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FLUORINATION OF THE SUPERCONDUCTING OXIDE YBCO WITH ELEMENTARY FLUORINE

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SUMMARY

$YBa_2Cu_3O_{6\ 93}$(YBCO) was fluorinated with elementary fluorine between room temperature and 450°C at 10 Torr in a batch system Fluorine was incorporated into YBCO without destroying its structure to give $YBa_2Cu_3O_{6\ 93-x/2}F_x (0<x<2)(YBCF_xO_y)$, in which x could be controlled by reaction temperature and time

X-ray diffraction profiles reflected the fluorine content For $0<x<0\ 5$, the structure of $YBCF_xO_y$ was orthorhombic as the original YBCO, for $0\ 5<x<1\ 0$, the orthorhombic phase gradually changed to tetragonal , for $1\ 0<x<2\ 0$, the tetragonal structure was retained Dilution of fluorine gave $YBCF_xO_y$ with a small x

Diamagnetic properties of the samples were measured with a specially designed magnetic balance The results indicated that the mole fraction of the superconducting phase went down to 0 as x exceeded 1 0 For all fluorinated samples, DC-4probe measurement indicated that there was no enhancement in onset temperature Tc brought about by fluorination

INTRODUCTION

Since the epoch-making discovery of Zurich type superconducting oxides by Bednortz and Muller [1], many efforts have been devoted to get compounds with higher transition onset temperatures Tc Following their initial compound, Y-Ba-Cu-

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O(1:2:3:7) was found to have a Tc higher than liquid nitrogen temperature,95 K [2]. Many trials to raise Tc were concentrated on the replacement of Y by another lanthanide[3] or Ba by other alkaline earth metals [4]. However, the Tc of such compounds still remained around that of the original YBCO. The idea of fluorine modification of YBCO was first considered by Ovshinsky et al. [5] and there was large enhancement of Tc in their compounds to 155 K. Follow-up experiments on these systems however cast some doubt on their results. Following their method solid reactions did not succeed in preparing fluorine-containing YBCO, because the formation of BaF_2 was inevitable at the solid phase reaction temperatures [6] [7].

Recently reliable reports were published by several authors using F_2 [6], NH_4HF_2 [7] and ZnF_2 [8] as fluorinating reagents and succeeding in making $YBCF_xO_y$. However, they did not record how the fluorine content influenced superconducting properties. In this report, we will discuss the interesting correlation between the fluorine content, the crystal structure and superconducting properties. A newly invented Meissner Effect Evaluation Device (MEED) was adopted to quantitatively determine the mole fraction of superconductor in powder samples.

RESULTS & DISCUSSION

YBCO in powder form was used as a starting material to get homogeneous $YBCF_xO_y$. Pelletized samples were used for DC-4 probe resistivity measurements for the reason that will be described later. Fig.1 shows thermogravimetric curves for the fluorination of powdered YBCO(5 μm in diameter) under various fluorine pressures. The fluorination reaction occurred gradually from room temperature and rapidly from 200 °C.

From X-ray diffraction, the optimum fluorine pressure to get single phase $YBCF_xO_y$ was found to be lower than 10 Torr(Fig.2). When P_{F2}=10 Torr no other peaks except for those of $YBCF_xO_y$ were observed. Broad peaks which could be assigned to a cubic phase (a=5.9 Å) appeared in the case of P_{F2}>100 Torr and the original YBCO peaks completely disappeared at x=8.3 (P_{F2}=150 Torr). The characteristic behavior of high pressure (P_{F2} >100 Torr)

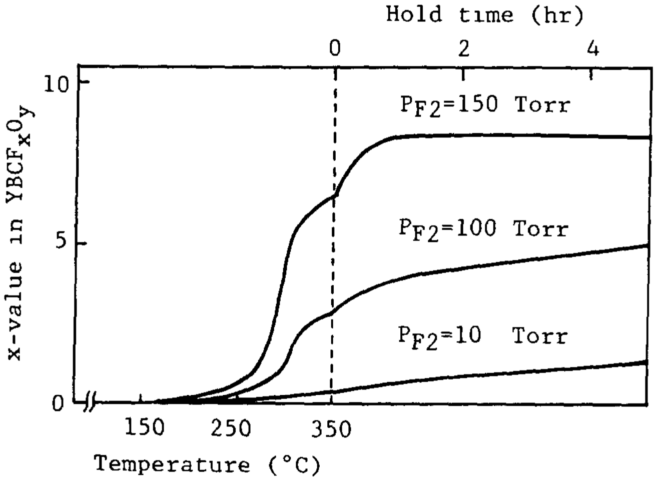


Fig 1 Thermogravimetric curves under various fluorine pressures(r t -350°C, 5°C/min)

