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Solid-State Chemistry of High-Temperature Oxide Superconductors: The Experimental Situation*

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High-temperature superconductivity in oxides of the type (La, $Ln)_{2-x}Ba_x(Sr)_xCuO_4$, $Y(Ln)Ba_2Cu_3O_{7-\delta}$, $La_{3-x}Ba_{3+x}Cu_6O_{14}$, and related systems is discussed with emphasis on aspects related to experimental solid-state chemistry. All of these oxides possess perovskite-related structures. Oxygen-excess and La-deficient La_2CuO_4 also exhibit superconductivity in the 20–40 K just as $La_{2-x}Ba_x(Sr_x)CuO_4$; these oxides are orthorhombic in the superconductivity phase. The crucial role of oxygen stoichiometry in the superconductivity of $YBa_2Cu_3O_{7-\delta}$ ($T_c = 95 \pm 5$ K) is examined; this oxide remains orthorhombic up to $\delta \approx 0.6$ and becomes tetragonal and nonsuperconducting beyond this value of δ. Oxygen stoichiometry in this and related oxides has to be understood in terms of structure and disorder. The structure of $La_{3-x}Ba_{3+x}Cu_6O_{14}$ is related to that of $YBa_2Cu_3O_7$, the orthorhombic structure manifesting itself when the population of O1 oxygens (along the Cu–O–Cu chains) is preponderant compared to that of O5 oxygens (along the *a*-axis); nearly equal populations of O1 and O5 sites give rise to the tetragonal structure. A transition from a high-T_c (95 K) superconductivity regime to a low-T_c (~60 K) regime occurs in $YBa_2Cu_3O_{7-\delta}$ accompanying a change in δ. There is no evidence for Cu^{3+} in these nominally mixed valent copper oxides. Instead, holes are present on oxygens giving rise to O^- or O_2^{2-} species, the concentration of these species increasing with the lowering of temperature. Certain interesting aspects of the superconducting oxides such as domain or twin boundaries, Raman spectra, microwave absorption, and anomalous high-temperature resistivity drops are presented along with the important material parameters. Preparative aspects of the superconducting oxides are briefly discussed. Phase transitions seem to occur at T_c as well as at ~240 K in $YBa_2Cu_3O_7$.

1. Introduction

The phenomenon of superconductivity has been an area of vital interest for the past few decades. Metals, alloys, molecular compounds, and polymers have been investigated for superconductivity, but the transition temperature did not cross the 23 K threshold until the beginning of 1987. The average rate of increase in T_c was about 3 K per decade. The highest T_c's in the 20 K region were exhibited by A15 compounds such as Nb_3Ge. Some of the more interesting chemical systems examined were Chevrel phases, organic donor–acceptor systems, and charge-transfer salts. Among the metal oxides, the highest T_c's were found in $LiTi_2O_4$ (*1*) and $BaPb_{1-x}Bi_xO_3$ (*2*), both close to 13 K. The possibility of high-temperature superconductivity in metal oxides was first demonstrated by Bednorz and

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Müller (*3*) in the La–Ba–Cu–O system. It was soon found that these oxides had the general formula $La_{2-x}Ba_xCuO_4$ and possessed the quasi-two-dimensional K_2NiF_4 structure; the analogous Sr compounds also showed high T_c superconductivity, the maximum T_c (20–40 K) in the Sr and Ba systems being at $x = 0.2$ and 0.15, respectively (*4–6*). Soon after this discovery, superconductivity above liquid nitrogen temperature was reported in the Y–Ba–Cu–O system (*7*); the phase responsible for superconductivity in this system was found to have the composition $YBa_2Cu_3O_{7-\delta}$ with a defect perovskite structure (*8, 9*).

The discovery of superconductivity above the liquid nitrogen temperature in metal oxides has raised much hope because of obvious technological implications. Of equal importance is the fact that this has given a big boost to research in the solid-state chemistry of metal oxides. The unprecedented excitement caused by the discovery of high T_c oxide superconductors as well as the flood of research publications and conference proceedings on the subject appearing in the last few months have prompted me to write this brief overview article, to highlight the major experimental findings (up to November 1987) of relevance to solid-state chemistry. In writing such an article, it was necessary to exercise the difficult discipline of quoting only representative references which would permit the reader to obtain the necessary details. If I have ignored some important references, I apologize for any errors in judgment.

2. La_2CuO_4 and Its Derivatives

Oxides of the general formula A_2BO_4 possess the K_2NiF_4 structure wherein the *B* ions interact only in the *ab* plane. The structure and properties of oxides of the K_2NiF_4 structure have been examined in some detail recently (*10*). La_2CuO_4 which is a member of this family, exhibits low resistivity (~1 ohm · cm) at room temperature, but the resistivity increases with decreasing temperatures, with a tendency to become antiferromagnetic. Electrical and magnetic properties of La_2CuO_4 are very sensitive to oxygen stoichiometry. Antiferromagnetism in La_2CuO_4 has been recently established by neutron diffraction and scattering; T_N is close to 290 K with a low-temperature Cu moment of 0.43 μ_B (*11*). The oxide undergoes an orthorhombic-tetragonal distortion at 505 K. It has been suggested that La_2CuO_4 is in a two-dimensional quantum fluid state wherein the spins are ordered instantaneously over long distances, but no measurable time-averaged moment has been detected (*11*). More interestingly, oxygen-excess La_2CuO_4 prepared under high oxygen pressure or by plasma oxidation becomes superconducting near 40 K (*12, 13*); lanthanum deficiency (e.g., $La_{1.9}CuO_4$) gives rise to superconductivity even with ordinary ceramic preparations (*14*) as shown in Fig. 1. It is to be noted that both oxygen-excess and La-deficiency give rise to a nominal mixed valency of Cu as in $La_{2-x}Ba_xCuO_4$.

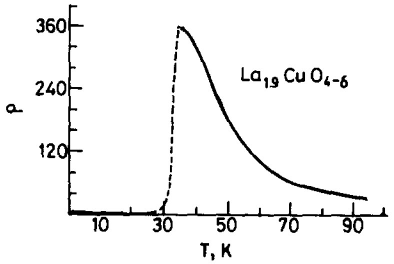

FIG. 1. Superconducting transition in La-deficient La_2CuO_4 [from Ref. (*14*)].

When La in orthorhombic La_2CuO_4 is partly replaced by Sr or Ba, the structure becomes tetragonal at room temperature, for $x > 0.05$ in $La_{2-x}Ba_x(Sr_x)CuO_4$. These oxides exhibit superconductivity in the 20–40 K range (*4–6*), the T_c peaking near $x = 0.15$ and 0.2 (nom.) for Ba and Sr, respectively. A Meissner effect up to 70% of the

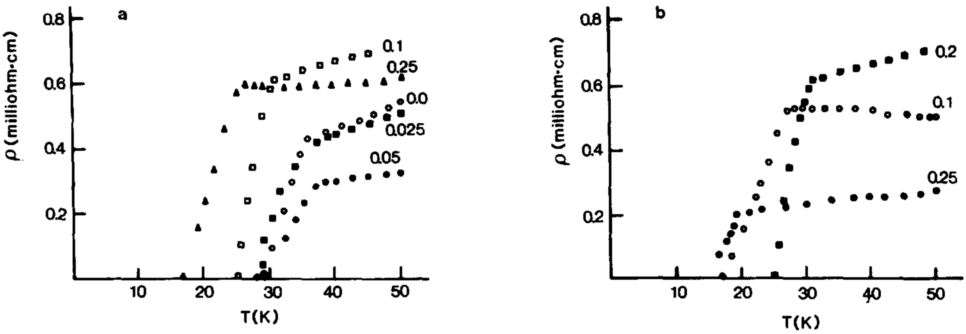

FIG. 2. (a) Resistivity data of $(La_{1-y}Pr_y)_{1.8}Sr_{0.2}CuO_4$ for different values of y. (b) Resistivity data of $(La_{0.9}Pr_{0.1})_{2-x}Sr_xCuO_4$ for different values of x [Ref. (*15*)].

ideal value has been reported in these oxides. $La_{2-x}Ca_xCuO_4$ also exhibits superconductivity, but the T_c values are much lower (*15, 16*); for example, the maximum value of T_c is 20 K for $x = 0.1$ (compared to 26 K when $x = 0.2$ Sr). The room-temperature structure of $La_{1.85}Sr_{0.15}CuO_4$ involves copper atoms with a tetragonally elongated octahedral coordination and Cu–O distances of 1.898 and 2.406 Å; La and Sr sites have ninefold oxygen coordination (*17*). Superconductivity is found in the 15–30 K region in oxides of the type $(La_{1-y}Ln_y)_{2-x}Ba_x(Sr_x)CuO_4$ where Ln = Pr, Nd, Eu, Gd, etc. (*15, 16, 18*) as shown in Fig. 2. In all such systems, T_c reaches a maximum at a particular value of x suggesting the importance of strong correlations (*19*).

