

Structural and Physical Properties of the $(\text{Cu,C,B})\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ Superconductors with T_C up to 130K under pressure.

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By reduction treatments, the T_C of $\text{Cu}_{1-y}\text{C}_y\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ ($y \approx 0.5$) was raised from 67K up to 120K. As for the other high- T_C cuprates, the highest value for the family is then obtained for the $n=3$ member when the doping of the CuO_2 planes is optimum.

We have also prepared the $n=3$ and $n=4$ members of the $\text{B}_{1-y}\text{C}_y\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$ family, showing superconducting transitions at $\approx 100\text{K}$ and $\approx 115\text{K}$, respectively. From resistivity measurements under pressure, the T_C of both phases increased. Considering a charge transfer model without intrinsic structural effects, these as-prepared phases appear underdoped.

1. $\text{Cu}_{1-y}\text{C}_y\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$

In 1994, a new superconducting homologous series, $\text{Cu}_{1-y}\text{C}_y\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_x$ ($(\text{Cu,C})-12(n-1)n$) ($y \approx 0.5$) was synthesized at high pressure and high temperature [1]. Superconducting transition temperatures around 67K and 117K were measured for the $n=3$ and $n=4$ members, respectively. From measurements of T_C as a function of applied pressure, we have shown that the as-prepared samples of $n=3$ and $n=4$ were in an overdoped state and close to optimal doping, respectively [2]. This motivated us to study the possibility of changing the doping of the $n=3$ sample by reduction treatments.

The first samples were prepared according to a method described in [3] in which the carbon content was not controlled. Then, we developed a new synthesis process which enabled us to adjust the carbon stoichiometry. The carbon content of the precursors, subsequently checked using a carbon determinator (LECO, type WR12), was slightly higher than the nominal content. For the reduction, the samples were either heat-treated in argon at $\approx 400^\circ\text{C}$ for a few hours or heated with Zr metal in an evacuated quartz tube.

For samples with $y \leq 0.5$, the reduction treatment led to an enhancement of T_C from 67K to 120K (figure 1), that was attributed to a loss of oxygen. The lattice parameters increased concomitantly, and the pressure dependence of T_C indicated that the sample had reached the optimal doping. T_C decreased when the sample was subsequently heated in an oxygen

flow. The samples with $y \geq 0.5$ showed values of T_C as well as c lattice parameters somewhat larger than the previous ones (77K). After reduction, the maximum of T_C reached was between 112 and 118K. It should be mentioned, however, that the extend of the Cu/C solid solution range is rather narrow.

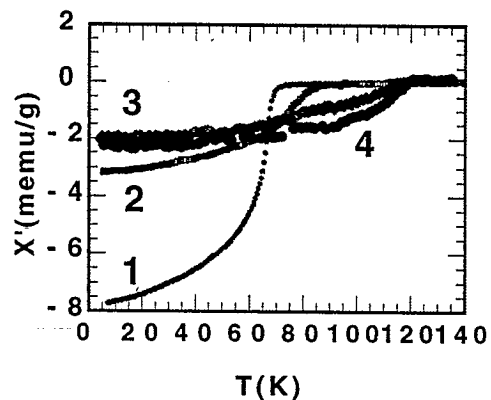


Figure 1 : χ_{ac} susceptibility as a function of temperature for an as-prepared sample (1) and after the successive heat-treatments under Ar at 400°C (2: 2hrs; 3: 4hrs; 4: 4.5hrs)

As for the other high T_C cuprates, the highest T_C of the family is then obtained for the $n=3$ member, and the lower the carbon content is the higher T_C is.

