1-D ribbons are coupled to two adjacent 2-dimensional networks of Cu-O sheets which lie in the a-b plane of the unit cell (Figure 1).

The ordering of the oxygens in these 1-D ribbons is intimately dependant on the processing of $Y_1Ba_2Cu_3O_{9-y}$. Further, the amount of oxygen can also be varied by different processing conditions. These compounds belong to a more general class of oxygen defect copper perovskites which are well-known to accommodate variable oxygen depending on the temperature at which they are prepared (10).
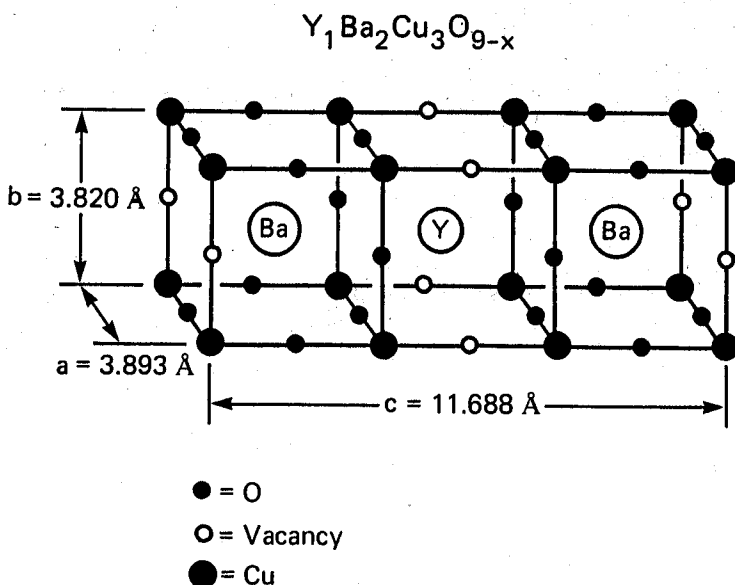
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$$Y_1Ba_2Cu_3O_{9-x}$$

$b = 3.820\ \text{Å}$

$a = 3.893\ \text{Å}$

$c = 11.688\ \text{Å}$

● = O

○ = Vacancy

⬤ = Cu

Figure 1.

Thermal gravimetric analysis (TGA) reveals facile and reversible movement of oxygen in the 500-600 C range for $Y_1Ba_2Cu_3O_{9-y}$ (7,9,11) which decreases with increasing temperature. If samples are cooled too rapidly from high temperature to permit thermodynamic equilibrium to be obtained, then, lower amounts and disordering of oxygen in the structure can occur.

The sensitivity of the superconducting transition to processing is shown in Figure 2 where resistance vs. temperature plots are given for different preparative conditions. The highest and sharpest transition is obtained when the sample is heated in oxygen at 900 C and then allowed to cool slowly to room temperature over about 5 hours (2). More rapid cooling gives superconducting transitions which are considerably depressed and broadened. The partial pressure of oxygen is also important, since even with slow cooling, air annealed samples have lower and broader transitions. These changes in Tc appear to be intrinsic to the electronic structure of $Y_1Ba_2Cu_3O_{9-y}$ and not simply due to changes in the granular nature of the samples. This is seen in magnetic measurements which are plotted in Figure 3 on the same samples shown in Figure 2. The temperature of the diamagnetic shift moves to lower temperatures as would be expected if superconductivity is being changed on a microscopic scale (12). The magnitude of the diamagnetic shift is also considerably reduced.

