Chapter 9

Broad Search for Higher Critical Temperature in Copper Oxides

Effects of Higher Reaction Temperatures

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A wide variety of the ternary (L-M-Cu) and binary (L-Cu and M-Cu) oxides involving rare earths (L = Y, La, Lu, and Sc) and alkaline earths (M = Sr, Ba) with copper were prepared. The vast majority of the 300 samples prepared were not metallic. Several contained known superconducting phases. In the Y-Ba-Cu-O system, many samples prepared at 1050 and 1200 C show some partial melting and deviate strongly from the predictions of the phase diagram determined at 950 C. In a few samples, anomalous resistance decreases were observed at temperatures as high as 260K. In each case, however, these anomalies could be directly traced to problems with strongly temperature dependent contact resistance and phase problems due to high degree of sample inhomogeneity. Multiphase samples prepared at the higher temperatures (i.e. 1050 and 1200 C) appear most prone to such resistance artifacts.

Since the initial discovery of higher temperature superconductivity in perovskite copper oxide compounds (1), the race for further improving T_c has gone on unabated. The superconducting behavior of $La_{2-x}\ Ba_x\ Cu\ O_{4-y}$ and $Y\ Ba_2\ Cu_3\ O_{9-y}$ and their isostructural derivatives has been well documented by numerous research groups (2). Superconductivity in these compounds is reproducible, stable and confirmed by a variety of physical measurements in many laboratories. The typical value of T_c for $Y\ Ba_2\ Cu_3\ O_{9-y}$ lies between 95 and 100K. In contrast, a small, but growing number of isolated reports have appeared (3-9), where much higher superconducting transitions are claimed in short-lived and irreproducible samples. Considering the unprecedented breakthroughs of the last six months, such fleeting behavior might be signalling another round of increases in T_c.

With the hope that there exist copper oxide compounds with higher T_c, we have undertaken an extensive matrix experiment, in which composition and processing conditions were varied for a wide variety of rare earth-alkaline earth-copper-oxide combinations. Most of the higher T_c, reports have involved Y-Ba-Cu-O compositions, and so this system received the major portion of our attention. We also examined other isoelectronic elements such as Sc, La, and Lu substituting for Y and, to a lesser extent, Sr for Ba. Binary rare earth-

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copper and alkaline earth-copper and ternary rare earth-alkaline earth-copper combinations were prepared.

Sample Preparation

The starting compositions that were prepared are outlined in Figure 1. Figures 2 and 3 provide the pseudo-ternary phase diagram for La-Ba-Cu and Y-Ba-Cu. For La-Ba-Cu, we concentrated on the unexplored Cu-rich region (Figure 2), neglecting other areas where there has been extensive work. For Y-Ba-Cu, most of the compositions were chosen outside of the shaded area of Figure 3, since in that area the known $Y Ba_2 Cu_3 O_x$ phase is expected to be formed (10-12). We searched in the "$K_2 Ni F_4$" region (where several high temperature anomalies have been reported (3-6)) as well as the unexplored Cu-rich compositions. All compositions were initially calcined in flowing O_2 for 12 hours at 700 C, cooled, reground, and then pressed into pellets for a final firing under O_2. The main process parameters examined were temperature and quench rate. Each composition was heated at 875 and 1050 C for 16 hours in flowing oxygen. Most of the Y-Ba-Cu compositions were also fired at 1200 C for several hours. Quench rate effects were studied by either removing the sample rapidly from the oven or by allowing the oven to slowly cool to room temperature over about 5 hours. Since some reports of higher T_c claim the behavior is time dependent, disappearing after a few hours to a few days, our electrical measurements were carried out typically within 2-12 hours after removal from the oven. In our experiments, reaction temperature was found to be a more important variable than the cooling rate and most of our effort was concentrated on the effects of the former.

