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Oxide Superconductors and Their Applications

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ABSTRACT

Since the discovery of 30 K Superconducting oxide system Ba-La-Cu-O last year, there have appeared two classes of copper based oxide materials to exhibit the critical temperature up to 95 K. The physical properties of these oxides have been cleared to a certain degree and research effort has also been directed to the practical application of these materials. The current status of the efforts is discussed briefly.

I. Discovery of High T_c Superconductors

The following six successive break throughs in finding the new materials have led us to the present excitement in the wide spread fields both of basic and applied researches of superconductivity.

1) Indication of the presence of high T_c superconductivity, up to 35 K, in a mixed phase system of Ba-La-Cu-O by IBM Zurich group (Apr. -Oct. 1986).[1,2]

2) Confirmation of the superconductivity in the same system and the subsequent identification of the superconducting phase as $(La_{1-x}Ba_x)_2CuO_4$ by Univ. of Tokyo group (Nov.-Dec. 1986).[3,4]

3) Substitution of the component ions to create a higher T_c material $(La_{1-x}Sr_x)_2CuO_4$ of 40 K-class by Univ. of Tokyo Group (Dec. 1986).[5]

4) Substitution of the component ions to create even a higher T_c Y-Ba-Cu-O system of 90K-class by Alabama-Houston Univ. group (Feb. 1987).[6]

5) Determination of the phase and crystal structure of $Ba_2YCu_3O_7$ (Mar.-Apr.1987)[7-10]

6) Discovery of magnetic superconductors of the same90 K class as $Ba_2LnCu_3O_7$ with Ln = every rare earth elements except Pr and Ce. (Mar. 1987)[11-14]

Although, reports of finding higher T_c superconductors with T_c's up to 50 K have been presented, they still await reliable experiments.

II. Properties of the High T_c Oxide Superconductors.

Various properties are similar for the 40 K and 90 K-class oxides and will be summarized for the 90 K-class materials.

1) The crystal structure is basically of perovskite type. Ba and Y (Ln) are preferentially sited to form layers of Ba to sandwich the one of Y, resulting in a triple-layer structure. Oxygen ions on the Y plane are essentially missing. On the Cu-O layer between the two adjacent Ba layers, oxygen ions are preferentially depleted to create inequivalent unit cell parameters a and b as shown in Fig. 1.

2) The low carrier density of p-type in the range of $5\times10^{21}cm^{-3}$ as indicated by the Hall measurements (Fig. 2) and plasma edge observation in the near infrared region reflectivity (Fig. 3). This low density of carriers seems to raise potential barriers at interfaces due to the weak screening of the interface charges. Also it should affect the device characteristics when the material is used as the non-equilibrium superconducting devices as well as proximity effect transistors.

3) A moderate value of the density of states at the Fermi energy N(0) as indicated by specific heat measurements (Fig. 4)[15] and Pauli paramagnetism. In Fig. 4 is illustrated a relationship between T_c and the electronic specific heat coefficient γ which is in proportion with N(0). The N(0) values of the high T_c oxides are in the range 1-2 states$\cdot eV^{-1}\cdot$Cu-atom$^{-1}\cdot$spin^{-1} which are in the typical range of the d-band metal superconductors, although they become smaller when compared per volume. They are slightly larger than expected from band calculations.[16]

4) Apparently large electron-correlation interaction as suggested by the temperature dependence of the thermo-electromotive force (Fig. 5). Because of this, the superconductivity is closely situated in the neighborhood of Mott-Hubbard type metal-to-insulator transition as well as of magnetism.

5) A large superconducting gap Δ. In the case of BCS superconductors, the factor $2\Delta/kT_c$ is expected to be 3.52. The recent tunneling measurements mostly find this factor in the range 4 to 7, indicating the superconductivity in the strong coupling region[17], although it is still controversial. This large factor as well as the high T_c make the gap much larger than that of the conventional superconductors, almost by a factor of ten. This should lead the electronic devices to be used in the much higher voltage region. But the energy consumption per switching should increase accordingly. Since the superconducting condensation energy is proportional to $N(0)\Delta^2$, thepresent material should have a much larger difference in the free energy change associated with the superconducting transition.

6) A strong anisotropy observed e.g. for upper critical field Hc_2 up to several times[18] and the critical current J_c up to 100 times.[19] This may cause some inconvenience for the device application, but may be more seriously for the polycrystalline wire application.