$La_{2-x}Ba_x(Sr_x)CuO_4$ undergoes a tetragonal-orthorhombic distortion near 180 K, the orthorhombic distortion increasing smoothly (through T_c) down to 30 K (*20*). Static and dynamic aspects of the tetragonal-orthorhombic distortion in $La_{2-x}Sr_xCuO_4$ have been studied by neuron scattering and other techniques and a classical soft phonon behavior involving CuO_6 octahedra has been observed (*21*). ESR studies have thrown light on the microscopic magnetic interactions in these oxides (*22*).

The replacement of Cu in $La_{2-x}Ba_x(Sr_x)CuO_4$ by Ni even to a small extent lowers the T_c and superconductivity is destroyed at ~5% substitution; Zn substitution has a similar effect although the ionic sizes of Zn^{2+} and Ni^{2+} differ from that of Cu^{2+} in the opposite directions (*13, 15*).

It is noteworthy that electrical resistivity values of $La_{2-x}Ba_x(Sr_x)CuO_4$ in the normal state are generally in the 10^{-2}–10^{-3} ohm · cm range which correspond to Mott's minimum metallic conductivity (*18*). These oxides are typical type II superconductors with H_{c1} = 400 Oe (4.7 K); H_{c2} is in the range 40–70 T (*23*). Far infrared measurements show the superconducting gap to be ~50 cm^{-1} (*24*). The magnetic penetration depth in $La_{1.85}Ba_{0.15}CuO_4$ is reported to be ~2000 Å (*25*).

3. $YBa_2Cu_3O_{7-\delta}$ and Related Oxides

Superconductivity above liquid N_2 temperature was reported in $Y_{1.2}Ba_{0.8}CuO_4$ by Wu *et al.* (*7*) who prepared this composition by analogy with the $La_{2-x}Ba_xCuO_4$ system, expecting that the smaller Y ion would increase T_c due to chemical pressure effects. This composition was actually biphasic consisting of green (insulating) Y_2BaCuO_5 and a black oxide. Since Y_2CuO_4 itself is not known to crystallize in the K_2NiF_4 structure, Rao and co-workers (*9*) examined the Y–Ba–Cu–O system starting with compositions of the type $Y_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$, by analogy with the defect perovskite $La_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ described by

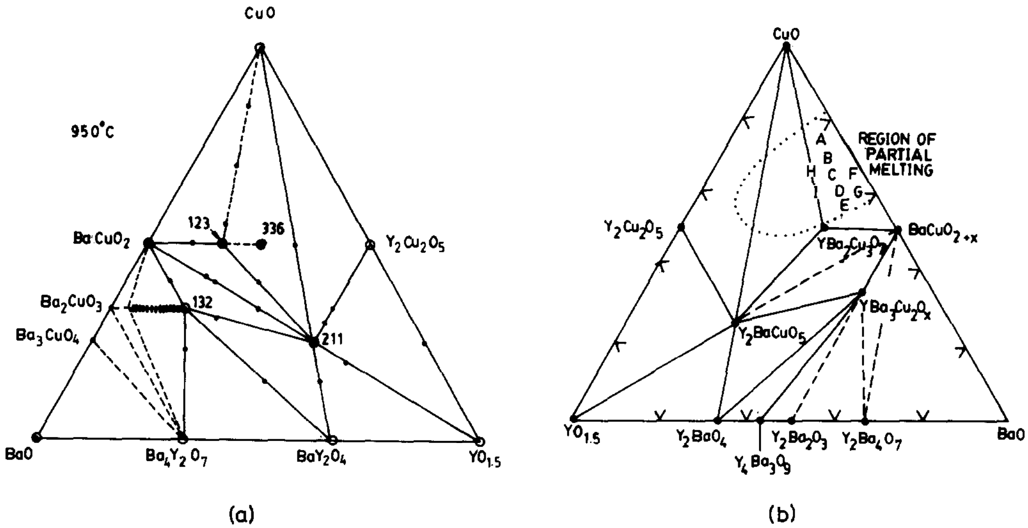

FIG. 3. (a) Pseudo-ternary phase diagram of the Y_2O_3–BaO–CuO system at 1220 K slightly modified from that published by Clarke (*75*). Here, 123, 211, and 132 refer to $YBa_2Cu_3O_{7-\delta}$, Y_2BaCuO_5, and $YBa_3Cu_2O_x$, respectively. The dashed line joining CuO to the superconducting phase (123) is a joint at 1170 K but is interrupted by melting 1200 K. The hatched line shows a region of apparent solid solution and the dotted lines emanating from it reflect uncertainty in end-member composition. We have shown the 336 oxide $Y_3Ba_3Cu_6O_{14}$ or the $Y(Ba_{2-x}Y_x)Cu_3O_7$ system although this system is likely to be stable around 1120 K or lower. (b) Phase diagram of the same system at 1240 K from Roth *et al.* (*76*).

Er-Rakho *et al.* (*26*). The perovskite phase responsible for high T_c (95 ± 5 K) superconductivity in the Y–Ba–Cu–O system is orthorhombic $YBa_2Cu_3O_{7-\delta}$ (*8*, *9*); the highest Meissner effect found hitherto in this oxide is ~80%. The phase diagram of the Y_2O_3–BaO–CuO system has been investigated by several workers [see, for example, Ref. (*27*)], and among the many phases, only $YBa_2Cu_3O_{7-\delta}$ has been clearly established to be a high-T_c superconductor (Fig. 3). $Y_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ with $x = 0.0$–0.5 also seems to be superconducting, although the phasic purity of these compositions is not fully established.

Superconductivity in $YBa_2Cu_3O_{7-\delta}$ is extremely sensitive to oxygen stoichiometry. Samples where the oxygen content is higher than 7 have also been made and they show $T_c \approx 90$ K up to 7.2 (*28*). When $\delta \geq 0.6$, the oxide becomes tetragonal and nonsuperconducting; oxygen is readily intercalated into the oxygen-deficient samples until the stoichiometry becomes close to $YBa_2Cu_3O_7$. In Fig. 4, the variation of the unit cell parameters of $YBa_2Cu_3O_{7-\delta}$ with δ is shown; notice how the structure becomes tetragonal at $\delta \approx 0.6$. The unit cell volume increases with δ from ~173.7 Å^3 ($\delta = 0.0$) to ~176.2 Å^3 ($\delta = 1.0$).

The structure of orthorhombic $YBa_2Cu_3O_{7-\delta}$ is interesting. It has corner-linked CuO_4 planar groups connected not only as sheets in the *ab* plane, but also as chains parallel to the *b*-axis (*29*, *30*) as shown in Fig. 5(a). Of the two sets of Cu atoms, one is surrounded by four oxygens at 1.929 and 1.960 Å; a fifth oxygen is located at 2.30 Å, giving rise to a square-pyramidal coordination for Cu, forming puckered CuO_2 sheets. In the other set, the Cu atoms are surrounded by four oxygens at 1.942 Å and 1.845 Å; here, the oxygen atoms form near rectangles connected by vertices, and resulting in the chains along the *b*-axis. These chains are responsible for the orthorhombic structure. In the tetragonal $YBa_2Cu_3O_6$ (δ = 1.0), the chains are missing as shown in Fig. 5(b) and the oxygens occupy only two-thirds of the perovskite anion sites and are ordered in such a manner that one-third of the Cu atoms is twofold coordinated while two-thirds is fivefold coordinated (*31, 32*); the Cu–O4 bond in this oxide is indeed very short (~1.80 Å). In Fig. 5(c), we also show a tetragonal phase where oxygen disorder (δ = 0.3–1.0) can give rise to distorted CuO_6 octahedra (*33*). Oxygen nonstoichiometry in $YBa_2Cu_3O_{7-\delta}$ has to be understood in terms of both disorder and structural distortion. If the O1 sites (oxygen along the chains) are predominently populated relative to the O5 sites (along *a*-axis) the structure is orthorhombic and the material is a superconductor. If the O1 and O5

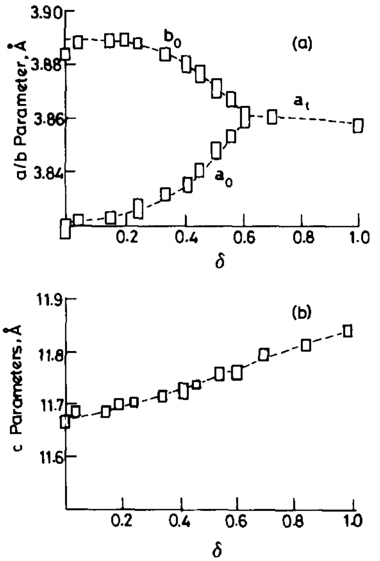

FIG. 4. Variation of the unit cell parameters of $YBa_2Cu_3O_{7-\delta}$ with δ. Notice that the orthorhombic a_0 and b_0 parameters merge to give the tetragonal a_t parameters around δ = 0.6.