We use phase sensitive detection as the basis of our four-probe measurements. The voltage source is the reference channel output of a Princeton Applied Research model 124A lock-in amplifier set to 1 volt rms at a frequency of 100 Hz. A typical value of Rs is 100 Kohm or 1M Ohm, yielding a nominal constant current through the sample of 10 or 1 microamperes, respectively, under conditions of low contact impedance. The voltmeter is the signal channel of the lock-in, a PAR model 116 differential amplifier with 100M Ohm input impedance. The phase angle between reference and signal channel is adjusted for maximum voltage signal. Normally the current and voltage are then in-phase if the contacts have no capacitive component. Our contacts are comprised of 10 mil Au wire imbedded into silver paste stripes painted on the sample. The current contacts completely cover the sample ends, while the voltage contacts are applied around the body of the material.

Results and Discussion

The preliminary results are summarized in Figures 2 and 3 for the La-Ba-Cu and Y-Ba-Cu systems, respectively. Semiconducting samples are marked with a solid triangle, metals with a circle, and superconductors with a square. Samples which melted are shown as a solid dot. The midpoint temperature of any resistance anomaly is indicated in the circle or square. From the point of view of discovering new superconducting systems, the results were disappointing and indicative of the difficulty of making such a discovery. We found no metallic samples in our limited search in the Lu-Ba-Cu, Sc-Ba-Cu, Sr-Cu, or Ba-Cu systems (under the conditions employed). The resistance anomaly at 32K in $La_2 Cu_5$ is probably associated with the superconductivity discovered at 40K in samples of nominal $La_2 Cu O_4$ (13-15). The other anomalies observed (Figure 2) may be associated with superconductivity reported in La_3

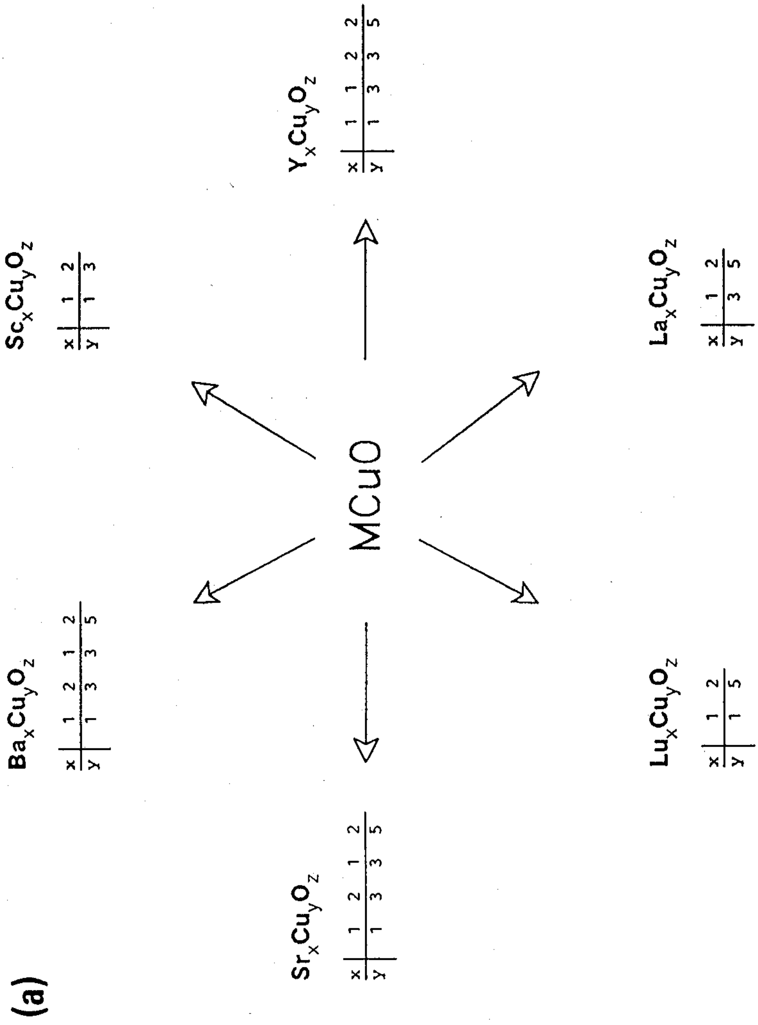

Figure 1a. Schematic diagram of compositions of pseudobinary copper oxides prepared using Ba, Sr, Lu, La, Y, and Sc.

