Superconductivity at 108 K in the simplest non-toxic double-layer cuprate of Ba$_2$CaCu$_2$O$_4$(O,F)$_2$

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Abstract. We report the superconductivity in apical fluorine system of Ba$_2$CaCu$_2$O$_{6-y}$F$_y$: the second member of Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$(O,F)$_2$ homologous series. The polycrystalline samples of Ba$_2$CaCu$_2$O$_{6-y}$F$_y$ (F-0212) were synthesized under high pressure as a parameter of nominal fluorine content ($y$). Samples with $y = 2.0 \sim 1.2$ elucidating the very sharp superconducting transitions in temperature dependence of susceptibility from under doping state to slightly over doping state via optimal doping state. A remarkable highest $T_c$ of 108 K has been achieved for the sample synthesized from a nominal composition of Ba$_2$CaCu$_2$O$_{4.4}$F$_{1.6}$. This $T_c$ is highest among the double CuO$_2$ layered system except for that including toxic elements such as Hg and Tl. The $T_c$ has been systematically controlled from 57 K to 108 K by controlling the doping state, by designing the starting composition of fluorine and oxygen. The strong dependence of the ‘$a$’ and ‘$c$’ lattice constants were found on the nominal F content. We propose the Ba$_2$CaCu$_2$O$_4$(O,F)$_2$ as a promising material for practical use due to its high $T_c$ and non-toxicity with a simple crystal structure.

1. Introduction

Since the historical discovery of high-$T_c$ superconductivity (HTSC) in the perovskite like cuprate oxides in 1986 by Bednorz and Muller [1], a large number of oxide HTSC have been reported. The origin of HTSC is still not well understood despite 20 years of intensive research. All HTSC compounds share a layered structure made up of one or more copper-oxygen (CuO$_2$) planes. Three or more layered cuprates consist of inequivalent types of CuO$_2$ layers: an outer CuO$_2$ plane (OP) in a fivefold pyramidal coordination and an inner plane (IP) in a fourfold square one. The presence of apical oxygen has been regarded as indispensable for the occurrence of superconductivity in hole-doped cuprate superconductors. Leaving the [CuO$_2$] plane unchanged but replacing the anion of the off-plane block by halide, would be an exciting quest for new HTSC [2-5]. In this paper, we report the successful synthesis and preliminary physical characterization of superconductivity in apical fluorine system of Ba$_2$CaCu$_2$O$_4$(O,F)$_2$: the second member of Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$(O,F)$_2$ homologous series [6-9].

The schematic view of the crystal structure of F-0212 is shown in Fig.1. It is isostructural with (La,Sr)$_2$CaCu$_2$O$_8$ [10] superconductors which is built of double [CuO$_2$] planes and two layers of rocksalt type off-plane block. The carrier concentration ($T_c$) is controlled by a substitution of fluorine (F$^-$)
for an apical oxygen site ($O^2$), which contrasts with structurally analogous compounds such as $La_2CuO_4$ and $Ca_2CuO_2Cl_2$ where the cation sites of $La^{3+}$ and $Ca^{2+}$ are substituted by $Sr^{2+}$ ($Ba^{2+}$) and $Na^+$, respectively [4,10].

**Figure 1** Crystal structure of $Ba_2CaCu_2O_4F_2$ (F-0212).

### 2. Experimental

High-pressure synthesis paves a unique pathway to approach high-$T_c$ superconducting cuprates (HTSC). Polycrystalline samples were synthesized using high-pressure synthetic route by controlling fluorine and oxygen content in the sample. $BaO_2$, $BaF_2$, $CaF_2$, $CuO$, $CuO$ and a precursor of $Ba_2CaCu_3O_x$ ($x \approx 7.39$) were used as the source materials. The precursor was prepared from $CuO$, $BaO_2$ and $Ca_2CuO_3$ by heating at 1,183 K for 12 hours in an oxygen flow. The $Ca_2CuO_3$ compound was prepared from $CaCO_3$ and $CuO$ by heating at 1,273 K for 24 h in oxygen flow with intermediate grinding. The oxygen content of the precursor was estimated from the weight change by heating. The source materials were weighed at nominal compositions of $Ba_2CaCu_2O_{6-y}F_y$ and mixed thoroughly by an agate mortar in a glove box filled with dry nitrogen gas. The mixtures were pressed into a pellet and sealed in a gold capsule. The gold capsule was heated at temperature 1,323 K and under pressure of 5 GPa for 120 min, using a cubic-anvil-type (Riken CAP-07) high pressure apparatus. Phase identification was done by means of powder X-ray diffraction (XRD) carried out by Rigaku RINT 1100 using CuK$_\alpha$ radiation. The resistivity was measured by standard four-probe method. The DC magnetic susceptibility was measured with decreasing temperature in a magnetic field of 10 Oe (field cooling) using a SQUID magnetometer (Quantum Design MPMS). Elemental analyses of polycrystalline F-0212 samples were performed in scanning electron microscope (Hitachi S-3000) using energy dispersive X-ray spectrometer (SEM-EDX).

