

A New Series of Oxycarbonate Superconductors (Cu_{0.5}C_{0.5})_mBa_{m+1}Ca_{n-1}Cu_nO_{2(m+n)+1}

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We found a new series of oxycarbonate superconductors in the Ba-Ca-Cu-C-O system under high pressure of 5 GPa. Their ideal formula is (Cu_{0.5}C_{0.5})_mBa_{m+1}Ca_{n-1}Cu_nO_{2(m+n)+1} ((Cu,C)-_{m(m+1)(n-1)n}). Thus far, n=3, 4 members of the m=1 series, (Cu,C)-1223 and (Cu,C)-1234, have been prepared in bulk while n=4, 5 members, (Cu,C)-2334 and (Cu,C)-2345, have been prepared for the m=2 series. (Cu,C)-1223 shows superconductivity below 67 K while T_c's of other compounds are above 110 K. In particular, (Cu,C)-1234 has the highest T_c of 117 K.

1. Introduction

Since the first discovery of the superconductor including carbon, (Ba,Sr)₂(Cu,C)₂O_y by Kinoshita and Yamada [1], various kinds of oxycarbonate superconductors have been reported; for instance, oxycarbonates based on the 123-type structure (e.g., (Y,Sr)Sr₂(C,Cu)Cu₂O_y [2]), Bi-oxycarbonates (e.g., Bi₂Sr₄Cu₂CO₃O_y [3]), Tl-oxycarbonates (e.g., Tl(Sr,Ba)₄Cu₂CO₃O_y [4]) and Hg-oxycarbonates (e.g., HgBa₂Sr₂Cu₂CO₃O_y [5]). These compounds have structures closely related to the mother superconductors, 123, Bi-2223, Tl-1223 and Hg-1223, respectively.

In this report, we discuss a new series of oxycarbonate superconductors, (Cu_{0.5}C_{0.5})_mBa_{m+1}Ca_{n-1}Cu_nO_{2(m+n)+1} ((Cu,C)-_{m(m+1)(n-1)n}) which are stable only under high pressure. The m=1 series of compounds have structures closely related to those of Hg(or Tl)-12(n-1)n [6]. The Hg (Tl) site is replaced by mixed atom of Cu and C in this series. The m=2 series have unique structures where three Ba planes are stacked in a charge reservoir block separated by the (Cu,C) ones [7].

Thus far, n=3,4 members of the m=1 series and n=4,5 members of the m=2 series have been prepared in bulk [6-7]. The highest T_c, 117 K was observed in (Cu,C)-1234 [6].

2. (Cu,C)-12(n-1)n series

The m=1 series of superconductors have been prepared under 5 GPa and 1200° C by using Ag₂O as an oxidizing agent [6]. In Fig. 1, crystal structures of the m=1 series are shown for n=3 and 4. These structures are closely related to those of Hg(or Tl)-12(n-1)n, n=3 and 4, respectively. Three and four CuO₂ planes are stacked separated by the Ca planes. The Hg(or Tl) site is replaced by the (Cu,C) mixed atoms. The interesting