With rapid cooling, both the amount and ordering of oxygen in the sample decreases in the basal planes. In the X-ray patterns shown in Figure 4, these changes are manifested by a decrease in the orthorhombic character of the unit cell ($a \neq b$). By following diffraction lines near 46-48 °, which are sensitive to changes in the a and b lattice dimensions in the unit cell, one can follow the trend to a more tetragonal unit cell ($a = b$). When the sample is heated in argon, the unit cell appears tetragonal and an insulating material is obtained. This pattern of
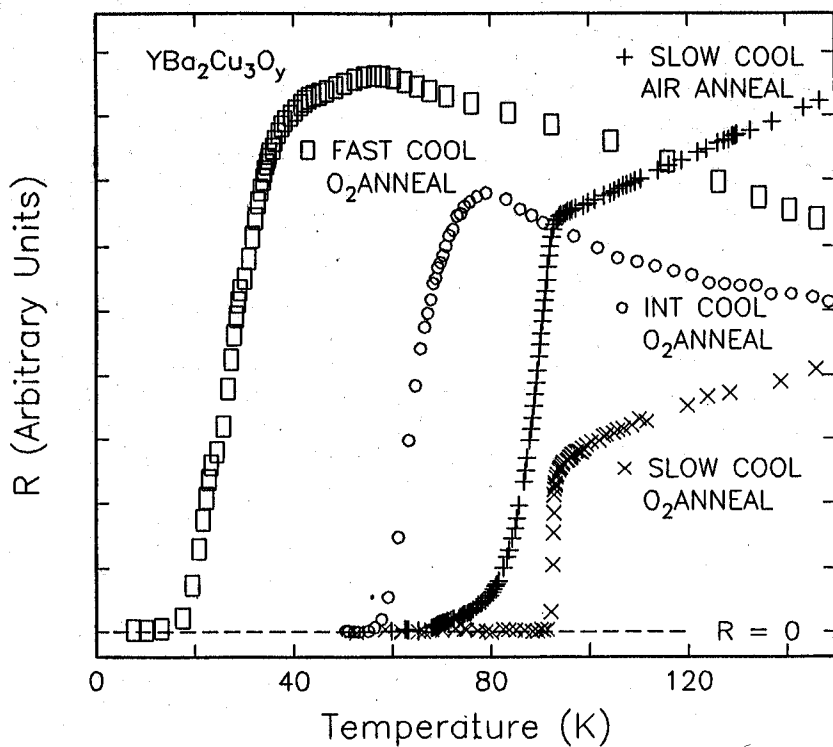
Figure 2.

change in the unit cell is paralleled in high temperature X-ray analysis of $Y_1Ba_2Cu_3O_{9-y}$ which shows the same transformation to a tetragonal unit cell around 700 C (7,9). Further, derivatives of $Y_1Ba_2Cu_3O_{9-y}$, where Y is replaced by rare earth elements, also show similar behavior as illustrated in Figure 5. Again the trend to a more tetragonal unit cell leads to degraded and superconducting behavior. In fact, in the case of $Pr_1Ba_2Cu_3O_{9-y}$, the orthorhombic splittings seen in the Y compound are not evident (4) and this compound displays insulating electrical properties.

The fact that Tc is essentially unchanged by replacement of Y with the magnetic rare earth elements points to the Cu-O sublattice as the source of the superconducting properties of $Y_1Ba_2Cu_3O_{9-y}$. Mixtures of rare earths or alkaline earths (2,13) also do not affect Tc, again emphasizing the key role of the Cu-O sublattice.

The sensitivity of superconductivity to processing appears to be important in another newly discovered perovskite compound. Undoped La_2CuO_{4-y} has been extensively studied since its initial preparation in 1961. However, it is only recently that superconductivity has been found in this material (4-6). In this compound only a small fraction of the sample is actually going superconducting and the structure responsible for this behavior is unknown. The presence of small amounts of unreacted lanthanum oxide in our final product, suggests that some lanthanum deficient phases might be forming. This could give rise to Cu+3, a factor which

has been recognized since Bednorz and Muller's initial discovery (1,3,14) as important to superconductivity in these copper oxide compounds. On standing, samples of La_2CuO_{4-y} slowly lose oxygen, and eventually become non-superconducting which may account for this behavior not being discovered earlier (14).

The field of perovskite superconductors has witnesses an explosion of interest and activity over this past year. While much remains to be done to better understand these compounds, some general structural and chemical features necessary for the superconducting behavior are beginning to emerge. These can be summarized as:

1. The Cu-O sublattice is the source of the superconducting behavior. The ordering of this sublattice is very dependent on the processing.

2. The low dimensional electronic structure of the Cu-O sublattice appears to be a general and important feature in all of the perovskite superconductors.