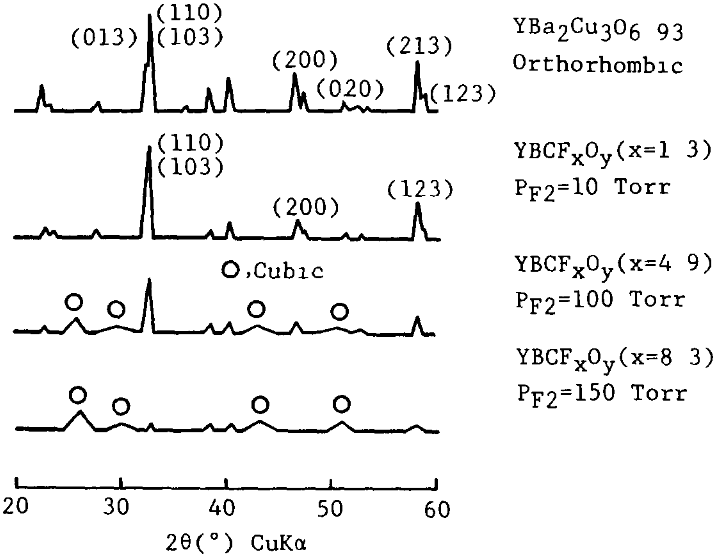


Fig 2 XRD patterns for products under various fluorine pressures

fluorination was seen in the surface properties of the pelletized sample X-ray diffraction, conductivity measurement and X-ray fluorescent analysis were carried out for the pelletized $YBCF_xO_y$ fluorinated at P_{F2}=150 Torr, r t -350 °C (5 °C/min) At the center of the pellet, although the x value was estimated to be around 0 5 from X-ray fluorescent analysis, the resistivity was still as high as $\sim 10^4$ ohm cm and indicated semiconducting properties at 50-200 K This suggested that fluorine gas attacked oxygen in YBCO at random to give a dense semiconducting layer at P_{F2}>100 Torr

We next attempted to prepare $YBCF_xO_y$ with various x values(0<x<2) in 10 Torr fluorine gas We found that x could be controlled between 0 and 2 to give $YBCF_xO_y$ without destroying its structure by taking the appropriate condition from thermogravimetric curve (Fig 3)

X-ray diffraction profiles(Fig 4) gave an interesting correlation between x and the structure For 0<x<0 32 fluorine was incorporated into the YBCO lattice to give an orthorhombic phase without change of lattice constants(a_0=3 823 Å, b_0=3 891 Å, c_0=11 675 Å) For 0 32<x<1 03 three doublet peaks (2θ=32 7°,46 7°, 58 3°) corresponding to the orthorhombic phase

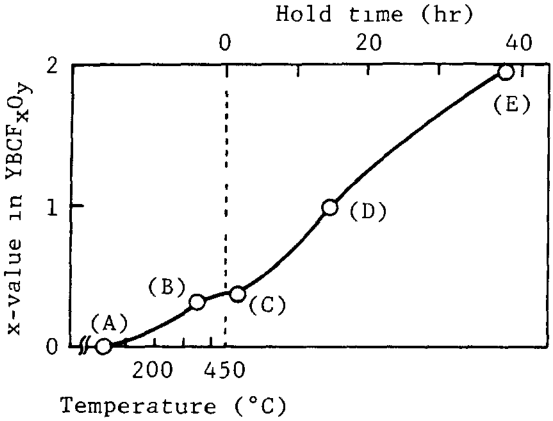


Fig 3 Thermogravimetric curve for fluorination of YBCO (P_{F2}=10 Torr, hold at 450°C, heating rate 1 3°C/min)

became singlets as x increased A pseudo-tetragonal structure was observed when x=1 03 with lattice constants a=3 863 Å, b=3 878 Å and c=11 685 Å (TABLE 1) This means that the YBCO lattice is becoming isotropic with the incorporation of fluorine For 1 03<x<1 95 the pseudo-tetragonal structure was retained until x reached 1 95 when weak unresolved peaks appeared and the ordering along the c-axis was almost lost X=2 is the critical composition to get $YBCF_xO_y$ without damaging the triple layered perovskite structure