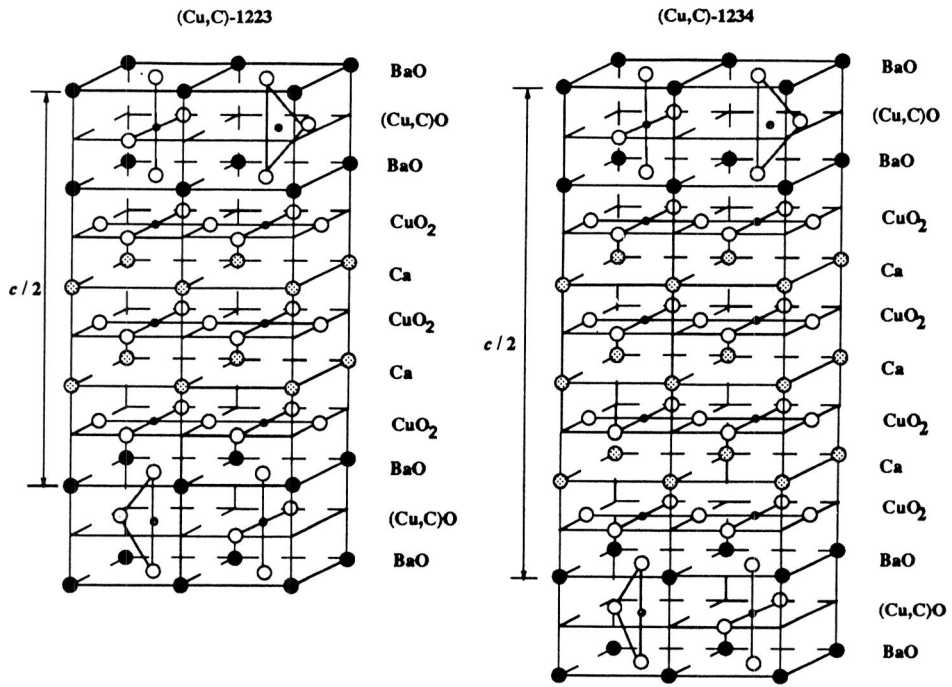
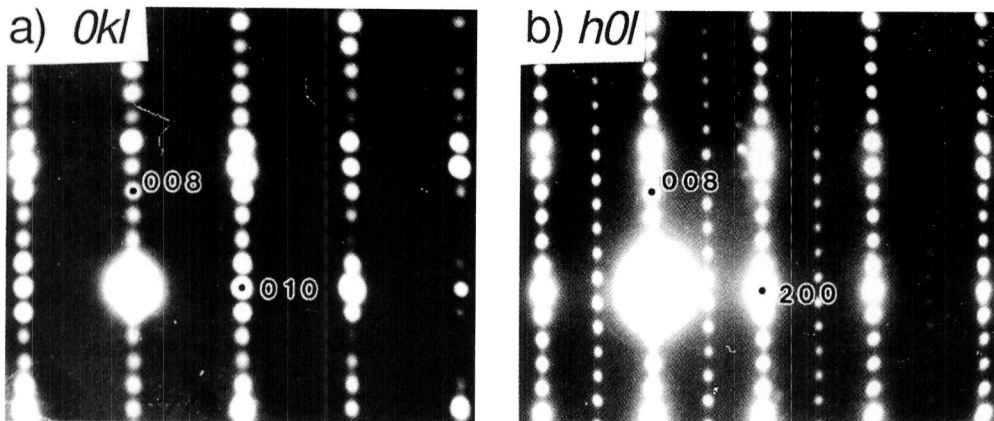