3. The stabilization of the Cu+3/Cu+2 mixed valent states in the Cu-O sublattice appears to be a key reason why these materials exhibit high temperature superconductivity.
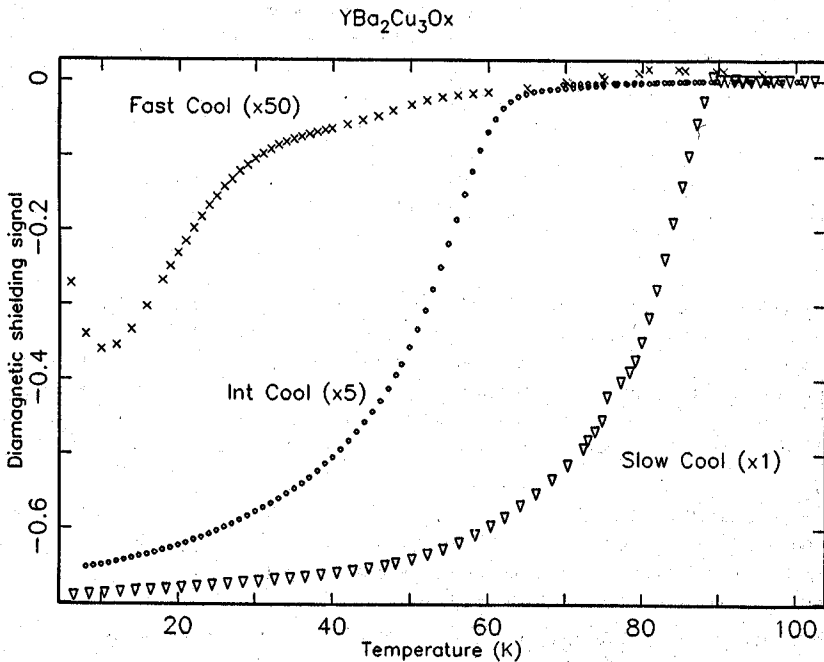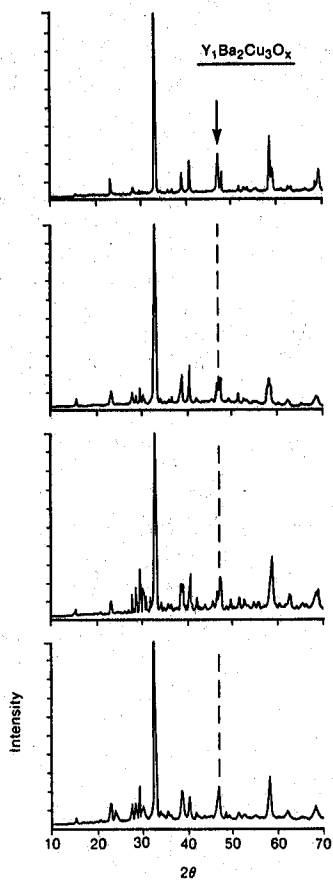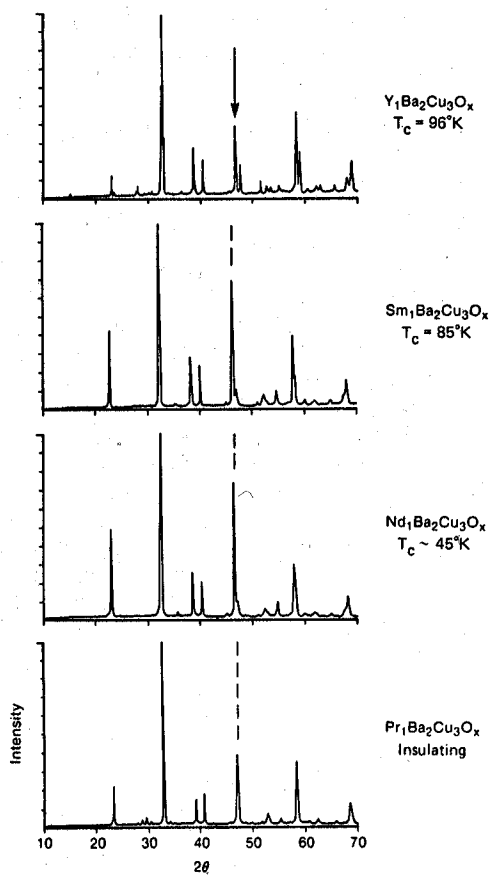

Figure 3.

Figure 4.

Figure 5.

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