Iodine intercalation into $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}(\text{O,F})_2$ multilayered superconductors

A Iyo$^1$, P M Shirage$^1$, D D Shivagan$^1$, Y Tanaka$^1$, H Kito$^1$, Y Kodama$^1$, K Tokiwa$^2$, and T Watanabe$^2$

$^1$National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Umezono, Tsukuba, Ibaraki 305-8568, Japan

$^2$Department of Applied Electronics, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-3510, Japan

iyo-akira@aist.go.jp

Abstract. We have synthesized an iodine-intercalated superconductor $\text{I}_x\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}(\text{O,F})_2$. The intercalation was performed by heating a host compound of $\text{Ba}_2\text{Ca}_3\text{Cu}_4\text{O}_{8}(\text{O,F})_2$ with $\text{I}_2$ in an evacuated quartz tube. The $T_c$ significantly increased from 82 K to 121 K by the iodine intercalation. The $T_c$ is the highest in four CuO$_2$ layered cuprates excluding Hg- and Tl-system. The iodine will be intercalated between Ba-(O,F) layers. Composition analysis indicated that nearly stage-I iodine intercalation (about $x=0.9$) was realized. The iodine atoms expand the spacing between the double Ba-(O,F) layers by about 4.0 Å which is comparable to the value of 3.5 Å for the iodine intercalation to Bi-system.

1. Introduction

Apical-fluorine system (F-system) is written by the chemical formula of $\text{Ba}_2\text{Ca}_n\text{Cu}_{2n}\text{O}_{n+2}(\text{O,F})_2$ for $n=2$ (F-02), $n=3$ (F-03), and $n=4$ (F-04) where “$n$” is the number of CuO$_2$ layers between the double Ba(O,F) layers. Figure 1 shows the crystal structure model for $n=4$, $\text{Ba}_2\text{Ca}_4\text{Cu}_8\text{O}_{10}(\text{O,F})_2$ (F-0234). It includes four CuO$_2$ layers between the charge reservoir layer (CRL) of (Ba(O,F))$_2$. There are some similarities between the F-system and Bi-system as follows. The stacking of layers across the CRL is staggered configuration. The Bi-system is known to show a cleavage between weakly coupled double Bi-O layers. The F-system also shows cleavage most probably between the double Ba(O,F) layers. An angle resolved photoemission spectroscopy (ARPES) has been performed using clean surface obtained by cleaving the single crystals [1,2,3]. The F-system prefers to stay on under-doped region. In case of $n=2$ (F-02), the doping state can attain to optimal with $T_c=108$ K [4]. For the F-0234 case, however, the doping state does not attain optimal although the $T_c$ can be changed widely in the under-doped region from 55K to 105K [5]. The CuO$_2$ planes are almost flat comparably to Hg-system having highest $T_c$ in cuprates [6]. The flatness of CuO$_2$ planes is known to an important factor for higher $T_c$. We, therefore, thought that F-system must have a potential for higher $T_c$ if carriers could be doped enough to attain a maximum $T_c$. We tried to change fluorine/oxygen content at apical site to dope more holes. But we had not succeeded to synthesize samples having $T_c$ higher than 105 K so that we had to select an alternative route to dope carriers. Then we attempted to introduce carriers to CuO$_2$ planes by an iodine intercalation between the...
weakly-connected double Ba(O,F) layers following the example of Bi-system whose hole concentration is increased by ionized iodine atoms intercalated between double BiO layers [7,8,9].

**Figure 1.** Crystal structure model for $n=4$, Ba$_2$Ca$_3$Cu$_4$O$_{2n}$(O,F)$_2$ (F-0234). There are four CuO$_2$ layers between the double Ba(O,F) layers. The atomic stacking across double Ba(O,F) layers is staggered configuration like as Bi-system.

2. **Experimental**

Samples of Ba$_2$Ca$_{2n-1}$Cu$_n$O$_{2n}$(O,F)$_3$ are synthesized using high-pressure technique. Details of sample preparation are written in elsewhere. We have selected a polycrystalline sample synthesized from a nominal composition of Ba$_2$Ca$_3$Cu$_4$O$_{8n}$O$_{0.4}$F$_{1.6}$ (F-0234, $T_c = 82$ K) as the host compound for iodine intercalation because the purest sample can be obtained from the above nominal composition.

The sample was ground into a powder in an agate mortar. The 40 mg of the powder was pressed into a pellet with 4.3 mm in diameter. The sample was sealed with about 10 mg of I$_2$ in an evacuated quartz tube with 8 mm in inside diameter and about 100 mm in length. The quartz tube was heated at 230°C for 240 h. We will refer to the obtained sample as IF-0234.

Powder X-ray diffraction (XRD) patterns were measured using CuK$\alpha$ radiation (RINT-1100, Rigaku). Magnetic susceptibility was measured with decreasing temperature in a magnetic field of 10 Oe (field cooling) (MPMS, Quantum Design). To estimate the amount of iodine intercalated into the host crystal, composition ratios of grains were measured using an energy dispersive x-ray analyzer attached to a scanning electron microscope (SEM-EDX). The composition ratio was obtained by averaging the data for several grains.

3. **Results and discussion**

Figure 2 shows the XRD patterns of the host and IF-0234 samples. Most of the diffraction peaks of the host sample could be assigned by I4/mmm space group with $a=3.863$ Å and $c=33.74$ Å. The XRD pattern of the IF-0234 is obviously different from that of the host sample. The major peaks was indexed assuming P4/mmm space group with $a=3.855$Å and $c=20.84$Å because in case of Bi-system the stacking of layers across double BiO layers changes from the staggered configuration to a vertically aligned one by the iodine intercalation [10]. Compared with the host sample, the (00l) peaks of IF-0234 is broad and weak and the other peaks such as (10l) are weak or unclear. This would be due to an incomplete intercalation and imperfect change of the atomic stacking along the $c$-axis between the double Ba(O,F) layers, from the staggered configuration to the vertically aligned one. Similar results were reported in the iodine-intercalated Bi-system [11].