It is impossible to sinter $YBCF_xO_y$ powder samples, because of inevitable formation of BaF_2 Thus a contactless method is required to measure the superconducting properties in powder samples A specially designed Meissner Effect Evaluation Device (MEED) was employed to measure the onset Tc and the mole

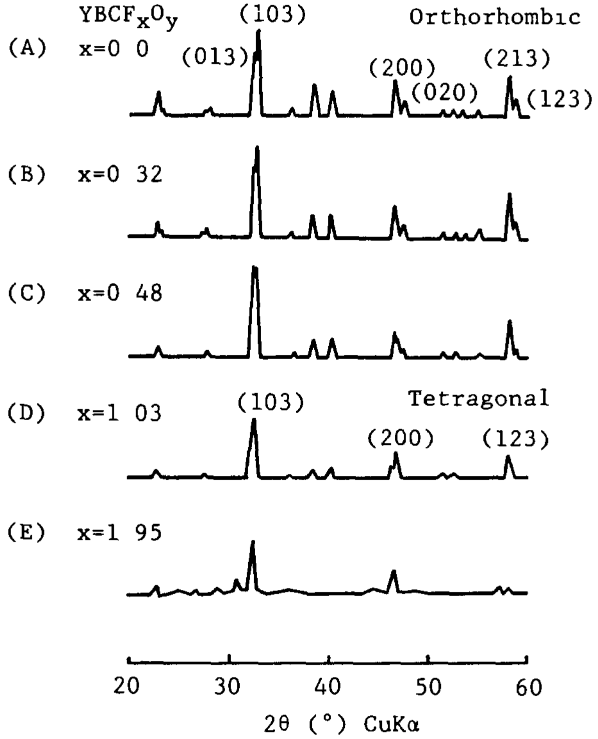


Fig 4 XRD patterns for $YBCF_xO_y$ with various x

TABLE 1

Lattice constant calculation for $YBCF_xO_y$ (x=1 03)

2θ(deg)	d(obsd)(Å)	(hkl)	d(cald)
22 800	3 8969	(003)	3 8950
32 690	2 7370	(110)	2 7368
38 490	2 3369	(005)	2 3370
40 310	2 2355	(113)	2 2393
46 620	1 9465	(006)	1 9475
47 000	1 9317	(200)	1 9315
58 270	1 5821	(123)	1 5833

based on a=3 863, b=3 878, c=11 685 (Å)

fraction of superconducting phase at 84 5 K (Fig 5) All Tcs of these samples were still around that of pristine YBCO, 94 ± 1 K The mole fraction of the superconducting phase reduced drastically from x=0 5 and fell to 0 at x=1 This corresponds to the structural change (orthorhombic to tetragonal) in the fluorination process

The location of fluorine in the $YBCF_xO_y$ lattice is still ambiguous but deserves discussion YBCO has nonstoichiometric properties, oxygen coordinating the second layer copper, which is sandwiched by Ba layers, is easily lost to bring about defects, it is so-called " labile " oxygen The defect sites, the number of which depend on the condition of synthesis of the YBCO, are supposed to be first oxidatively occupied in a fluorine atmosphere because of the strong oxidizing power of the fluorine The formation of orthorhombic $YBCF_xO_y$(0<x<0 32) can be interpreted as the occupation of the site of defects Labile oxygen atoms are more easily oxidized than others so that they are expected to be attacked in the next step It must be recognized that there is enough space around the second layer Cu to allow the incorporation of fluorine After the critical