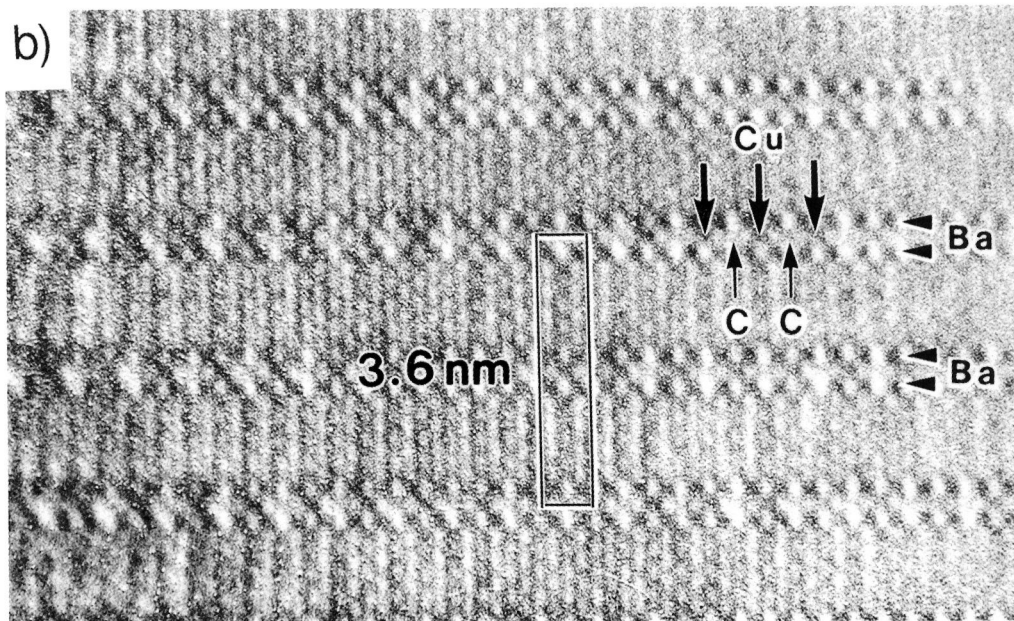
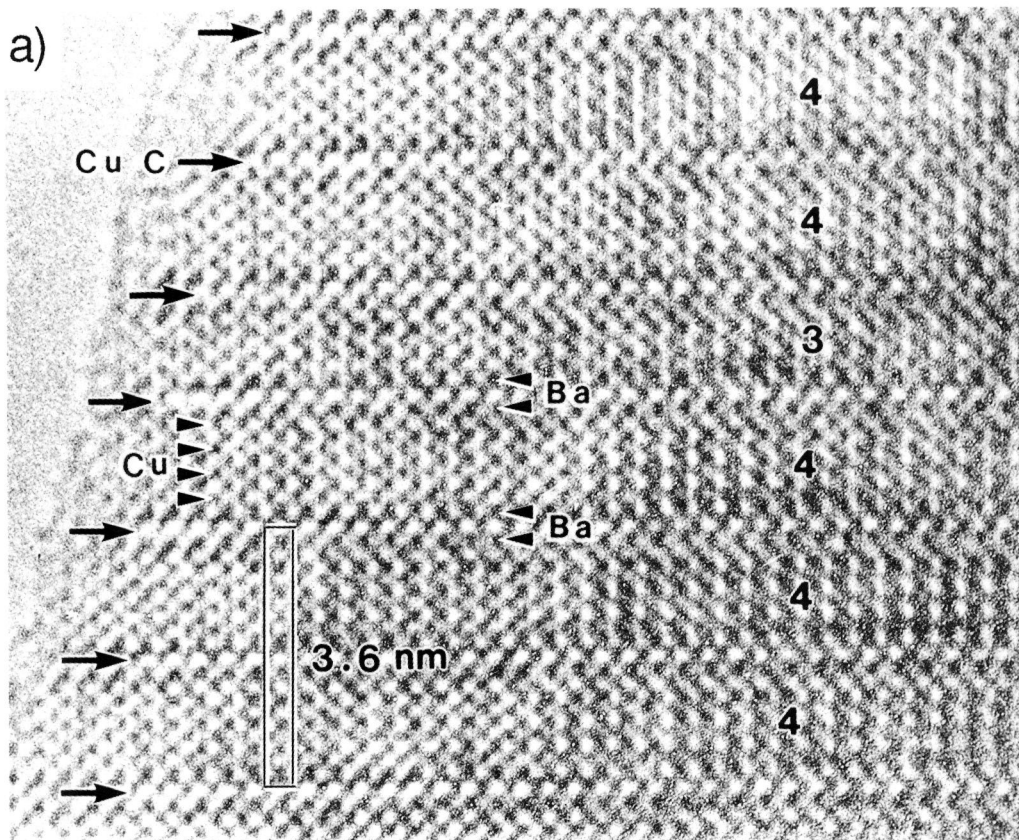