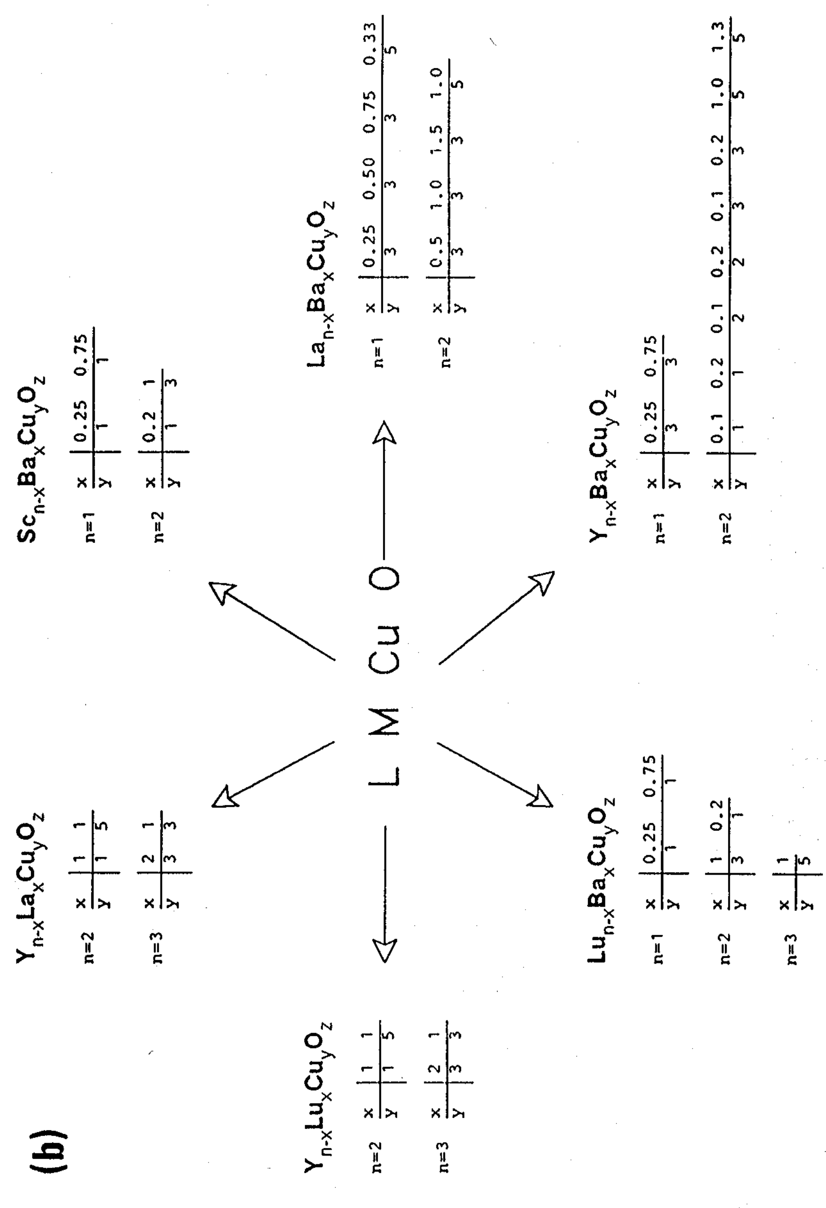

Figure 1b. Schematic diagram of pseudoternary copper oxides prepared in this work.