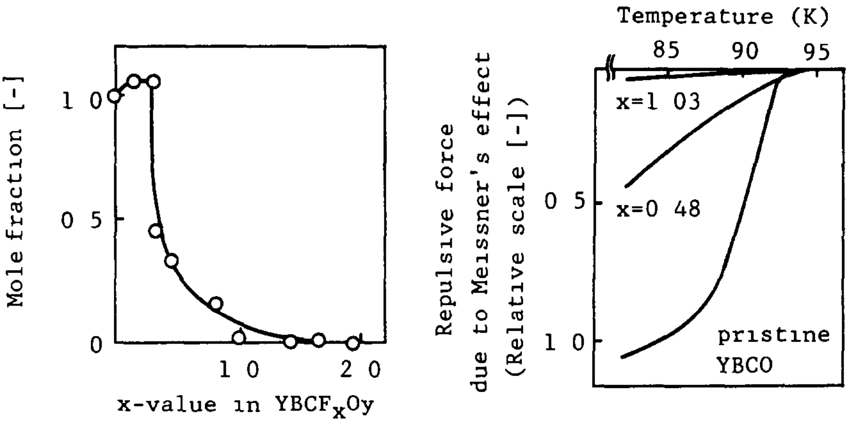


Fig 5 Perfect-diamagnetic properties of YBCF$_x$O$_y$

(a) Mole fraction of superconducting phase in YBCF$_x$O$_y$

(b) MEED profiles of YBCF$_x$O$_y$

x value, x=2, for the single phase YBCF$_x$O$_y$ all possible sites around Cu are fully occupied by fluorine After the occupation around the second Cu site, fluorine will start out to attack other oxygens and to destroy the YBCO structure The results favor such occurrence when x>2

DC 4-probe resistivity measurements were carried out for the pelletized samples prepared under various conditions(Fig 6) The addition of oxygen gas is expected to influence the formation of YBCF$_x$O$_y$ because of the reversibility of oxidation This leads us to use F_2/O_2 system aiming at simultaneous fluorination and annealing Comparing this system with one in which Ar gas was used instead of oxygen should establish the role of oxygen Preparation conditions were as follows, sample 1, P_{F2}=10 Torr, 450°C 12hr, sample 2,P_{F2}/P_{O2}=10/50 Torr, 450°C 12 hr, sample 3, P_{F2}/P_{Ar}=10/50 Torr, 450 °C 12hr, respectively X-ray fluorescent analysis indicated that the content of fluorine was x=4 in sample 1, x=3 6 in sample 2 and x=2 1 in sample 3 The x-value of fluorine declined more sharply under dilute conditions, samples 2 and 3, than in sample 1 In the case of samples 2 and 3 the fluorine content settled down to 0 5 from 50 μm to the center of the pellet, and in sample 1,from 200 μm to the center of the pellet

The products on the surface were dependent on the reaction gas The YBCO orthorhombic structure was almost destroyed on the surface of sample 1 In sample 2 BaF_2 was observed Only a pseudo-tetragonal structure was observed in sample 3

The resistivity of all these samples are low enough even on the reaction surface to be measured by the 4-probe method The resistivity measurements were made on the reaction surface and at the center of pellets, after filing off the surface Both were very similar, although the fluorine content was much higher on the reaction surface than that at the center The superconducting transition onset temperatures Tcs at the center are between 90-95 K(TABLE 2) The zero resistivity temperature

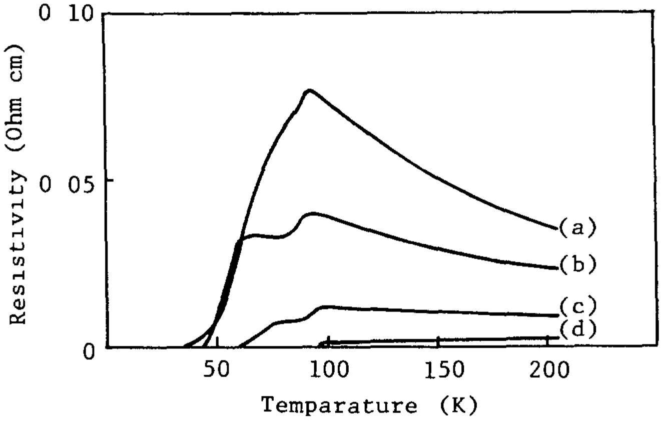


Fig 6 Temparature dependence of resistivity of $YBCF_xO_y$ fluorinated under various conditions (at the center of pellet, 450°C, 12hr hold)

(a) P_{F2}=10 Torr, P_{Ar}=50 Torr
(b) P_{F2}=10 Torr
(c) P_{F2}=10 Torr, P_{O2}=50 Torr
(d) YBCO

were found to decrease in every sample, and the difference between the zero resistivity temperature and the onset Tc reached a maximum of 62 K (sample 3) This indicates that these compounds were multiphasic with various Tc Unfortunately we cannot give a clear explanation on the effects of dilute gases on the properties of samples Further F_2/O_2=38 Torr/722 Torr, 100°C, 40 days fluorination was carried out, but there was no sign of improvement in the Tc of this sample even under these mild conditions, though the presence of fluorine was confirmed in the bulk phase by ESCA