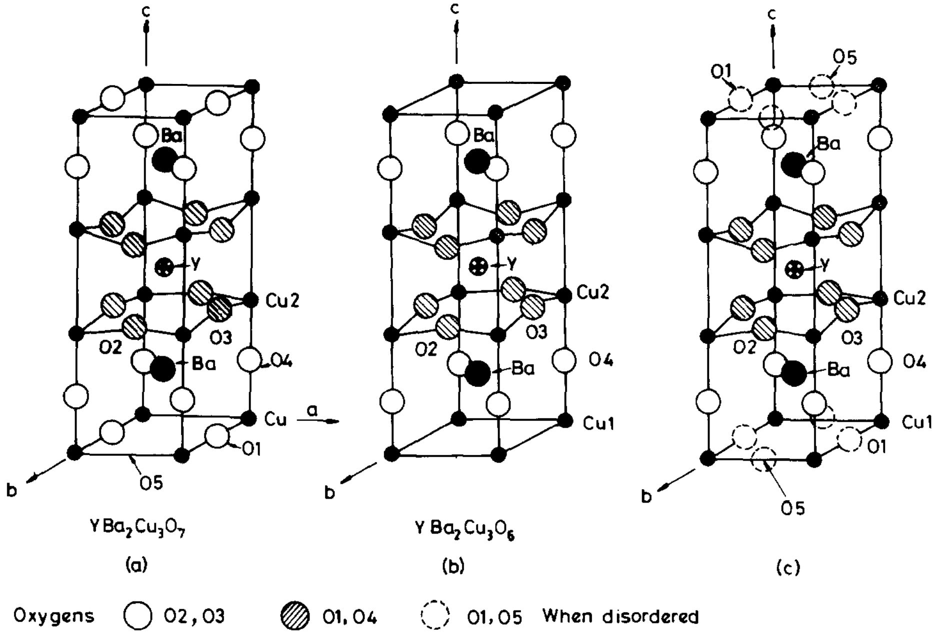

FIG. 5. Structures of $YBa_2Cu_3O_{7-\delta}$: (a) orthorhombic structure of the superconducting phase with δ = 0.0; (b) tetragonal structure of the nonsuperconducting phase with δ = 1.0; (c) disordered structure of the tetragonal phase involving CuO_6 octahedra with a small site occupancy. If the chain oxygen (O1) sites are predominantly occupied relative to oxygens along the *a*-axis (O5 sites), the structure will be orthorhombic; equal population of O1 and O5 sites makes it tetragonal. The Cu–O4 distance varies with stoichiometry. In (a) the O1–O4 distance is quite short (~2.6 Å).

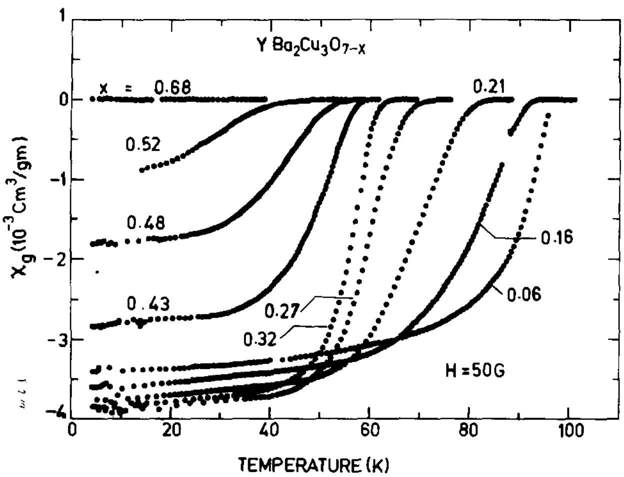

FIG. 6. Meissner effect (at 50 G) of $YBa_2Cu_3O_{7-\delta}$ for different values of δ [from Ref. (*39*)].

sites are equally populated, the structure is tetragonal. Ordering of oxygens in the chains seems crucial for high-T_c superconductivity. A slight off-site displacement of the O1 (possibly of O5) oxygens also must be considered. Quenching $YBa_2Cu_3O_7$ from high temperature results in oxygen loss and the associated orthorhombic-tetragonal transition occurs in the 620–700 K range, depending on the oxygen pressure, around $\delta \approx 0.5$ (*33*).

Superconducting oxides of the general formula $LnBa_2Cu_3O_7$ with Ln = Nd, Sm, Eu, Gd, Dy, Ho, Er, Tm, Yb, Lu have all been prepared; they are all orthorhombic similar to $YBa_2Cu_3O_7$ with $T_c \approx 90$ K (*34–37*). Magnetic states seem to coexist along with superconductivity in the oxides containing paramagnetic lanthanides such as Gd (*38*). Oxides of this general composition with the variable valence elements Ce, Pr, and Tb are not superconducting and their structures seems to be different. $LaBa_2Cu_3O_{7-\delta}$ (orthorhombic) also contains Cu–O–Cu chains and is superconducting; the T_c, however, varies widely (40–90 K) depending on the preparative conditions. Observation of high-T_c superconductivity in a number of lanthanide compounds analogous to $YBa_2Cu_3O_7$ indicates that the Y/Ln ion does not have a major role to play in the superconductivity except to hold the structure together. At T_c, there appears to be an isostructural phase transition, at least in $YBa_2Cu_3O_7$, as revealed by specific heat, nuclear quadrupole resonance, thermal expansion, and other measurements.

The variation of the superconducting transition temperature of orthohombic $YBa_2Cu_3O_{7-\delta}$ with δ(0.0–0.6) is most interesting. In Fig. 6, the magnetic susceptibility data of $YBa_2Cu_3O_{7-\delta}$ for different values of δ (*39*) are shown. In Fig. 7, resistivity data (*40*) of different compositions are presented. We have plotted the T_c values from resistivity and susceptibility data against δ in Fig. 8. While T_c remains nearly constant near 90 K when δ = 0.0–0.2 it drops to a lower value (~60 K) above δ = 0.2 showing a plateau-like behavior. Since in this plateau region, the Cu–O–Cu chains of $YBa_2Cu_3O_7$ are deficient in oxygen, it is possible that the ~60 K plateau is more characteristic of the CuO_2 sheets in the orthorhombic structure, the 90 K T_c being more characteristic of the Cu–O–Cu chains in the presence of the CuO_2 sheets (the sheets getting coupled through the chains). Figure 8 may

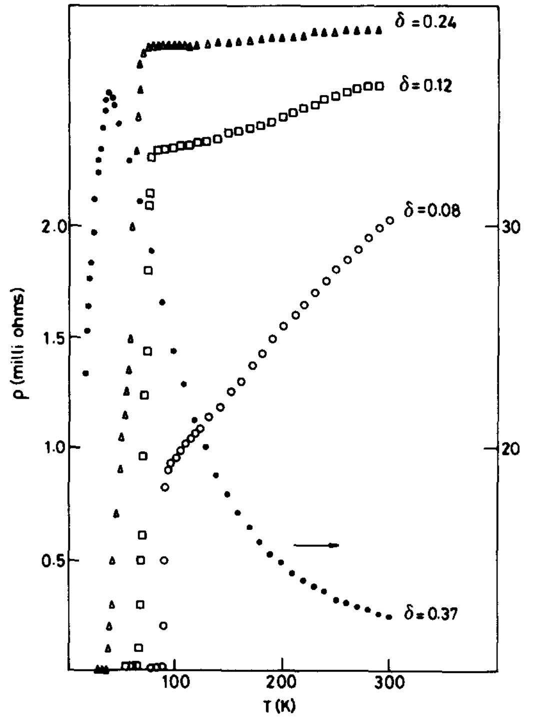

FIG. 7. Electrical resistivity behavior of $YBa_2Cu_3O_{7-\delta}$ for different values of δ [from Ref. (*40*)].

be taken to signify a transition from chain-type superconductivity to sheet-type superconductivity in $YBa_2Cu_3O_{7-\delta}$, brought about by a change in oxygen stoichiometry. Accordingly, the Hall coefficient and the volume fraction subject to the Meissner effect are also insensitive in the plateau region; Although the actual T_c values at different δ vary slightly among different workers (*41*), there is little doubt regarding the presence of the constant low-T_c plateau at ~0.2 ≤ δ ≲ 0.5. Whether there is a unique structural feature in the plateau region is not yet certain, although certain superlattice spots in diffraction patterns (or diffuse scattering) seem to have been noticed in this composition range. Electrical resistivity and magnetic susceptibility reflect the unique nature of the compositions in the plateau region.