### 3. Results and discussion

Fig. 2 shows the X-ray diffraction patterns of $Ba_2CaCu_2O_{6-y}F_y$ samples with ‘$y$ = 2.2, 2.0, 1.8, 1.6, 1.4 and 1.2. Most peaks could be indexed on the basis of tetragonal $I4/mmm$ symmetry. Obvious impurity phases were not recognized from X-ray diffraction (XRD) patterns of ‘$y$ = 2.0 and 1.8 samples (Fig. 2 d and e respectively). Several impurity peaks observed to increase in the XRD pattern of ‘$y$ = 1.2, 1.4, 1.6 and 2.2 samples as shown in (Fig. 2 a, b, c and f respectively).
Along with minor F-0223 phase, unknown impurity peaks were also recognized in ‘y’ = 2.2 sample. The tendency of sample quality is similar to the case of Ba$_2$Ca$_3$Cu$_4$O$_{10-y}$F$_y$ (F-0234)[9]. In case of F-0234, namely, the sample of ‘y’ = 1.6 is nearly single phase and unknown impurity peaks increases apart from ‘y’ = 1.6 [9].

![Figure 2](image)

**Figure 2.** X-ray diffraction patterns of Ba$_2$Ca$_2$Cu$_2$O$_{6-y}$F$_y$ samples with (a) y = 1.2 , (b) y = 1.4, (c) y = 1.6, (d) y = 1.8, (d) y = 2.0 and (f) y = 2.2 (* = F-0223 and x = impurity peaks)

![Figure 3](image)

**Figure 3** The variation of the lattice parameters ‘a’ and ‘c’ are plotted against the nominal ‘y’ content in the Ba$_2$Ca$_2$Cu$_2$O$_{6-y}$F$_y$ sample.

The variation of the lattice parameters are plotted in Fig. 3, against the nominal ‘y’ content in the Ba$_2$Ca$_2$Cu$_2$O$_{6-y}$F$_y$ sample. As ‘y’ decreases, the a-axis length decreases monotonically, while ‘c’-axis length increases. This attributes that carrier (hole) concentration increases with decreasing ‘y’, and
thus the carrier concentration in the CuO$_2$ planes is controlled systematically by changing the oxygen and fluorine composition. The increase of $c$-axis length on going from Ba$_2$CaCu$_2$O$_3$F$_2$ ($a = 3.885 \text{ Å}, c = 20.961 \text{ Å}$) to Ba$_2$CaCu$_2$O$_4$F$_2$ ($a = 3.869 \text{ Å}, c = 21.170 \text{ Å}$) can be explained by the expansion of the (Ba,Ca)-F rock-salt block due to the enhanced Coulomb repulsion between the adjacent (monovalent) F layers resulting from the introduction of (divalent) oxygen. The reduction in the ‘$a$’ parameter is expected for $p$-type carrier doping. The lattice parameter for highly unstable system Ba$_2$CaCu$_2$O$_6$ ($a = 3.85 \text{ Å}, c = 22.0 \text{ Å}$) by Yamauchi et al. [11] supports to our above conclusion. The $a$-parameter of F-0212 (3.873Å for $\gamma = 1.6$) is relatively large compared with the other double-layered system; for example, HgBa$_2$CaCu$_2$O$_y$ and Tl$_2$Ba$_2$CaCu$_2$O$_y$ have $a$-parameter of 3.85~3.86Å.

According to Adachi et al. [12], the ‘$c$’ parameter of Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$($n+1$) series with ($n = 2$) is 20.4 Å. In the present studies, ‘$c$-axis’ of Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$F$_2$ series with ($n = 2$) is 20.977 Å. This seems to reflect that this increase in ‘$c$’ parameter is due to the replacement of Sr in Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$($n+1$) by Ba in Ba$_2$Ca$_{n-1}$Cu$_n$O$_{2n}$F$_2$ system.

In order to evaluate the micro-structural features of F-0212 polycrystalline sample, they were subjected to scanning electron microscopic (SEM) characterization. The typical scanning electron microscopy (SEM) images of F-0212 with $\gamma = 2.0$ and $\gamma = 1.6$ samples are shown in figure 4. The micrograph reveals the continuous nature of grains in F-0212 polycrystalline sample. The grains are almost randomly aligned, rectangular-shaped platelets with a typical size of 25 μm for $\gamma = 2.0$ and 7μm for $\gamma = 1.6$ were estimated.

The EDX analyses of $\gamma = 2.0$ sample revealed that the average Ba:Ca:Cu ratio was 2.05:0.99:1.94. The cation ratio was averaged for several grains shows good agreement with the nominal chemical composition. Although the cuprate superconductors, whose crystal structures are analogous to F-0212 phase, have a tendency to decompose in the air [11], the F-0212 phase was observed relatively stable. A striking degradation of the superconducting properties was not found in F-0212 polycrystalline sample. The grains are almost randomly aligned, rectangular-shaped platelets with a typical size of 25 μm for $\gamma = 2.0$ and 7μm for $\gamma = 1.6$ were estimated.

