

- Until recently, the alloy Nb₃Ge had the highest known critical temperature, 23.2 K.
- Early in 1986, J.Georg Bednorz, and Karl Alex Muller, made a remarkable discovery that has resulted in a revolution in the field of superconductivity. They found that an oxide of lanthanum, barium, and copper in a mixed-phase form of a ceramic became superconducting at about 30 K.

- ✤ The temperature dependence of the resistivity for their samples taken from their original paper is shown in the following figure.
- ★ The superconducting phase was identified as the compound La_{2-x} Ba_xCuO₄, where x ≈ 0.2.
- ***** By replacing **Ba** with **Sr**, the **T**_c value was raised to about **36 K**.



- Early in 1987, K. Wu and P. Chu at the University of Alabama and the University of Houston announced the discovery of superconductivity near 92 K in a mixed-phase sample containing yttrium, barium, copper, and oxygen.
- * The superconductivity phase was soon identified to be the compound YBa₂Cu₃O_{7-δ}. A plot of the resistivity versus temperature for this compound is shown in the next Figure.



This was an important milestone, since the transition temperature of this compound is above the boiling point of liquid nitrogen (77 K), a coolant that is readily available, inexpensive, and simple to handle compared to liquid helium.

- Recently, several complex metallic oxides in the form of ceramics have been investigated, and critical temperatures above 100K (triple-digit super conductivity) have been observed.
- Early in 1988, researchers reported the onset of superconductivity at about 120 K in a Bi-Sr-Ca-Cu-O compound and about 125 K in a TI-Ba-Ca- Cu-O compound.
- ***** Some properties of high-T_c cuprate superconductors in the form of bulk polycrystalline are summarized in the Table.

Superconductor	T _c (K)	B _{c2} (0) in Tesla
$La-Ba-Cu-0\\La_{1.85}Sr_{0.15}CuO_5\\La_2CuO_4\\YBa_2Cu_3O_{7-\delta}\\ErBa_2Cu_3O_{9-\delta}\\DyBa_2Cu_3O_7\\Bi-Sr-Ca-Cu-O\\Tl-Ba-Ca-Cu-O$	30 36.2 40 92 94 92.5 120 125	>36 ≈160 >28

- As you can see, the new high-T_c materials are all copper oxides of one form original or another.
- The exceptional interest in these novel materials is due to at least four factors:

1. The metallic oxides are relatively easy to fabricate and hence can be investigated at smaller laboratories.

2. They have very high T_c values, and very high upper critical magnetic fields, estimated to be greater than 100 T in several materials.

3. Their properties and the mechanisms responsible for their superconducting behavior represent a great challenge to theoreticians.

4. They may be of considerable technological importance and large-scale applications such as superconducting electronics, energy generation, and magnetic levitation for high-speed transportation.

The various cuprate superconducting compounds that have been extensively studied to date can be classified in terms of the so-called perovskite crystal structures.



- > The first class is (Fig. a), the cubic perovskite (a = b = c) such as BaPb_{1-x}Bi_xO₃, one of the original "high-T_c materials," which has T_c ≈ 10 k.
- ➤ The second class, known as the K₂NiF₄ structure (Fig. b) is a single layer perovskite having a tetragonal distortion $(a = b \neq c)$, such as La_{1.85}Sr_{0.15}CuO₄, having T_c ≈ 38 K.
- ➤ The third class is a multi-layer perovskite (Fig. c), such as Yba₂Cu₃O₇ ($T_c \approx 92K$), with orthorhombic structure ($a \neq b \neq c$). Compounds in this class are sometimes called 1-2-3 materials because of their relative metallic composition.
- The oxygen stoichiometry of $YBa_2Cu_3O_{\delta}$ can vary over the range $6 < \delta < 7$ while retaining the triple perovskite structure. Properties range from superconducting at $6.5 < \delta < 7.0$ to semiconducting with $\delta < 6.4$.

• YBa₂Cu₃O₇ (Y123) is orthorhombic, but as the oxygen content decreases, the structure undergoes a phase transition to tetragonal symmetry.



• The following figure shows the change in structure: in (a) for $\delta = 7.0$, all the O(1) sites are occupied, and O(5) sites are empty. On removal of oxygen from O(1), the O(5) sites becomes partially occupied, untill at (b) the orthorhombic-tetragonal (O/T) phase transition occurs when the O(1) and O(5) sites are equally occupied. (c) Shows the structure of YBa₂Cu₃O₆ in which all the oxygen is missing from the basal plane.



- □ The critical temperature T_c is found to be strongly dependent on oxygen content. The next figure shows the variation of T_c vs. δ for YBa₂Cu₃O_{7- δ}.
- □ These illustrate the "double plateau" behavior, where T_c remains constant at ~90 K for 6.8 < δ < 7.0 and drops to another plateau at 60 K for 6.5 < δ < 6.7.



□ It is evident from recent literatures that the thermal treatment and the variety of preparation techniques are playing the crucial role in determining the physical properties of the newly discovered high Tc- cuprate superconductors.

- ✤ It is now well established that the maximum supercurrents in these structures are high in the copper-oxygen planes, and much lower in the direction perpendicular to these planes.
- The critical current densities in the copper oxygen (a, b) planes of thin films of about 10¹⁰ A/ m² have been reported in YBa₂Cu₃O_{7-δ} as compared to much smaller values along the c direction.
- * The critical current density in bulk polycrystalline samples of YBa₂Cu₃O_{7-δ} is in the range 10⁵ –10⁷ A/m², which is much lower because of grain boundary effects. Since these materials consist of tiny grains compacted together, the current must pass through both the grains and the grain boundaries. Most scientists believe that this factor limits the critical current in these materials.

- It has been well established that these new copper oxides exhibit the two characteristic properties of superconductors, namely zero resistivity and diamagnetism. In addition, they are known to have the following properties:
- 1. They have been determined to be type II superconductors with very high upper critical fields, greater than 100 T.
- 2. They are very an isotropic in nature, as evidenced by their small resistivity in the copper–oxygen planes, and much higher resistivities in the direction perpendicular to these planes.
- 3. They have a granular composition, and it is very brittle and inflexible.
- 4. There appears to be a direct correlation between their superconducting properties and their crystallographic structures that contain oxygen-deficient copper oxide layers and chains.

- 5. Substitution of atoms on the copper oxide layers degrades or destroys the superconductivity, while atomic substitution at other sites has little effect on the superconductivity.
- 6. Almost all the 1-2-3 materials have T_c value close to 90 K, even though they differ in their band gaps, high-temperature resistivity, critical current densities, critical magnetic fields, and so on.
- 7. The critical current densities in bulk polycrystalline samples are very low (of the order of 10⁶ A/m²), but much higher in well-oriented thin films.