Several workers have in recent months synthesized a variety of derivatives of $YBa_2Cu_3O_{7-\delta}$. The Y/Ba or *Ln*/Ba ratio in Y(*Ln*)$Ba_2Cu_3O_7$ has been varied (*37, 42*), with a slight alteration of T_c. Ba has been partly replaced by La causing a decrease in the lability of oxygen. Substitution of Ba by Sr or *Ln* in $YBa_2Cu_3O_{7-\delta}$ lowers the T_c (*43*). Cu in $YBa_2Cu_3O_{7-\delta}$ has been partly substituted by Zn, Ni, Co, Fe, and other ions, and such substitutions generally lower T_c or destroy the superconductivity, the structure tending to be tetragonal or/and oxygen-deficient (see, for example, Refs. (*13, 44*)). Weakly orthorhombic or nearly tetragonal samples prepared by low-temperature methods exhibit low T_c or no superconductivity. Oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ (δ up to 0.7) have been prepared in the orthorhombic structure by the low-temperature Zr-getter technique; these samples show superconductivity with T_c exhibiting a plateau in the δ = 0.3–0.45 region (*45*); T_c, however, decreases markedly when δ > 0.45. The question then arises as to whether the orthorhombic structure (with Cu–O–Cu chains) is necessary to achieve a high T_c. There are some unconfirmed reports of tetragonal analogs of $YBa_2Cu_3O_7$ exhibiting

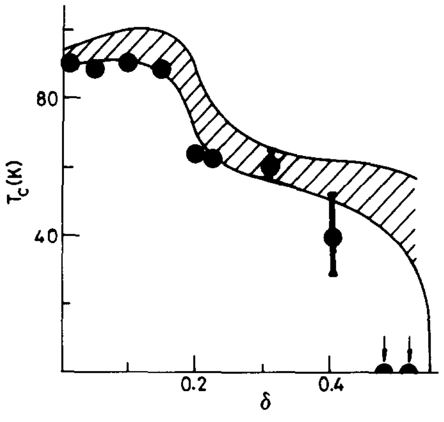

FIG. 8. Variation of T_c with δ. Magnetic measurements of Johnston *et al.* [Ref. (*39*)] are indicated by the cross-hatched region. Our resistivity data is shown by full dark circles.

high T_c in the 80–90 K range (e.g., $YBa_2Cu_{3-x}Ga_xO_7$); structures of such oxides however need to be confirmed by neutron studies, since X-ray diffraction alone would not be able to establish unequivocally the tetragonality of the structure. Another possibility is that the tetragonal structure arises from a randomness of Cu–O chains (along *a*- and *b*-axes) or that it is due to the absence of long-range order with respect to the Cu–O chains.

Samples of $YBa_2Cu_3O_{7-\delta}$ which show high-T_c superconductivity exhibit fairly high resistivity (Mott's minimum metallic conductivity range) in the normal state (*18*). The absolute thermopower and Hall effect measurements of the samples with $\delta < 0.5$ show that oxides of these compositions are *p*-type (hole) conductors. The electronic properties of $YBa_2Cu_3O_{7-\delta}$ [as well as of $La_{2-x}Ba_x(Sr_x)CuO_4$] are anisotropic. A "superconducting glass-type" behavior has been noticed in these oxides by Müller and others based on magnetic measurements.

Some of the important properties of this type II superconductor are summarized below (*46*):

Hall carrier density: 4×10^{21} cm^{-3} (for a material of resistivity $\sim$ 400 $\mu\Omega$ cm just above the T_c).

$dH_{c2}/dT = 2T/\mathrm{K}$; BCS coherence length $\approx$ 1.4 nm; London penetration depth $\approx$ 200 nm; mean free path $\approx$ 1.2 nm.

$H_c(\mathrm{O}) \approx 1T$.

$H_{c2}(\mathrm{O}) \approx 120T$.

Critical current density: In ceramic samples, $\sim 10^3$ A/cm^2 at 77 K; in films (on $SrTiO_3$) $\sim$ 10^5 A/cm^2 at 77 K; at 4.2 K, $\sim 10^6$ A/cm^2 (in crystals and films).

Depairing current density: 10^7–10^8 A/cm^2 (estimated).

A critical current density of $\sim 10^5$ A/cm^2 is essential for viable magnet and other applications at 77 K. A magnetic penetration depth of 225 ± 75 Å has been recently reported as an upper limit for $YBa_2Cu_3O_7$ (*25*). Recent specific heat (*c*) measurements on $YBa_2Cu_3O_7$ show $\Delta c/T_c$ to be $\sim$48 mJ/mol · K^2 giving rise to a $\Delta c/\gamma T_c$ of 1.33; there is a large temperature dependence of the Debye temperature, probably due to the large vibrational amplitudes of the loosely bound O1 and O2 oxygens in the orthorhombic structure (*47*). It is interesting to consider whether this feature has a bearing on the tendency to form peroxide species (see Section 4). It is to be noted that the O1–O4 distance is rather short (Fig. 5a).

Oriented thin films of superconducting $YBa_2Cu_3O_{7-\delta}$ have been prepared by employing electron beam or pulsed laser evaporation (*48*). The substrate used is generally $SrTiO_3$. Since these films show sharp transitions and high critical currents, their potential in electronic applications seems promising.

Raman and infrared spectra of $YBa_2Cu_3O_{7-\delta}$ and related oxides have been examined by several workers (*49–51*). There has however been considerable disagreement in the assignments. Many workers report Raman bands close to 340, 440, 500, 580, and 630 cm^{-1}, of which the last is somewhat of a mystery peak with variable intensity from sample to sample. The 630-cm^{-1} band has not been reported by some workers; the band is also not found in $YBa_2Cu_3O_6$. The 630-cm^{-1} Raman band has been assigned to the Raman-inactive Cu–O chain stretching mode and also to "defect clusters," but this band could also arise from the O–O stretching mode of a peroxide-like species or due to an impurity such as $Y_2Cu_2O_5$. The 580-cm^{-1} band shows an increase in intensity with increasing δ, while the 500-cm^{-1} band shows evidence of softening. The 500-cm^{-1} band is most likely due to the Cu–O stretching mode involving the short Cu–O bonds along the *c*-axis. The 370- to 330-cm^{-1} bands are due to Cu–O deformation modes. There is some uncertainty regarding the assignment of the 430- and 580-cm^{-1} Raman bands which have been attributed to

Cu–O stretching in the sheets. The infrared spectrum of $YBa_2Cu_3O_7$ shows only a few bands instead of the expected 21. We are able to assign an infrared band around 580 cm^{-1} to a mode involving the Cu–O (chain) stretching in $YBa_2Cu_3O_7$ and a band close to 600 cm^{-1} in $YBa_2Cu_3O_6$ due to Cu–O stretching involving the short Cu–O bonds (along the *c*-axis or possibly the disordered CuO_6 octahedra in the tetragonal structure). In $YBa_2Cu_3O_7$ an IR band close to 190 cm^{-1} (associated with Y) and another at 140 cm^{-1} (associated with Ba or with a Cu–O chain bend) are seen clearly, just as in the Raman studies. Far infrared studies have been reported to show a superconducting gap starting at 210 cm^{-1} (*49*), but there seems to be some uncertainty about this observation.

4. Nature of the Cu Species and the Role of Oxygen

We have seen earlier how oxygen plays a crucial role in the superconductivity of $YBa_2Cu_3O_{7-\delta}$. Careful studies by employing photoelectron and Auger spectroscopies have thrown much light on this aspect. Ultraviolet photoemission spectroscopy studies show some changes in the 12-eV region in the case of $YBa_2Cu_3O_7$ on cooling the sample to 80 K. The valence band region clearly shows a low density of states at the Fermi level and indicates the presence of strong correlations. Variable-temperature X-ray photoelectron spectroscopy studies on $La_{1.8}Sr_{0.2}CuO_4$ and $YBa_2Cu_3O_7$ in the O(1s) and Cu(2p) regions (*52, 53*) indicate the presence of molecular oxygen species with a high O(1s) binding energy of ~533 eV alongside of features due to the oxide and O^- or/and impurity) ions around 529 and 531 eV, respectively (Fig. 9). The proportion of species responsible for the 533-eV feature increases with the lowering of temperature (Fig. 9). This oxygen species is identified as a peroxide-like unit (although it is close to the feature expected for ice) based on the knowledge of O(1*s*) binding energies of such species generated by oxygen adsorbed on transition metal surfaces as well as of traditional metal peroxides. The Cu(2*p*) spectrum shows the presence of a well-screened d^{10} state (Cu^{1+}) at 933 eV, along with a poorly screened d^9 state (Cu^{2+}) at 942 eV. The proportion of the d^{10} state increases with the lowering of temperature. There is, however, no evidence for Cu^{3+} in the Cu(2*p*) or Auger spectra; X-ray absorption edge measurements also provide no evidence for Cu^{3+} (*54*). Auger spectra, however, clearly show the presence of Cu^{1+} (Fig. 10).

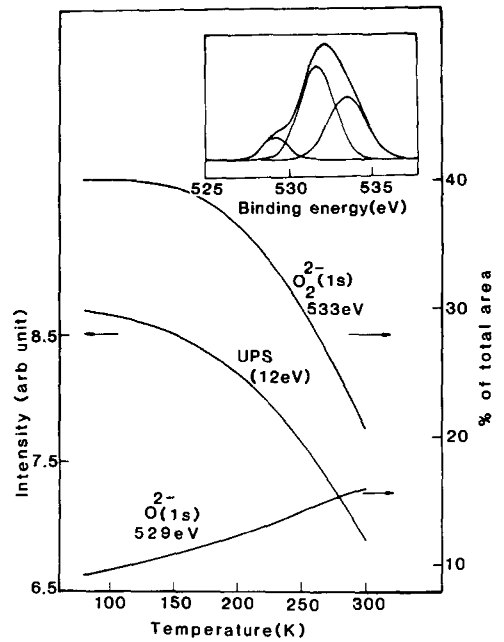

FIG. 9. Temperature-variation of O(1s) peak intensity due to O^{2-} and O_2^{2-} species (at 529 and 533 eV, respectively) in $YBa_2Cu_3O_7$. Temperature-variation of the intensity of He II spectrum at 12 eV is also shown. Inset shows the O(1*s*) signal at 80 K as consisting of three Gaussians peaking at 529, 531, and 533 eV; the one at 531 eV is due to O^- species [from Ref. (*52*)].