7) Very short coherence length ξ_0 in the range of 1nm to several nm.[20] This is due mainly to the large gap parameter and the narrow band width. The small ξ_0 value is regarded to require a more uniformity e.g. in the thickness of the ultra-thin insulating film for the J-J device.

8) An extremely large variation of oxygen content. The oxygen deficiency δ may vary from ca. 0 to 1 when the formula is expressed as $Ba_2YCu_3O_{7-\delta}$ as shown in Fig. 6.[21] Because of this, the material needs to be slow cooled for acquisition of sufficient oxygen to minimize the adverse effect of oxygen deficiency on the superconducting properties. The oxygen is depleted preferentially along b-axis as shown in Fig. 7.

9) A phase transition from tetragonal to orthorhombic structure takes place in association with the decrease in the oxygen deficiency. Above 500 °C, this transition occurs at

$\delta \sim 0.3$. At lower temperatures, the orthorhombic structure persists over $0 \lesssim \delta \lesssim 0.7$.

10) Weak Josephson coupling characteristics are observed in the polycrystalline specimen as well as along the c-axis in the nearly single crystalline specimens.[19] This is probably associated with grain boundaries or sub-boundaries but needs further studies for the clear explanation.

11) The material tends to react with water and carbon dioxide in the atmosphere which deteriorates the superconducting properties and hence should be avoided.

12) Concerning to the mechanisms of superconductivity, the negative or very small isotope effect has been reported on the substitution of oxygen 16 by oxygen 18. The phonon-mediated BCS mechanism has hence lost the support and various mechanisms are being assumed. These include those assuming a) charge transfer both intra- and inter-band, and b) spin fluctuation both of ferro- and antiferro-magnetic nature as the mediating excitations in the solid to create the Cooper pairs. It is also noted that a completely new type of concept called RVB-resonating valence bond theory has been proposed initially by Prof. P. W. Anderson of Princeton University in order to treat with the highly correlated electron system.

III. Applications

The crucial problem currently encountered for the application of polycrystalline superconducting wires is the very low critical current. This seems to be associated dominantly with the grain boundaries and the compositional inhomogeneity. No convincing proposals to overcome this difficulty have been made.

On the other hand, thin film process has achieved a moderate success in the sense that the critical current has exceeded 10^6 A/cm^2 level. Still a better process to obtain good epitaxial films at as low temperature as possible is being sought. Some proto-type devices such as SQUID and infrared sensors might appear in the near future.

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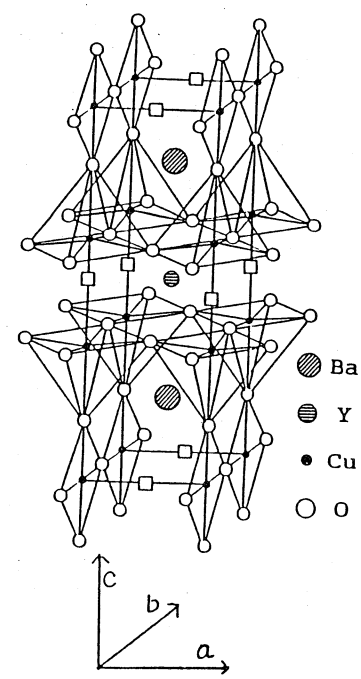

Fig. 1 Crystal structure of $Ba_2YCu_3O_7$.

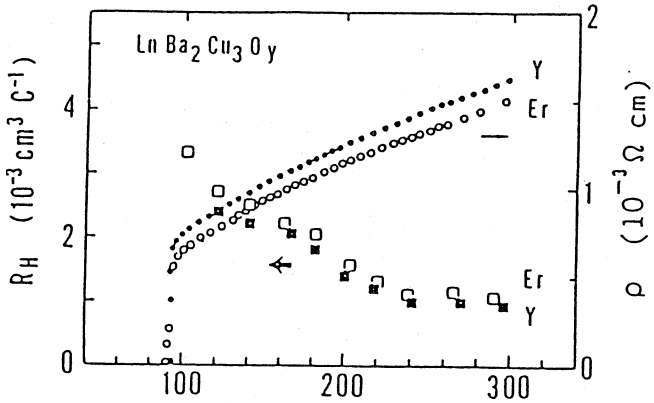

Fig. 2 Temperature dependence of the resistivity and the Hall coefficient for $Ba_2YCu_3O_7$ together with $Ba_2ErCu_3O_7$.