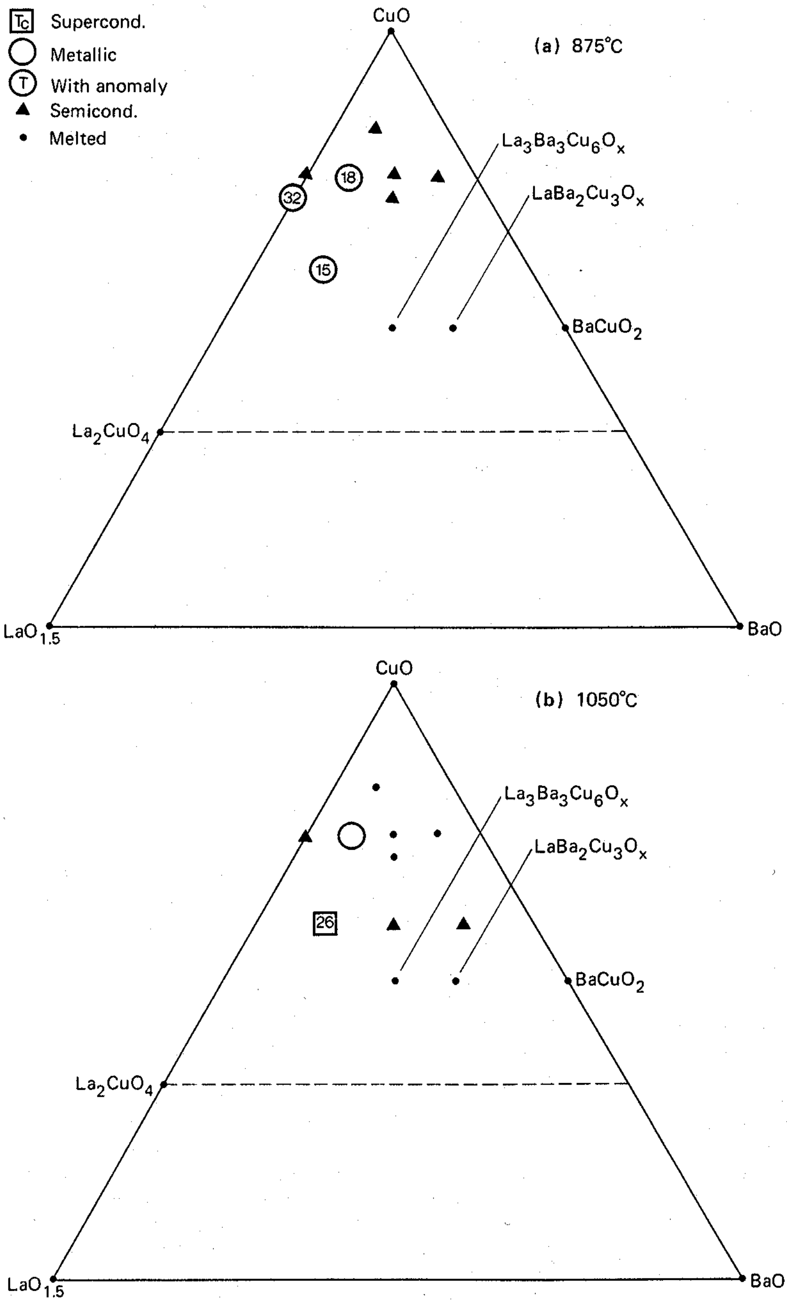

Figure 2. Compositions of La–Ba–Cu–O system and summary of results for samples prepared at (a) 875 °C and (b) 1050 °C.

Ba_3 Cu_6 O_x, (16) or La Ba_2 Cu_3 O_x (17-18). In the Y-Ba-Cu system (Figure 3), the anomalies observed near 90K are probably associated with the superconducting phase Y Ba_2 Cu_3 O_x (Tc=95K) (2).

The unexpected results of this study have come from the samples prepared at higher than normal temperatures (i.e. 1050 and 1200 C vs 950 C). The first result concerns the phase diagram for Y-Ba-Cu determined (10,11) at 950 C, some of the tie lines of which are shown in Figure 3a,b,c. Samples reacted at 875 (Fig.3a) behave as expected: that is, samples with compositions within the shaded area should contain some of the phase Y Ba_2 Cu_3 O_x and hence become superconducting near 90K, as observed. Compositions outside this shaded area were found to be semiconducting.