Based on the above findings, it has been proposed that holes are present on oxygen rather than on copper in $YBa_2Cu_3O_7$ and

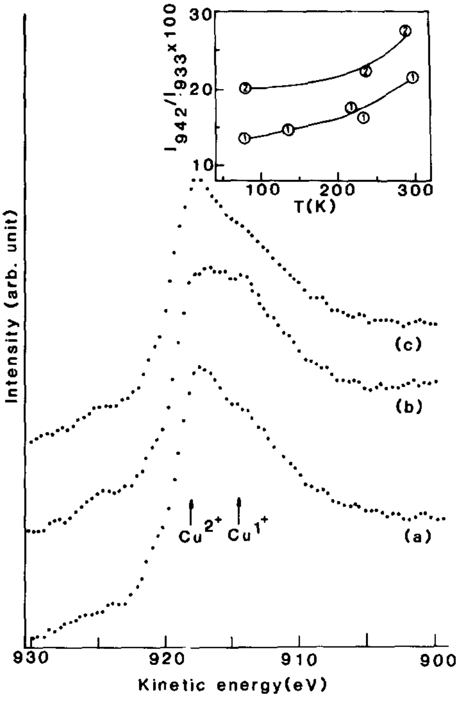

FIG. 10. Cu(L_3VV) Auger spectrum of $YBa_2Cu_3O_7$ at different temperatures. In the inset, the temperature variation of the intensity of the 942-eV feature relative to that of the 933-eV feature in the Cu($2p_{3/2}$) spectrum is shown. The circled numbers 1 and 2 refer to independent sets of measurements (results from this laboratory). (a), (b) and (c) are at 300, 80 and 300 K respectively.

$La_{2-x}Ba_x(Sr_x)CuO_4$ (note that both are hole conductors). The oxygen holes (O^-) could then dimerize to give peroxide-type species (O_2^{2-}). The pair of electrons released in the formation of such species from the oxide ions ($2O^{2-} \rightarrow 2O^-$ or $O_2^{2-} + 2e$) could be related to superconductivity. It is likely that the average charge on oxygen in these oxides is close to $-1.3 + 0.1$. Holes in the O($2p$) valence bands are favored by the Cu^{1+} (d^{10}) state, just as holes in the S($3p$) or Se($4p$) valence bands are generally favored in the Cu^{1+} chalcogenides (*52*). Since there is no real evidence for Cu^{3+} and the Cu–O bonds are highly covalent (1.8–1.95 Å), we conclude that the contribution from the state with the holes on Cu is indeed negligible. It may be noted here that peroxide-like species are likely to be common in many oxides which are supposed to contain metal ions in high-oxidation states (e.g., Pb^{4+}, Ni^{3+}, Cu^{3+}).

5. $La_{3-x}Ba_{3+x}Cu_6O_{14}$ and Related Oxides

High-T_c superconductivity up to 70 K in the $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ (the so-called 336) system (*55, 56*) created considerable interest since the structure was then known to be tetragonal (*26*) with no Cu–O–Cu chains in evidence. Oxygen treatment under pressure increases T_c; Sr substitution for Ba is also possible. Recent neutron diffraction studies (*57*) of a few members of this family have shown that these oxides are in fact disordered isomorphs of orthorhombic $YBa_2Cu_3O_{7-\delta}$ and that they do contain Cu–O–Cu chains. (A tetragonal structure has, however, been assigned to these materials by some workers, based on X-ray studies.) In these oxides, both the O1 and O5 sites are partially occupied, with more oxygen atoms in the O1 site. Equal occupation of the O1 and O5 sites would give rise to the tetragonal structure. If one takes the normalized difference in the O1 and O5 site occupancies as an order parameter, the zero-resistance T_c increases with the order parameter. The nonsuperconducting $x = 0$ compound corresponding to $La_3Ba_3Cu_6O_{14+\delta}$ itself has the tetragonal $YBa_2Cu_3O_{7-\delta}$ structure with partial substitution of La on the Ba sites (*58*). The $x = 1$ compound, $LaBa_2Cu_3O_{7-\delta}$, is orthorhombic, with a reported T_c as high as 90 K (*59*); a T_c of ~77 K is more commonly found in this laboratory. As mentioned earlier, T_c in this compound depends very markedly on the stoichiometry and ordering of oxygens especially in the chain (more so that in $YBa_2Cu_3O_{7-\delta}$), just as in the other members of the $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ family. We find $La_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ to be tetragonal with oxygen excess and low T_c.

The observation that the structure of $La_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ is related to that of $YBa_2Cu_3O_{7-\delta}$ (possessing Cu–O–Cu chains) is important. This relationship clearly justifies the very early characterization of $YBa_2Cu_3O_{7-\delta}$ (*9, 60*) on the basis of the structure of $La_{3-x}Ba_{3+x}Cu_6O_{14}$. This also makes it worthwhile to investigate the $Y_{3-x}Ba_{3+x}Cu_6O_{14}$ system (*9, 60*) carefully. By employing low-temperature methods, it has been possible to synthesize monophasic $Y_{3-x}Ba_{3+x}Cu_6O_{14}$ as well as $(Y, La)_{3-x}Ba_{3+x}Cu_6O_{14}$. These aspects as well as the synthesis of the $Ln_{3-x}Ba_{3+x}Cu_6O_{14}$ family of oxides are being examined in detail in this laboratory. It now appears as though all the oxides showing high-T_c superconductivity are orthorhombic. Where one apparently encounters tetragonality, it would be necessary to establish the structure unequivocally by neutron diffraction.

6. Some Novel Features

Nominal mixed valence, low-dimensionality, and marginal metallicity in the normal state are three of the important features of these oxide superconductors. Electronic and magnetic properties are anisotropic as expected of low-dimensional materials. While $La_{2-x}Sr_xCuO_4$ seems to exhibit measurable ^{18}O isotope effect on the T_c, there is essentially no isotope effect in the case of $YBa_2Cu_3O_{7-\delta}$ (*61*). There is some news that marginal isotope effect has been found in some laboratories. While we cannot entirely ignore electron–phonon interaction, its direct role as in the traditional BCS theory is not apparent. It is possible that if the relevant phonon mode softens in the temperature region of interest the isotope effect will be masked (K. P. Sinha, unpublished results). Excitonic bands around 0.5 and 1.0 eV seem to be present in $La_{2-x}Sr_xCuO_4$ and the significance of these bands needs to be further explored.

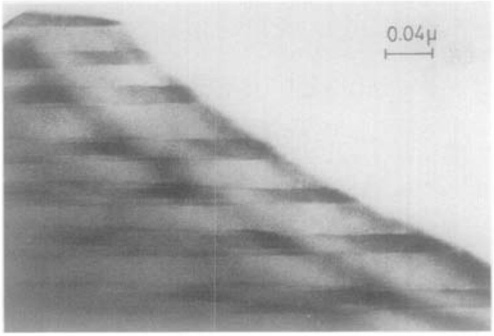

FIG. 11. Bands in electron micrographs of $YBa_2Cu_3O_7$ due to twins [from Ref. (*62*)].

Electron microscopic studies of $YBa_2Cu_3O_7$ show the presence of domain or twin boundaries (Fig. 11), in addition to other defects (*40, 42, 62–64*). It is important to understand the nature of such domains, since the coherence length is only a few angstroms. Twins such as those in Fig. 11 can arise from the different orientations of the $(CuO_2)_\infty$ units in the orthorhombic structure; along the boundaries, there could be oxygen excess compared to the bulk (*40, 64*). The possibility that the microstructural features arise from the separation of metallic and insulating phases in these borderline metals has to be considered. Control of the microstructure (twin density) provides a means of optimizing the critical density (*65*). It is to be noted that twins arise from the orthorhombic structure which in turn becomes possible due to the presence of Cu–O–Cu chains. Properties such as grain size (boundaries) and sample porosity are also crucial material parameters.