Fig.1. Structures of $(\text{Cu,C})\text{-}12(n-1)n$ [6].



Figs.2 (a,b). Electron diffraction patterns of $(\text{Cu,C})\text{-}1234$.
 Indexes are given based on the orthorhombic superlattice.



Figs.3 (a,b) Lattice images of (Cu,C)-1234.
 a) projected along [100] b) along [010]

feature of the present compounds is ordering between Cu and C in the (Cu,C) plane between the Ba ones; they are placed alternatively along the a-axis. This results in a superstructure having $a_s=2a$, $b_s=b$, $c_s=2c$ with respect to a tetragonal subcell, a, b, c.

This Cu-C ordering was confirmed by electron microscopic observation. As an example, Figs. 2(a,b) show $0kl$ and $h0l$ electron diffraction patterns of (Cu,C)-1234. The patterns are compatible with the above-mentioned superstructure with the space group Bmmm. Figures 3(a,b) indicate lattice images of (Cu,C)-1234 corresponding to the diffraction patterns in Figs. 2(a,b), respectively. The (Cu,C) plane between the Ba ones consists of two types of dots in Fig. 3(b); dark and less dark dots are placed alternatively indicating the ordered arrangement, -Cu-C-Cu-C along the a-axis. The adjacent (Cu,C) planes have a different phase with respect to the Cu-C sequence, C-Cu-C-Cu, which causes $2c$ periodicity. Shimakawa et al. analyzed the structure of (Cu,C)-1234 by neutron powder diffraction and suggested that the Cu/C ratio in the (Cu,C) plane is not exactly 0.5/0.5 but 0.68/0.32 [8]. The partial substitution of Cu for C or mutual substitution between them in the (Cu,C) plane might occur in the present series of compounds. In addition, EPMA measurement indicated that significant substitution of Ca for the Ba site occurs in (Cu,C)-1234 [6].

In Fig. 4. DC magnetic susceptibility data are shown for (Cu,C)-1223 and 1234. The (Cu,C)-1223 phase becomes superconducting below 67 K while the (Cu,C)-1234 phase below 117 K. Kumakura et al. determined critical current densities and irreversibility fields for (Cu,C)-1223 and 1234 [9]. According to them, temperature dependencies of J_c 's in a magnetic field are much smaller than that of Hg-1223 in the $m=1$ series of compounds. Moreover, the slopes of irreversibility lines for them are steeper than that of Hg-1223.

3. (Cu,C)-23(n-1)n series

The $m=2$ series of compounds have been prepared under 5 GPa and 1250° C using Ag₂O as an oxidizing agent [7]. Crystal structures of the $m=2$ series are shown in Fig. 5 for $n=4,5$. This series have unique structures where three Ba-planes are stacked in a charge reservoir block separated by the (Cu,C) planes. The Cu-C ordering in the (Cu,C) plane was confirmed by the electron microscopic observation as well as in the $n=1$ series [7]. The phase of the Cu-C-Cu-C sequence is the same in every (Cu,C) plane in contrast to the $m=1$ series which results in a superstructure, $a_s=2a$, $b_s=b$, $c_s=c$ with respect to a tetragonal subcell, a, b, c. The $m=2$ series of compounds are the first examples which include three Ba planes in a charge reservoir block. This type of block seems unstable because of highly active Ba ions. In the structures in Fig. 5, every Ba ion is bounded to at least one CO₃ group. This seems key factor to stabilize the Ba ion.

It is more difficult to prepare the $m=2$ series than $m=1$ series of compounds. At the present stage, a pretty good sample have been obtained for the $n=4$ member but the $n=5$ member was prepared only as