One can see large CuO peaks in the diffraction pattern of the IF-0234 sample. It means that not small part of the sample was decomposed during the heating with iodine. The heat treatment
conditions such as temperature, time and the amount of iodine enclosed with the sample may not be optimized yet. Anyhow, iodine should be successfully intercalated between the double Ba(O,F) layers because it is the only possible space for iodine intercalation. The XRD analysis indicates that the increase in spacing between the double Ba(O,F) layers through the iodine intercalation is about 4.0 Å (=20.84-33.74/2). The value is somewhat larger but comparable to the case of iodine intercalation to Bi-system (3.5 Å).

Figure 2. X-ray diffraction patterns of the host and iodine intercalated Ba$_2$Ca$_3$Cu$_4$O$_8$(O,F)$_2$ (F-0234). Most of the diffraction peaks of the host sample could be assigned by I4/mmm space group with $a=3.863$ Å and $c=33.74$ Å. The peaks of iodine intercalated sample were indexed assuming P4/mmm space group with $a=3.855$Å and $c=20.84$Å.

Figure 3. Temperature dependence of magnetic susceptibility for the host and iodine intercalated Ba$_2$Ca$_3$Cu$_4$O$_8$(O,F)$_2$ (F-0234). Inset shows the enlargement near the transition.

The SEM-EDX analysis showed that the grains of host sample has a cation ratio of Ba:Ca:Cu=2.07:3.06:3.87 (Ba+Ca+Cu=9), which is close to the ideal cation ratio of 2:3:4. On the other hand, the IF-0234 sample has a composition ratio of I:Ba:Ca:Cu = 0.88:2.06:3.14:3.80 (Ba+Ca+Cu=9). The cation ratios of Ba:Ca:Cu are almost same for both samples. It indicates that that iodine was incorporated into the host crystals keeping the unit (composition) of the host crystal unchanged. Thus, the $x$ in the I$_x$Ba$_2$Ca$_3$Cu$_4$O$_8$(O,F)$_2$ was estimated about 0.9. Namely, nearly stage-I iodine intercalation is realized in the IF-0234 sample.
Figure 3 shows the temperature dependence of magnetic susceptibility for the host and IF-0234 sample. The $T_c$ of the host sample is 82 K. A small transition at higher temperature (108K) is due to the minor phase of Ba$_2$Ca$_2$Cu$_3$O$_6$(O,F)$_2$ (F-0223). The IF-0234 sample showed a $T_c$ of 121 K. The $T_c$ increased as high as 39 K by the iodine intercalation. The transition width of the IF-0234 sample is sharper than that of the host. The volume fractions estimated from the susceptibility at low temperature are about 28% and 11% for the host and IF-0234 sample, respectively. The value of 28% for the host is quite normal as a pelletized powder sample. Although the volume fraction became small after the intercalation, the value of 11% is not small as a bulk superconductor taking account of the decomposition of the sample as seen in Fig. 2.

We believe that the main reason for enhancement of $T_c$ will result from increase of the carrier (hole) concentration in CuO$_2$ planes (the doping state moves from under doping toward optimal one) by the iodine intercalation like the case of the iodine intercalation into Bi-system. The decrease of $a$-parameter by the iodine intercalation seems to support the above idea.

4. Summary
The Bi-system had been known to the only high-$T_c$ superconductor that can be a host of iodine intercalation. We have shown that F-0234 also accepts iodine for the first time. Moreover, the F-0234 is the first four CuO$_2$ layered cuprates that can be a host for the iodine intercalation. The iodine was successfully introduced most probably between double Ba(O,F) layers. Consequently, the $T_c$ significantly increased from 82 K (the host compound) to 121 K.

Acknowledgments
This work was partially supported by Grant-in-Aid for Specially promoted Research (20001004) from The Ministry of Education, Culture, Sports, Science and Technology (MEXT).

References
[1] Iyo A, Hirai M, Tokiwa K, Watanabe T, Tanaka Y 2004 Supercond. Sci. Technol. 17 143
[2] Tokiwa K, Okumoto H, Kono S, Iga S, Takemura K, Watanabe T, Iyo A, Tanaka Y 2005 Int. J. Mod. Phys. B 19 263
[3] Chen Y, Iyo A, Yang W, Zhou X, Lu D, Eisaki H, Devereaux T P, Hussain Z, Shen Z X 2006 Phys. Rev. Lett. 97 236401
[4] Shirage P M, Shivagan D D, Tanaka Y, Kodama Y, Kito H, Iyo A 2008 Appl. Phys. Lett. 92 222501
[5] Iyo A, Hirai M, Tokiwa K, Watanabe T, Tanaka Y 2003 Physica C 392-396 140
[6] Yamaguchi H, private communication.
[7] Xiang X D, McKernan S, Vareka W A, Zettl A, Corkill J L, Barbee III T W, Cohen M L 1990 Nature 348 145
[8] Pooke D, Kishio K, Koga T, Fukuda Y, Sanada N, Nagoshi M, Kitazawa K, Yamafuji K 1992 Physica C 198 349
[9] Koike Y, Sasaki K, Fujiwara A, Mochida M, Noji T, Saito Y 1993 Physica C 208 363
[10] Kijima N, Gronsky R, Xiang X D, Vareka W A, Zettl A, Corkill J L, Cohen M L 1991 Physica C 181 18
[11] Fujiwara A, Koike Y, Sasaki K, Mochida M, Noji T, Saito Y 1993 Physica C 208 29