Many samples of $YBa_2Cu_3O_{7-\delta}$ and related oxides are reported to exhibit sharp resitivity anomalies at relatively high temperatures (200–300 K). Inverse AC Josephson effect has also been employed to examine this behavior (*66*). Such observations are generally irreproducible in the sense that these properties do not persist over repeated cycles or on standing for ex-

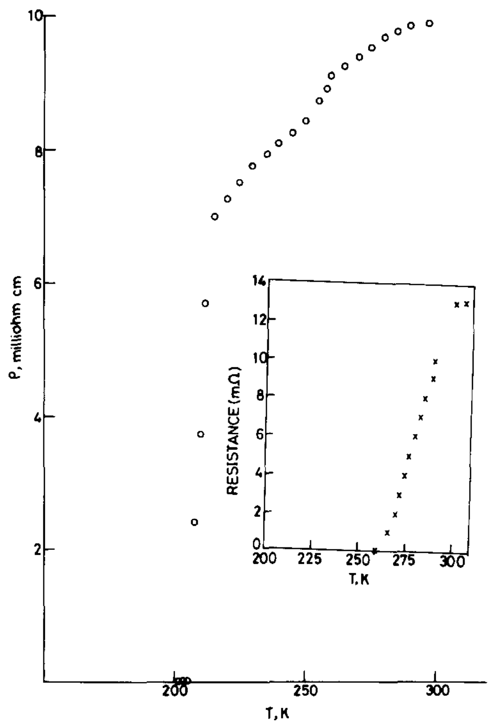

FIG. 12. A sample of $Y_2Ba_2Cu_3O_x$ where Ba sites are partly substituted by La prepared in the author's laboratory showing zero-resistance around 210 K. Inset shows a similar behavior seen in $ErBa_2Cu_3O_{7-\delta}$ by Ayyub *et al.* (*77*).

tended periods. It seems that many of these observations are artifacts of the electrical measurement techniques or of sample inhomogeneity, especially in samples prepared at high temperatures (*27*). "Zero-resistance" has also been occassionally observed at 200 K or above by some workers in certain oxide compositions; adequate Meissner effect measurements on such samples are lacking. In Fig. 12, we show such a transition found in this laboratory, but unfortunately this feature disappeared on recycling giving back the 95 K transition. It should be noted here that the volume fraction of the 95 K superconducting phase in $YBa_2Cu_3O_7$ itself is rather small (~15%). The phase responsible for T_c values of 200 K or higher may therefore be present only in small proportions. It is possible that intergrowths are responsible for such a behavior, but it is not clear why they should be unstable. The challenge is to obtain a stable, pure sample of such a really hot oxide superconductor, if it exists.

In the superconducting state, $YBa_2Cu_3O_7$ absorbs electromagnetic radiation over a wide range of frequencies from a few megahertz to a few gigahertz (*67*). The intensity of absorption is very sensitive to temperature, particle size, and magnetic field, and crucially depends on the presence of ambient oxygen. Josephson junctions formed by oxygen and the superconducting grains may be responsible for this effect.

A large increase in T_c (up to 160 K) has been found by cycling across 239 K (*71*) and this may be considered to be due to oxygen ordering or movement. It is equally possible that the microstructure (twin density) changes across this transition. A 234 K transition has been encountered, based on a temperature-variation study of the 640-cm^{-1} Raman band (*72*); this transition correlates with acoustic anomalies and may represent a continuous transition involving change in point group symmetry (D_{2h}–C_{2v}). The 234–239 K transition needs to be investigated in detail by acoustic and other measurements since such a transition (also found in $La_{2-x}Ba_xCuO_4$) may be fundamental to superconductivity in these oxides.

7. Preparative and Related Aspects

The synthesis of superconducting oxides provides many opportunities and challenges. The most common method employed is the ceramic method involving the high-temperature reaction of an appropriate mixture of oxides and carbonates. Citrates and oxalates have also been employed with no definitive advantage in the case of $La_{2-x}Ba_x(Sr_x)CuO_4$ and $YBa_2Cu_3O_7$; nitrates, however, seem to have a definitive advantage (*68*). In the synthesis of $YBa_2Cu_3O_7$ and related oxides, we have found it convenient to employ BaO_2 instead of $BaCO_3$.

Starting with a slight excess of CuO sharpens the transition. Addition of BaF_2 seems to have a similar effect. The effect of partial fluorination is yet to be carefully investigated, although there are indications that T_c increases significantly, in this process.

The precursor method (*69*) would be an ideal alternative route for the synthesis of these oxides. Unfortunately, no single precursor compound or a precursor solid solution has been found. Mixed nitrates, however, seem to be useful in preparing oxide superconductors which specially require low temperatures [e.g., $Y_{3-x}(La_{3-x})Ba_{3+x}Cu_6O_{14}$]. Precipitation from high alkaline media has not been successful. The sol–gel route in the traditional sense seems difficult because it is hard to get the alkoxides of Y(*Ln*), Ba, and Cu^{2+} to form a homogeneous mix. It may be worthwhile to examine the feasibility of using cuprous alkoxides (instead of cupric) for the sol–gel route. It has been possible to prepare gels by adding appropriate amounts of yttrium nitrate and copper acetate to a known amount of barium hydroxide (*13*). Oxides of the La–Ba–Cu–O system can similarly be prepared starting with lanthanum nitrate.

Heating under high oxygen pressure is found convenient for producing stoichiometric or oxygen-excess samples. Thus, superconducting $La_2CuO_{4+\delta}$ and $La_{3-x}Ba_{3+x}Cu_6O_{14-\delta}$ have been made by treatment under high oxygen pressure. Plasma oxidation offers another convenient way of preparing such materials. $La_2CuO_{4+\delta}$ has been prepared by plasma oxidation; $YBa_2Cu_3O_{7-\delta}$ ($\delta \approx 0.5$–1.0) is readily oxidized to the near-stoichiometric phase by plasma oxidation (*13*). Different workers have prepared $YBa_2Cu_3O_{7-\delta}$ by employing different treatments. The time of annealing (soaking) in oxygen varies quite markedly, from a few hours to a few days. In general, most preparations yield samples with T_c in the 90–95 K region. Some workers have reported much higher T_c values (>100 K) in samples annealed or soaked differently (*70*); for example, soaking samples of $YBa_2Cu_3O_7$ for extended periods in a helium or a nitrogen atmosphere has been reported to increase T_c up to 130 K, but the effect does not appear to be permanent. These results are generally based on electrical resistivity measurements. The chemistry of such treatments is not clear. One possibility is that oxygen in the Cu–O–Cu chains becomes perfectly ordered, causing an increase in T_c; it is worthwhile to examine the Meissner effect in such samples.

Exposure of $YBa_2Cu_3O_7$ and other oxide superconductors to laboratory atmosphere for extended periods seems to degrade the materials. In the case of $YBa_2Cu_3O_7$, hydroxides and carbonates of the component metals and surface carbonization have been noticed especially when samples are impure.

Samples of $YBa_2Cu_3O_7$ and other oxides prepared by low-temperature methods generally exhibit low T_c values. Part of the problem could be the small particle size which in turn determines the nature of grain boundaries. Single crystals of $La_{2-x}Ba_x(Sr_x)CuO_4$ and $YBa_2Cu_3O_{7-\delta}$ have been grown by the flux method by several workers. In particular, the recent work by Holtzberg *et al.* (*73*) on the growth of $YBa_2Cu_3O_{7-\delta}$ crystals is noteworthy.

8. Concluding Remarks

The tremendous possibilities of applications of $YBa_2Cu_3O_7$ and other yet-to-be-discovered high-T_c ceramic oxides make this area of research most exciting. Clearly, the high-temperature oxide superconductors constitute the most sensational discovery since the transistor. There is considerable scope for obtaining reliable data on these oxide superconductors. Theories and models will have to wait until the experimental findings are fully established and the future offers unlimited scope for research in metal oxide solid-state chemistry. Superconductivity near room temperature or above is often being reported, but no stable phase of this type has yet been isolated. It is possible that a stable room-temperature superconductor is lying somewhere in a solid-state chemistry laboratory. Many oxide systems, especially those containing V, Nb, and Ru, as well as intergrowth structures (*74*) such as $(Y, Ba, Sr)_{n+1}Cu_nO_{3n+1}$, need to be investigated. What is especially satisfying is that even in this short period, there is an appreciation of the role of structure and stoichiometry in superconductivity. Thus, Cu–O–Cu chains are responsible for the orthorhombic structure of $YBa_2Cu_3O_7$, and the orthorhombic structure is essential for the formation of twins which control many of the properties. Furthermore, all the high-T_c oxides discussed hitherto belong to the perovskite family and possess orthorhombic structures.

Acknowledgments

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Note added in proof. Linearity of normal-state resistivity of $YBa_2Cu_3O_7$ over a wide temperature range is noteworthy. Hitherto, there is no clear evidence for vacancy ordering in $YBa_2Cu_3O_{7-\delta}$, especially when $\delta = 0.33$ or 0.5. Incorporation of an extra Cu–O layer is supposed to increase T_c to 290 K (*78*), but we have not been able to confirm this observation. The 240 K transition in $YBa_2Cu_3O_7$ is confirmed by heat capacity measurements (*79*).

$Ln_{3-x}Ba_{3+x}Cu_6O_{14+\delta}$ (Ln = La, Nd, etc.) becomes tetragonal at a value of x depending on Ln; these members have low T_c compared to the 123 system. In the La member, only the $x = 1.0$, $\delta \approx 0.0$ shows high T_c (*80*).

Two-dimensional $Sr_2Bi_2Cu_2O_{7+\delta}$ is superconducting (*81*).