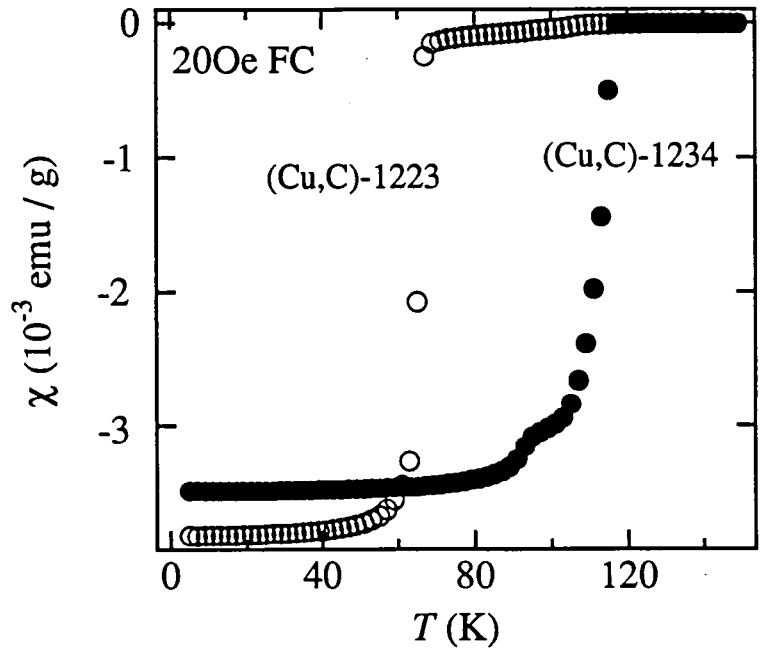


Fig. 4. DC susceptibility data for (Cu,C)-12(n-1)n [6].

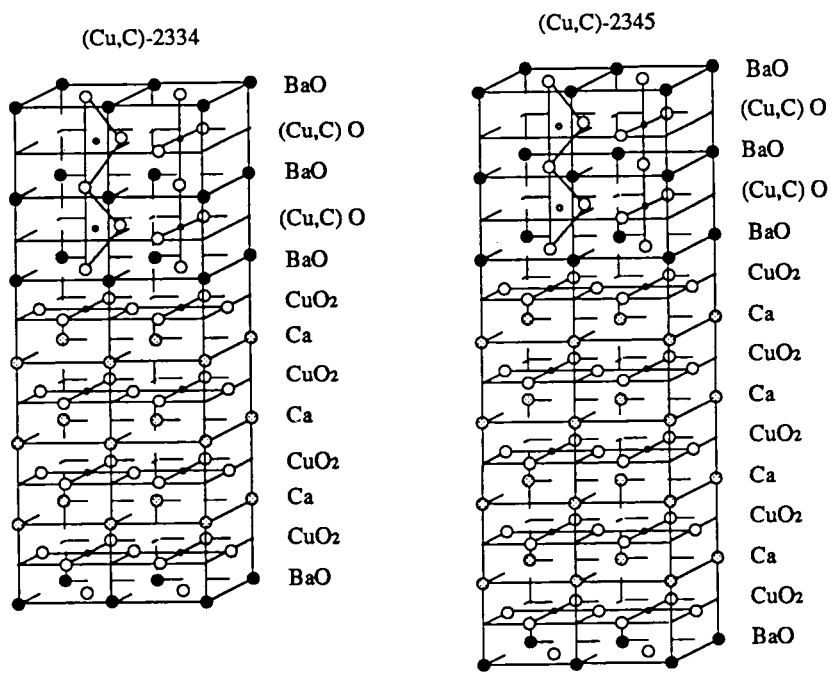


Fig. 5. Structures of (Cu,C)-23(n-1)n [7].