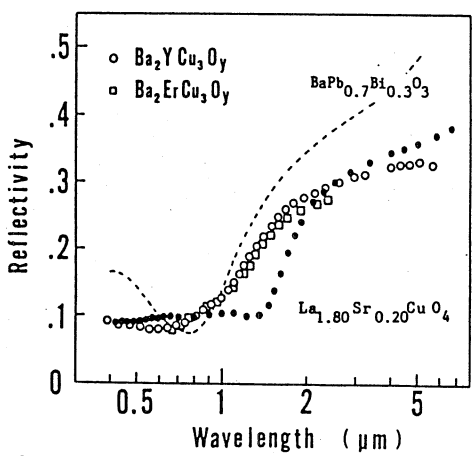

Fig. 3 Optical reflectivity of $Ba_2YCu_3O_7$ compared with the other oxide Super-conductors.

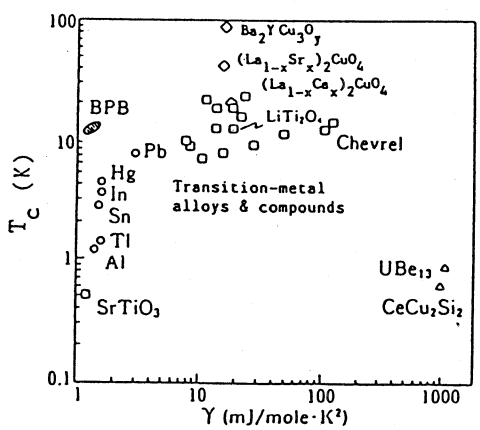

Fig. 4 Relationship between electronic specific heat coefficient Y and Tc for various superconductors.

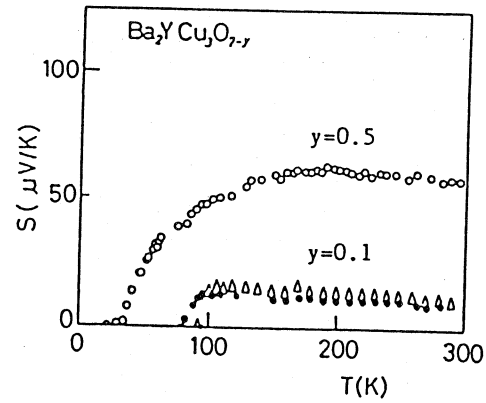

Fig. 5 Temperature dependence of the Seebeck coefficient for $Ba_2YCu_3O_{7-y}$ with various nonstoichiometry y.

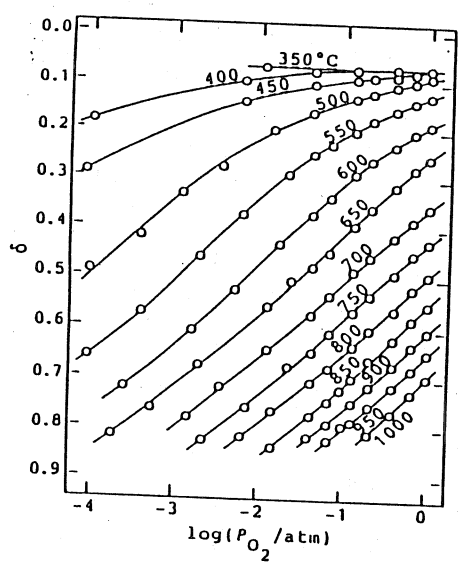

Fig. 6 Equilibrium oxygen deficiency δ in $Ba_2YCu_3O_{7-\delta}$ as a function of temperature and oxygen pressure.

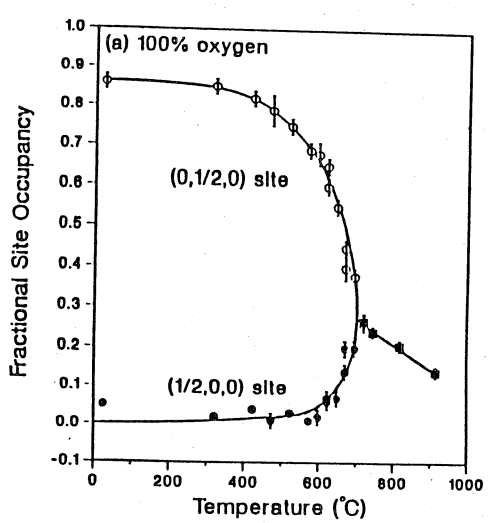

Fig. 7 Fractional site occupancy of oxygen on (0, 1/2, 0) site along b-axis and on (1/2, 0, 0) site along a-axis.