When these same compositions are prepared by reacting the material at 1050 and 1200 C, different results are obtained, as readily seen as shown in Figs. 3b and c, where a number of samples with compositions outside the shaded area exhibit superconductivity. Samples prepared at 1050 C tend to have superconducting transitions near 45K, while those prepared at 1200 C have T_c near 90K. Preliminary powder X-ray diffraction results indicated that $Y_{1.8}$ $Ba_{0.2}$ Cu_2 O_x prepared at 1050 C contains primarily Y_2 Cu_2 O_5 and Y Ba_2 Cu_3 O_x, with very little of the green Y_2 Ba Cu O_5. Large amounts of this latter phase would have been expected on the basis of the 950 C phase diagram. These data suggest that a quite different phase diagram which is appropriate for the 1050/1200 C samples. In fact, at these higher temperatures it appears that the tie line extends NOT from Y_2 Ba Cu O_5 to CuO, but from Y_2 Cu_2 O_5 to Y Ba_2 Cu_3 O_x. Partial melting of some of these samples indicates that this behavior may arise from complications of liquidus effects. More extensive measurements are necessary to confirm this conjecture.

For all the highly conducting samples made in this study, care was taken to measure the conductivity quickly after removal from the oven, and to look carefully between 300K and 90K. Generally, no indication of any resistance anomaly was observed, consistent with all previous work in our laboratory. On several samples prepared at 1050 and 1200 C, however, anomalies in the measured voltage were observed at high temperatures. In Fig. 4, an example of these data is shown for a sample with a composition of $Y_{1.5}$ $Ba_{.5}$ Cu O_x.

In this case, the effect observed is produced by temperature dependent current contacts and NOT by superconductivity. Here the room temperature current contact resistance was about 4K ohm. This resistance increased to around 10^9 ohms at 77 K, thus, over most of the temperature range of the measurement, the voltage source was not behaving as an ideal current source, resulting in an apparent drop in resistance as the temperature was lowered, producing the 220 K "onset" shown in Fig. 4.

In one of our samples of composition $Y_{1.2}$ $Ba_{0.8}$Cu O_x, the voltage contact resistance varied over several megaohms between room temperature and 77 K. Under these conditions, the 100 megaohm input impedance of the signal channel no longer represented an ideal voltmeter and significant fluctuating current was drawn through the voltage contacts resulting in an apparent resistive anomaly in the 200-300 K range. This anomaly disappeared under temperature cycling as the voltage contact impedance decreased.

These results demonstrate that high temperature resistive anomalies can be produced by temperature dependent contact resistance. Moreover, our experience has been that the contacts can become quite capacitive as the temperature is lowered, shifting the voltage output into quadrature, again producing an apparent drop in resistance.

Given the fact that resistive anomalies can arise from the above variety of measurement artifacts, we suggest that workers observing indications of

