A New Series of Oxycarbonate Superconductors
(Cu0.5C0.5)mBa(m+1)Can−1Cu(n+1)O2(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 (Cu0.5C0.5)mBa(m+1)Can−1Cu(n+1)O2(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 Tc's of other compounds are above 110 K. In particular, (Cu,C)-1234 has the highest Tc of 117 K.

1. Introduction

Since the first discovery of the superconductor including carbon, (Ba,Sr)2(Cu,C)2Oy 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)Cu2Oy [2]), Bi-oxycarbonates (e.g., Bi2Sr4Cu2CO3Oy [3]), Ti-oxycarbonates (e.g., Ti(Sr,Ba)4Cu2CO3Oy [4]) and Hg-oxycarbonates (e.g., HgBa2Sr2Cu2CO3Oy [5]). These compounds have structures closely related to the mother superconductors, 123, Bi-2223, Ti-1223 and Hg-1223, respectively.

In this report, we discuss a new series of oxycarbonate superconductors, (Cu0.5C0.5)mBa(m+1)Can−1Cu(n+1)O2(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 Ti)-12(n−1)n [6]. The Hg (Ti) 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 Tc, 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 Ti)-12(n−1)n, n=3 and 4, respectively. Three and four CuO2 planes are stacked separated by the Ca planes. The Hg(or Ti) site is replaced by the (Cu,C) mixed atoms. The interesting
Fig. 1. Structures of (Cu,C)-12(n-1)n [6].

Figs. 2 (a,b). Electron diffraction patterns of (Cu,C)-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 a
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 \(0k0\) 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
-Cu-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 \(Ag_2O\) 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 \(CO_3\) 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 Tc of (Cu,C)-2334 is 113 K. Although we can not determine Tc 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.

References