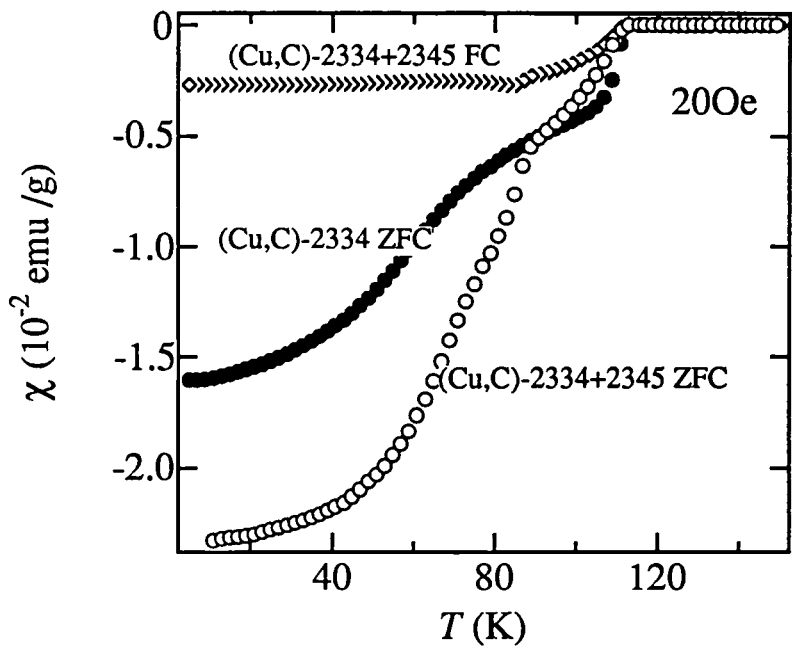


Fig. 6. DC susceptibility data for (Cu,C)-23(n-1)n [7].

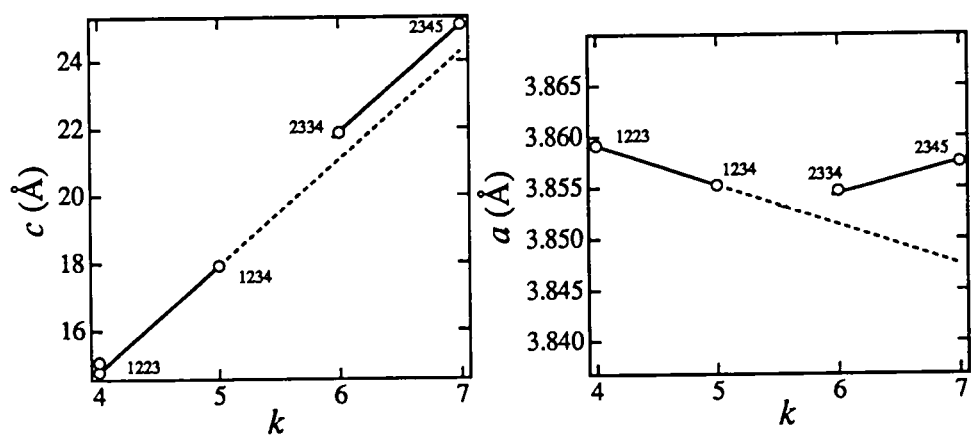


Fig. 7. Lattice parameters of (Cu,C)-m(m+1)(n-1)n [7].

mixture with the $n=4$ one [7]. Figure 6 shows DC magnetic susceptibility data for (Cu,C)-2334 and the mixture of (Cu,C)-2334 and 2345 [7]. Both samples show diamagnetic susceptibility below 113 K indicating that T_c of (Cu,C)-2334 is 113 K. Although we can not determine T_c of (Cu,C)-2345 definitely, it is suggested to be near 110 K since the mixture of (Cu,C)-2334 and 2345 indicated larger diamagnetic susceptibility at 5 K (see Fig. 6).

Lattice parameters of tetragonal subcells of (Cu,C)- $m(m+1)(n-1)n$ are plotted in Fig. 7 against k , sum of (Cu,C) and Cu planes in a unit formula. The c -dimensions of the $23(n-1)n$ deviate upward from the straight line obtained for the $12(n-1)n$ series. This is probably due to larger number of Ba planes included in a subcell of (Cu,C)- $23(n-1)n$ than in (Cu,C)- $12(n-1)n$. The a -axis of (Cu,C)- $23(n-1)n$ also changes in a different manner as a function of k ; it tends to increase with k while that of (Cu,C)- $12(n-1)n$ decreases with k .

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