Synchrotron powder diffraction data were collected at Brookhaven on an $n=3$ as-prepared sample. A preliminary refinement indicates that an oxygen atom, probably the mobile one, is present

between two Cu atoms along the edge of the cell as in $\text{YBa}_2\text{Cu}_3\text{O}_7$. The formula of the $n=3$ phase can be written as $\text{C}_y\text{Cu}_{1-y}\text{Ba}_2\text{Ca}_2\text{Cu}_3\text{O}_{8+y+x}$ where x represents the amount of mobile oxygen. The average valence of Cu in the CuO_2 planes is then given by $v(\text{Cu}) = (8+2x-2y-(1-y)v(\text{Cu}_1))/3$ where $v(\text{Cu}_1)$ is the average valence of the Cu atoms in the basal plane of the structure. After the maximum reduction, x is equal to 0 and the valence of Cu in the basal plane, which is linearly coordinated, can be taken as +1. If one enters these values in the above equation, one finds $v(\text{Cu}) = (7-y)/3$. For $y=0.5$, this gives $v(\text{Cu}) \approx +2.16$ which is the value commonly found for cuprates optimally doped, and therefore in agreement with the behavior of T_C under pressure. For as-prepared samples, according to structural refinements, the oxygen site would be fully occupied and the valence of the Cu in the basal plane can be taken as +2. Then $v(\text{Cu})$ is equal to $(8-2y)/3$. For $y=0.5$ this gives $v(\text{Cu}) = +2.33$ and for $y < 0.5$ the $v(\text{Cu})$ will be higher. This would explain why the T_C of the samples prepared with less carbon is lower than that of the $y=0.5$ samples.

2. $\text{B}_{1-y}\text{C}_y\text{Ba}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+2+\delta}$

One structural feature that may be detrimental for higher T_C 's in the family described above is the fact that, due to the large difference between C-O and Cu-O bonds, there exist two apical Cu-O distances and that the CuO_2 plane may be buckled. This idea lead us to study the $(\text{C},\text{B})-12(n-1)n$ system since the B-O and C-O bonds have a comparable length (for triangular coordination). In this case, the Cu valence is adjusted by the C/B ratio. The $n=3$ member has been reported in [4].

We have prepared a sample with $n=3$ nominal composition. However, from x-ray diffraction about 1/3 of the sample corresponded to the $n=4$ member. The lattice parameters of the $n=3$ and $n=4$ phases were respectively $a=3.883(4)$ $c=14.71(3)$ Å and $a=3.875(5)$ $c=17.78(8)$ Å. For both phases the a value is much larger than for (Cu,C) samples, whereas the c parameter is shorter in agreement with the short B-O bond compared with the Cu-O one. Two T_C (onset) at $\approx 100\text{K}$ and $\approx 115\text{K}$ were measured from a.c. susceptibility and attributed from superconducting volume considerations to the $n=3$ and $n=4$ members, respectively.

When the sample was heated in reducing conditions, T_C decreased, whereas under an O_2 flow neither T_C nor the cell parameters changed.

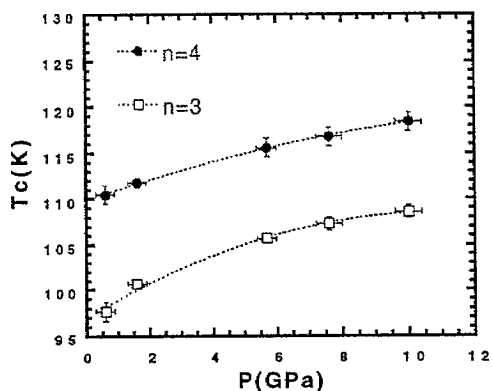


Figure 2 : Superconducting critical temperature (defined as the peak of dR/dT) as a function of pressure.

When measured as a function of applied pressure, these two T_C increased (figure 2) up to 109K and 118K (onset at 128K) at 10GPa. We even registered a point at 130K (onset) for the highest T_C for a pressure around 15 GPa. If the increase of T_C is only due to a charge transfer, as in $(\text{Cu},\text{C})-12(n-1)n$ samples, this indicates that both phases are underdoped. Otherwise, samples can be near the optimum doping, and an additional intrinsic structural effect should be considered, as in the Hg based phases [5], to account for this $T_C(P)$ behavior.

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