References

1. D. C. Johnston, H. Prakash, W. H. Zachariasen, and R. Viswanathan, *Mater. Res. Bull.* **8,** 777 (1973).
2. A. W. Sleight, J. L. Gillson, and F. E. Bierstedt, *Solid State Commun.* **17,** 27 (1975).
3. J. G. Bednorz and K. A. Müller, *Z. Phys. B* **64,** 187 (1986).
4. R. J. Cava, R. B. van Dover, B. Batlogg, and E. A. Reitman, *Phys. Rev. Lett.* **58,** 408 (1987).
5. C. W. Chu, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, and Y. Q. Wang, *Phys. Rev. Lett.* **58,** 405 (1987).
6. S. Uchida, H. Takagi, K. Kitazawa, and S. Tanaka, *Japan. J. Appl. Phys.* **26,** L1 (1987).
7. M. K. Wu, J. R. Ashburgn, C. J. Torng, P. H. Hor, R. L. Meng, L. L. Gao, Z. J. Huang, Y. Q. Wang, and C. W. Chu, *Phys. Rev. Lett.* **58,** 908 (1987); Z. Zhao *et al. Kexue Tongbao,* No. 6 (1987).
8. T. Siegrist, S. Sunshine, D. W. Murphy, R. J. Cava, and S. M. Zahurak, *Phys. Rev. B* **35,** 7137 (1987); R. J. Cava, B. Batlogg, R. B. van Dover, D. W. Murphy, S. Sunshine, T. Siegrist, J. P. Remeika, E. A. Rietman, S. Zahurak, and G. P. Espinosa, *Phys. Rev. Lett.* **58,** 1676 (1987).
9. C. N. R. Rao, P. Ganguly, A. K. Raychaudhuri, R. A. Mohan Ram, and K. Sreedhar, *Nature* (*London*) **326,** 856 (1987).
10. P. Ganguly and C. N. R. Rao, *J. Solid State Chem.* **53,** 193 (1984).
11. S. Mitsuda, G. Shirane, S. K. Sinha, D. C. Johnston, M. S. Alvarez, D. Vaknin, and D. E. Moncton, *Phys. Rev. B* **36,** 822 (1987); G. Shirane, Y. Endoh, R. J. Birgeneau, M. A. Katsner, Y. Hidaka, M. Oda, M. Suzuki, and T. Murakami, *Phys. Rev. Lett.* **59,** 1613 (1987).
12. J. Beille, R. Cabanel, C. Chaillout, B. Chevalier, G. Demazeau, F. Deslandes, J. Etorneau, P. Le Jay, C. Michel, J. Provost, B. Raveau, A. Sulpice, J. Tholence, and R. Tournier, *C. R. Acad. Sci. Paris* **18,** 304 (1987).
13. J. M. Tarascon, P. Bardoux, B. G. Bagley, L. H. Greene, W. R. McKinnon, and G. W. Hull, *ACS Symp. Ser.* **351,** Chap. 20 (1987).
14. S. M. Fine, M. Greenblatt, S. Simizu, and S. A. Friedberg, *ACS Symp. Ser.* **351,** Chap. 10 (1987).
15. P. Ganguly, R. A. Mohan Ram, K. Sreedhar, and C. N. R. Rao, *Solid State Commun.* **62,** 807 (1987); R. A. Mohan Ram, P. Ganguly, and C. N. R. Rao, *Phase Transitions* **10,** 107 (1987).
16. A. K. Grover, S. K. Dhar, P. L. Paulose, V. Nagarajan, E. V. Sampath Kumaran and R. Nagarajan, *Solid State Comm.* **63,** 1003 (1987).
17. H. H. Wang, U. Geiser, R. J. Thorn, K. D. Carlson, M. A. Beno, M. R. Monaghan, T. J. Allen, R. B. Proksch, D. L. Stupka, W. K. Kwok, G. W. Crabtree, and J. M. Williams, *Inorg. Chem.* **26,** 1190, 1474 (1987).
18. C. N. R. Rao, *Int. J. Mod. Phys. B* **1,** 721 (1987).
19. K. Sreedhar, T. V. Ramakrishnan, and C. N. R. Rao, *Solid State Commun.* **63,** 835 (1987).

20. P. Day, M. Resseinsky, K. Prassides, W. I. F. David, O. Moze, and A. Soper, *J. Phys. C. Solid State* **20,** L429 (1987).

21. R. J. Birgeneau, C. Y. Chen, D. R. Grabbe, H. P. Jenssen, M. A. Kastner, C. J. Peters, P. J. Picone, T. Thio, T. R. Thurston, and H. L. Tuller, to be published.

22. H. Thomann, D. C. Johnston, P. J. Tindall, D. P. Goshorn, and R. A. Klemm, *Phys. Rev. Lett,* in press.

23. K. Nakao, N. Miura, S. Uchida, H. Takagi, S. Tanaka, K. Kishio, J. Shimoyama, K. Kitazawa, and K. Fueki, *Japan. J. Appl. Phys.* **26** (1987); D. W. Capone, D. G. Hinks, J. D. Jorgensen, and K. Zhang, to be published.

24. Z. Schlesinger, R. L. Greene, J. D. Bednorz, and K. A. Muller, *Phys. Rev. B* **35,** 7232 (1987).

25. R. Felici, J. Penfold, R. C. Ward, E. Olsi, and C. Matacotta, "RAL-87-062," Rutherford Appleton Laboratory Report (1987); *Nature (London)* **329,** 523 (1987).

26. L. Er-Rakho, C. Michel, J. Provost, and B. Raveau, *J. Solid State Chem.* **37,** 151 (1981).

27. J. B. Torrance, E. M. Engler, V. Y. Lee, A. I. Nazzal, Y. Tokura, M. L. Ramirez, J. E. Vazquez, R. D. Jacowitz, and P. M. Grant, *ACS Symp. Ser.* **351,** Chap. 9 (1987).

28. S. W. Keller, K. J. Leary, T. A. Faltens, J. N. Michaels, and A. M. Stacey, *ACS Symp. Ser.* **351,** Chap. 12 (1987).

29. W. I. F. David, W. T. A. Harrison, J. M. F. Gunn, O. Moze, A. K. Soper, P. Day, J. D. Jorgensen, M. A. Beno, D. W. Capone, D. G. Hinks, I. K. Schuller, L. Soderholm, C. U. Segre, K. Zhang, and J. D. Grace, *Nature (London)* 327, 310 (1987).

30. F. Beech, S. Miraglia, A. Santoro, and R. S. Roth, *Phys. Rev. B* **35,** 8778 (1987).

31. P. Bordet, C. Chaillout, J. J. Capponi, J. Chenavas, and M. Marezio, *Nature (London)* **327,** 687 (1987).

32. A. Santoro, S. Miraglia, F. Beech, S. A. Sunshine, D. W. Murphy, L. F. Schneemeyer, and J. V. Waszczak, *Mater. Res. Bull.* **22,** 1009 (1987).

33. J. D. Jorgensen, M. A. Beno, D. G. Hinks, L. Soderholm, K. J. Volin, R. L. Hitterman, J. D. Grace, I. K. Schuller, C. U. Segre, K. Zhang, and M. S. Kleefisch, *Phys. Rev. B* **35,** 7915 (1987).

34. R. A. Mohan Ram, N. Y. Vasantacharya, and C. N. R. Rao, *J. Solid State Chem.* **69,** 186 (1987); J. M. Tarascon, W. R. McKinnon, L. H. Greene, G. W. Hull, and E. M. Vogel, *Phys. Rev. B* **36,** 226 (1987).

35. D. W. Murphy, S. A. Sunshine, R. B. van Dover, R. J. Cava, B. Batlogg, S. M. Zahurak, and L. F. Schneemeyer, *Phys. Rev. Lett.* **58,** 1888 (1987).

36. K. N. Yang, Y. Dalichaouch, J. M. Ferriera, B. W. Lee, J. J. Neumeier, M. S. Torikachvili, H. Zhou, M. B. Maple, and R. R. Hake, *Solid State Commun.* (1987).

37. C. C. Torardi, E. M. McCarron, M. A. Subramanian, H. S. Horowitz, J. B. Michel, A. W. Sleight, and D. E. Cox, *ACS Symp. Ser.* **351,** Chap. 15 (1987).

38. B. D. Dunlap, M. Slaski, D. G. Hinks, L. Soderholm, M. Beno, K. Zhang, C. Segre, G. W. Grabtree, W. K. Kwok, S. K. Malik, I. K. Schuller, J. D. Jorgensen, and Z. Sungaila, *J. Magn. Magn. Mater.* **68,** 139 (1987); G. V. Subbarao, U. V. Varadaraju, R. Vijayashree, K. Padmanabhan, R. Balakrishnan, T. A. Mary, N. P. Raju, R. Srinivasan, U. De, J. Janaki, and T. S. Radhakrishnan, *Proc. Yamada Conf. Low-Temp.* (1987).

39. D. C. Johnston, A. J. Jacobson, J. M. Newsam, J. T. Lewandowski, D. P. Goshorn, D. Xie, and W. B. Yelon, *ACS Symp. Ser.* **351,** Chap. 14 (1987).

40. C. N. R. Rao, L. Ganapathi, and R. A. Mohan Ram, *Mater. Res. Bull,* in press.

41. Z. Z. Wang, J. Calyhold, N. Pong, J. M. Tarascon, L. H. Greene, W. R. McKinnon, and G. W. Hull, *Phys. Rev. B* **36,** 7222 (1987); R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature (London)* **329,** 423 (1987).