![SEM photographs of Ba$_2$CaCu$_2$O$_6$F$_y$ (F-0212) with (a) $\gamma = 2.0$ and (b) $\gamma = 1.6$](image)

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The temperature dependence of the susceptibility for Ba$_2$CaCu$_2$O$_6$F$_y$ samples with ‘$\gamma$’ = 1.2 ~ 2.2. The observed superconducting transition temperatures ( $T_c$’s) for ‘$\gamma$’ = 1.2, 1.4,1.6, 1.8, 2.0 and 2.2 were 106 K, 106 K, 108 K, 87 K, 82 K and 57 K, respectively. Samples with ‘$\gamma$’ = 1.2 ~ 2.0 (Fig.4 a–d) have shown sharp superconducting transitions, representing that F-0212 phase has an aptitude as an inherent homogeneous superconductor. The cations of Ba, Ca and Cu do not substitute each other, and there is no disorder coming from the inter-atomic substitution in this phase. This is one of the facts that F-0212 system shows higher $T_c$ and sharp superconducting transition. An inhomogeneous distribution of anions and/or cations in samples causes the $T_c$ to distribute widely. Broad transition observed in the ‘$\gamma$’ = 2.2, means that the nominal composition ‘$\gamma$’ = 2.2 is not suitable for preparation of homogeneous sample.
The absolute values of susceptibility of ‘y’ = 1.2 ~ 1.6 at low temperature (5K) is smaller than that of ‘y’ = 1.8 ~ 2.0 although they are large enough as bulk superconductors. It might be due to the fact that the difference of pinning properties rather than sample purity. Namely, pinning forces of ‘y’ = 1.6, 1.4 and 1.2 are stronger than that of ‘y’ = 2.0 ~ 2.2 due to their higher carrier concentrations as reported in ref [13].

If all of the apical oxygen sites are replaced by fluorine ions (F−) a nominal Cu valence is +2 on average. In this case, an antiferromagnetic insulating state is expected to occur, but, superconductivity with $T_c = 82$ K takes place. Hole carriers might be introduced by the existence of apical oxygen and/or interstitial fluorine/oxygen anions even in the case that the nominal composition is Ba$_2$CaCu$_2$O$_6$F$_{y}$. In order to understand the mechanism of the carrier doping, the actual oxygen and fluorine content has to be elucidated. However, the over all composition of the samples synthesized under high-pressure is the same as that of nominal composition. When the sample include some impurity phases, it is quite difficult to measure actual anions ratio by titration method. It is also difficult to know oxygen and fluorine content by neutron and X-ray diffraction analysis because the scatting factor of oxygen and fluorine are almost same. By considering that the real composition of ‘y’ = 1.8 is the same as the nominal composition of sample Ba$_2$CaCu$_2$O$_{4.2}$F$_{1.8}$, the Cu valence becomes 2.1+ which is a reasonable value for superconductivity.

Starting from ‘y’ = 2.2, the $T_c$ increases with decreasing ‘y’ and has a maximum value of 108 K for ‘y’ = 1.6, then, the $T_c$ deceases for the sample ‘y’ = 1.4. As far as we know, the maximum $T_c$ of 108 K is the highest among the double CuO$_2$ layered system without Tl- and Hg-system as well as among the isostructural cuprates such as (La,Sr)$_2$CaCu$_2$O$_6$ ($T_c = 60$ K), (Cu,Na)$_2$CaCu$_2$O$_4$Cl$_2$ ($T_c = 49$ K), (Sr,Ca)$_2$Cu$_3$O$_4$+$\delta$Cl$_{2\nu}$ ($T_c = 80$ K) and Sr$_2$CaCu$_2$O$_{4+\delta}$F$_{2\nu}$ ($T_c = 99$ K) [14]. Cation site substitutions for carrier doping or mixing of Sr and Ca have been pointed out to decrease the $T_c$ [15,16]. The realization of highest $T_c$ in Ba$_2$CaCu$_2$O$_y$(F,O)$_2$ might be the fact that the disorder accompanied by carrier doping (apical fluorine substitutions) is small. Toxicity and high vapor pressure of Tl and Hg sometimes becomes an obstacle for application of Tl- and Hg-system. Compared to Hg- and Tl- based superconductor, F-0212 superconductor has much thinner “blocking layer”, leading to intermediate anisotropy compared with Cu-1212 (Y-123) and Hg-system. Therefore, this system would be a potential candidate as practical materials for application, if we can synthesize the sample either without high pressure or films of this system [17].
Conclusions:
We have successfully synthesized the F-0212 superconductor with a maximum $T_c$ of 108 K. This $T_c$ is the highest among the double CuO$_2$ layered system without Tl and Hg-system. The ability to fine tune the crystal structure and change the charge-carrier concentration in these materials by varying the fluorine and oxygen content gave plenty of room for manoeuvre to optimize $T_c$. It should be noted that the $T_c$'s of the present series of phases are very high in spite of the presence of the apical fluorine atom. In particular, $T_c$ of $'y'$ = 1.6, 108K, is comparable to the highest $T_c$ observed in halogen-free oxide superconductors. This fact clearly indicates that the structure and the carrier density of the CuO$_2$ planes are essential to determine $T_c$ and the blocking layer is important as long as it is concerned with the creation of the carriers.

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