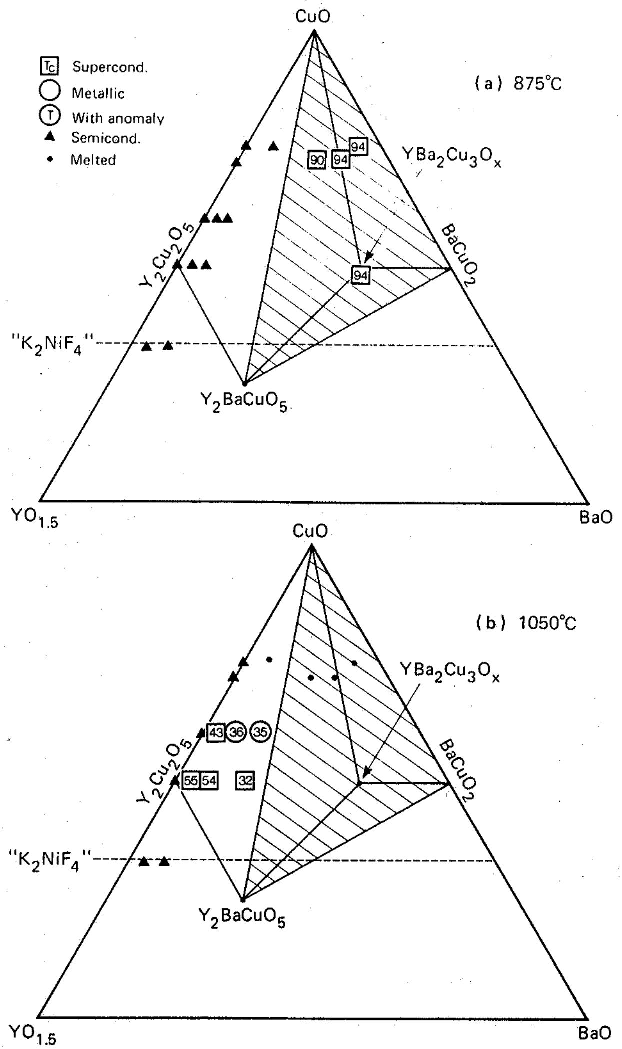

Figure 3. Compositions of Y–Ba–Cu–O system and summary of results for samples prepared at (a) 875 °C and (b) 1050 °C. *Continued on next page.*

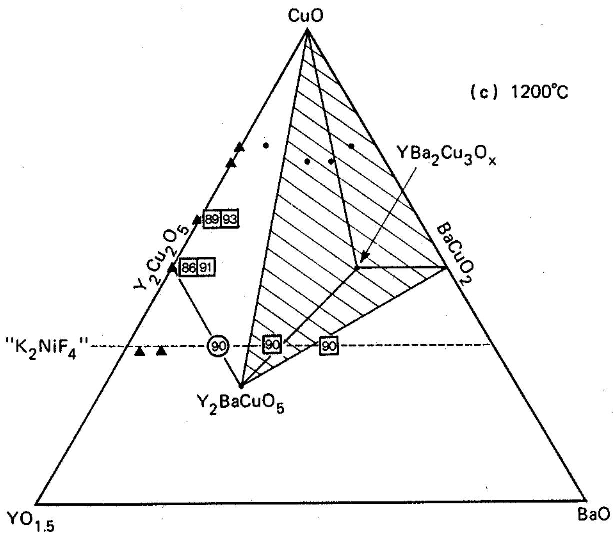

Figure 3. *Continued.* Compositions of Y–Ba–Cu–O system and summary of results for samples prepared at (c) 1200 °C.

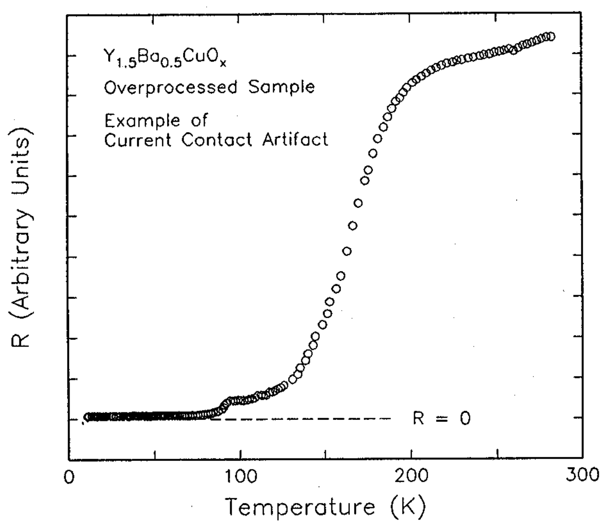

Figure 4. Resistance of sample prepared at 1200 °C exhibiting anomalous drop at 170 K. It is shown that the behavior observed in this sample is caused by an artifact rather than superconductivity.

superconductivity above 100 K during four-probe measurements follow the following guidelines in reporting their results:

- Measure temperature dependence of contacts by two-probe pairwise measurements and report numerical values.
- Permute current and voltage contacts to check for topological artifacts (19-20).
- Monitor quadrature signal throughout temperature scan for capacitive effects and report results.
- If anomalies are observed, try several different sample currents and signal frequencies.
- Look at second harmonic component via oscilloscope for evidence of contact/sample nonlinearities.
- Report fully on all observations listed above.

Conclusion

A broad search of 57 copper oxide compositions prepared at three different temperatures has indicated the difficulty of discovering new superconducting compounds. The dependence of the results on the preparation temperature suggests that the effective phase diagram may be quite different at different temperatures. Finally, it was found that samples prepared with multiple phases at too high temperatures can show resistivity anomalies at temperatures as high as 260K, which are not an indication of superconductivity. Rather, they are artifacts caused by the extreme microscopic inhomogenity of such samples and the difficulties of making good contacts to them.

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