42. C. N. R. Rao, P. Ganguly, K. Sreedhar, R. A. Mohan Ram, and P. R. Sarode, *Mater. Res. Bull.* **22,** 849 (1987).

43. K. Fueki, K. Kitazawa, K. Kishio, T. Hasegawa, S. Uchida, H. Takagi, and S. Tanaka, *ACS Symp. Ser.* **351,** Chapter 4 (1987).

44. J. Thiel, S. N. Song, J. B. Ketterson, and K. R. Poeppelmeier, *ACS Symp. Ser.* **351,** Chap. 17 (1987); Y. Maeno *et al.*, *Nature (London)* **328,** 512 (1987).

45. R. J. Cava, B. Batlogg, C. H. Chen, E. A. Rietman, S. M. Zahurak, and D. Werder, *Nature (London)* **329,** 423 (1987).

46. A. P. Malozemoff, W. J. Gallagher, and R. E. Schwall, *ACS Symp. Ser.* **351,** Chap. 27 (1987).

47. K. Kadowaki *et al.* to be published.

48. P. Chaudhari, R. H. Koch, R. B. Laibowitz, T. R. McGuire, and R. J. Gambino, *Phys. Rev. Lett.* **55,** 2684 (1987); X. D. Wu, D. Dijkkamp, S. B. Ogale, A. Inam, E. W. Chase, P. F. Miceli, C. C. Chang, J. M. Tarascon, and T. Venkatesan, *Appl. Phys. Lett.* **51,** 861 (1987).

49. M. Cardona, L. Genzel, R. Liu, A. Wittlin, H. Mattausch, F. Garcia-Alvarado, and F.

GARUA-GONZALEZ, *Solid State Commun.* **64,** 727 (1987).

50. Z. IQBAL, S. W. STEINHAUSER, A. BOSE, N. CIPOLLINI, AND H. ECKARDT, *Phys. Rev. B* **36,** 2283 (1987); G. A. KOUROUKLIS, A. JAYARAMAN, B. BATLOGG, R. J. CAVA, M. STAVOLA, D. M. KROL, E. A. RIETMAN, AND L. F. SCHNEEM EYER, to be published.
51. Y. DAI, J. S. SWINNEA, H. STEINFINK, J. B. GOODENOUGH, AND A. CAMPION, *J. Amer. Chem. Soc.* **109,** 5291 (1987).
52. C. N. R. RAO, P. GANGULY, M. S. HEGDE, AND D. D. SARMA, *J. Amer. Chem. Soc.* **109,** 6983 (1987); C. N. R. RAO, P. GANGULY, J. GOPALAKRISHNAN, AND D. D. SARMA, *Mater. Res. Bull.* **22,** 1159 (1987).
53. D. D. SARMA AND C. N. R. RAO, *J. Phys. C.* **20,** L659 (1987); D. D. SARMA, K. SREEDHAR, P. GANGULY, AND C. N. R. RAO, *Phys. Rev. B* **36,** 2371 (1987).
54. P. STEINER, V. KINSINGER, I. SANDER, B. SIEGWART, S. HÜFNER, C. POLITIS, R. HOPPE, AND H. P. MÜLLER, *Z. Phys. B* **67,** 497 (1987); A. BIANCONI, A. CLOZZA, A. C. CASTELLANO, S. D. LONGA, M. DE SANTIS, P. DELONGU, A. GARGANO, R. GIORGI, P. LAGARDE, A. M. FLANK, AND A. MACEILI, *Int. J. Mod. Phys.* **1,** 853 (1987).
55. D. B. MITZI, A. F. MARSHALL, J. Z. SUN, D. J. WEBB, M. R. BEASLEY, T. H. GEBALLE, AND A. KAPITULNIK, to be published.
56. A. K. GANGULI, L. GANAPATHI, K. SREEDHAR, R. A. MOHAN RAM, P. GANGULY, AND C. N. R. RAO, *Pramana* **29,** 335 (1987).
57. C. U. SEGRE, B. DABROWSKI, D. G. HINKS, K. ZHANG, J. D. JORGENSEN, M. A. BENO, AND I. K. SCHULLER, *Nature (London)* **329,** 227 (1987).
58. W. I. F. DAVID, W. T. A. HARRISON, R. M. IBBERSON, M. T. WELLER, J. R. GRASMEDER, AND P. LANCHESTER, *Nature (London)* **328,** 328 (1987).
59. A. MAEDA *et al., Japan. J. Appl. Phys.* **26,** L1366 (1987).
60. R. A. MOHAN RAM, K. SREEDHAR, A. K. RAY CHAUDHURI, P. GANGULY, AND C. N. R. RAO, *Philos. Mag. Lett.* **55,** 257 (1987); P. GANGULY, K. SREEDHAR, A. K. RAYCHAUDHURI, AND C. N. R. RAO, *Pramana* **27,** 229 (1987).
61. B. BATLOGG, R. J. CAVA, J. JAYARAMAN, R. B. VAN DOVER, G. A. KOUROKIS, S. SUNSHINE, D. W. MURPHY, L. W. RUPP, H. S. CHEN, A. WHITE, K. T. SHORT, A. M. MUJSCE, AND R. A. RIETMAN, *Phys. Rev. Lett.* **58,** 2333 (1987); D. L. C. BORUNE *et al., Phys. Rev. Lett.* **58,** 2337 (1987); B. BATLOGG *et al., Phys. Rev. Lett.* **59,** 912 (1987); T. A. FALTENS *et al., Phys. Rev. Lett.* **59,** 915 (1987).
62. G. N. SUBBANNA, P. GANGULY, AND C. N. R. RAO, *Mod. Phys. Lett. B* **1,** 155 (1987).
63. Y. MATSUI, E. T. MUROMACHI, A. ONO, S. HORIUCHI, AND K. KATO, *Japan J. Appl. Phys.* **26,** L777 (1987).
64. B. RAVEAU, C. MICHEL, AND M. HERVIEU, *ACS Symp. Ser.* **351,** Chap. 13 (1987).
65. R. A. CAMPS, J. E. EVETTS, B. A. GLOWACKI, S. B. NEWCOMB, R. E. SOMEKH, AND W. M. STOBBS, *Nature (London)* **329,** 229 (1987).
66. A. K. GUPTA, B. JAYARAM, S. K. AGARWAL, A. GUPTA, AND A. V. NARLIKAR, *Phase Transitions* **10,** 29 (1987).
67. S. V. BHAT, P. GANGULY, T. V. RAMAKRISHNAN, AND C. N. R. RAO, *J. Phys. C* **20,** L559 (1987).
68. V. BHAT, A. K. GANGULI, K. S. NANJUNDA SWAMY, R. A. MOHAN RAM, J. GOPALAKRISHNAN, AND C. N. R. RAO, *Phase Transitions* **10,** 87 (1987); S. DAVISON, K. SMITH, Y. C. ZHANG, J. H. LIU, R. KERSHAW, K. DWIGHT, P. H. RIEGER, AND A. WOLD, *ACS Symp. Ser.* **351,** Chap. 7 (1987).
69. C. N. R. RAO AND J. GOPALAKRISHNAN, *Acc. Chem. Res.* **20,** 228 (1987).
70. I. K. GOPALAKRISHNAN, J. V. YAKHMI, AND R. M. IYER, *Nature (London)* **327,** 604 (1987); D. N. MATHEWS, A. BAILEY, R. A. VAILE, G. J. RUSSELL, AND K. N. R. TAYLOR, *Nature (London)* **328,** 786 (1987).
71. R. N. BHARGAVA, S. P. HERKO, AND W. N. OSBORNE, *Phys. Rev. Lett.* **59,** 1468 (1987).
72. M. ZHANG, C. QIANG, S. DAKUN, J. RONG-FU, Q. ZHENG-HAO, Y. ZHENG, AND J. F. SCOTT, to be published.
73. F. HOTZBERG, D. L. KAISER, B. A. SCOTT, T. R. MCGUIRE, T. N. JACKSON, A. KLEINSASSER, AND S. TOZER, *ACS Symp. Ser.* **351,** Chap. 8 (1987).
74. C. N. R. RAO AND J. M. THOMAS, *Acc. Chem. Res.* **18,** 113 (1985).
75. D. R. CLARK, *Int. J. Mod. Phys. B* **1,** 170 (1987).
76. R. S. ROTH *et al., Adv. Ceram. Mater.* **2,** 303 (1987).
77. AYYUB *et al., J. Phys. C* **20,** L673 (1987).
78. J. NARAYAN *et al., Appl. Phys. Lett.* **51,** 941 (1987).
79. T. LAEGREID, K. FOSSHEIM, E. SANDVOLD, AND S. JULSRUD, *Nature,* in press.
80. L. GANAPATHI, A. K. GANGULI, R. A. MOHAN RAM, AND C. N. R. RAO, *J. Solid State Chem.,* in press.
81. C. MICHEL *et al., Z. Phys. B* **68,** 421 (1987).