Apart from the mechanism of fluorination, an important issue in this study was to consider how fluorine incorporation influences the superconducting properties of YBCO A three

TABLE 2

Onset and zero resistivity temperature for $YBCF_xO_y$ prepared under various conditions

Preparation condition	^{a}Tc on (K)	Zero resistivity temp (K)
YBCO (authentic)	95 0	89 0
P_{F2}=10 Torr 450°C 12hr	92 0 *^{b}63 0	42 5
P_{F2}/P_{O2} =10/50 Torr 450°C 12hr	95 0 *^{b}81 5	54 0
P_{F2}/P_{Ar} =10/50 Torr 450°C 12hr	94 0	32 5
P_{F2}/P_{O2} =38/722 Torr 100°C 40days	92 0	85 0

measured by DC 4-probe method at the center of pellets

[a] onset temperature

[b] temperature at shoulder

dimensional network consisting of a O-Cu-O array is believed to play an important role in the superconducting mechanism All of our results show that fluorine degrades the superconducting properties Taking the fluorination process into the consideration, the superconducting properties seem to depend on not only the framing expansion of O-Cu-O in the first and the third layer but also the one dimensional sequence in the second layer It is still uncertain whether fluorine modulates the frequency of phonons or changes the band structure of YBCO

EXPERIMENTAL

1 Fluorination of YBCO

After mixing Y_2O_3 $BaCO_3$ CuO=0 5 2 3,the mixture was sintered at 920 °C for 6hr in an oxygen flow to give $YBa_2Cu_3O_{7-\delta}$, in which δ was determined by iodometry to be 0 07 $YBCO_{6\ 93}$ was ground to 5 μm particles and used in fluorination The x-value in $YBCF_xO_y$ was calculated from the weight increase of thermogravimetric curve based on the equation

$$YBCO_{6\ 93} + x/2F_2 \longrightarrow YBCF_xO_{6\ 93-x/2} + x/4O_2$$

$YBCO_{6\ 93}$, which was pressed in a pellet(13mm Φ) and sintered at 920 °C for 3hr in oxygen, was fluorinated for conductivity measurement The x-value of the pelletized $YBCF_xO_y$ was determined by X-ray fluorescent analysis on the surface

The fluorination reaction was carried out in the thermobalance (Shimadzu,TG-35), which could be used up to 650 °C under a fluorine atmosphere A platinum dish and quartz reactor were used to avoid contamination from HF sources

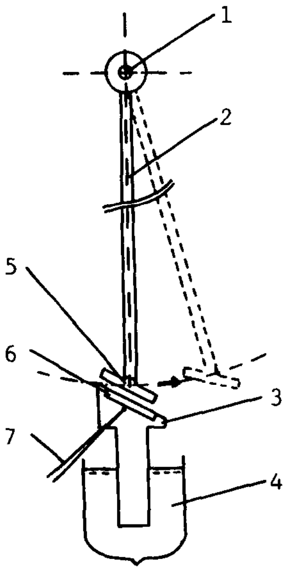
2 DC 4-probe resistivity measurement

The resistivity of pelletized samples were measured by the DC 4-probe method in a liquid helium Dewar(20K < T < r t)

3 Meissner Effect Evaluation Device(**MEED**)

Onset temperature and mole fraction of superconducting phase in powder samples were determined by the Meissner Effect Evaluation Device (**MEED**)(Fig 7)[9] The MEED takes advantage of the repulsive force arising from the diamagnetism of the sample It has a Sm-Co magnet at the bottom of a rod, which was supported by a Ruby edge The sample, after being pressed into a pellet, is put on a copper sample holder which is cooled by liquid nitrogen to 77 K Below the Tc of the sample, the repulsive force between the sample and the magnet is brought about by transition into perfect diamagnetism, the so-called Meissner Effect

The intensity of the repulsive force is converted into the movement of a magnetic core at the top of the rod, which is detected by a differential transformer The proportional relationship between the movement and the quantity of sample make it possible to estimate the mole fraction of the sample (Fig 8) The repulsive force was measured at 84 5 K and normalized to the same quantity for plotting The mole fraction of $YBCF_xO_y$ was estimated by comparison with YBCO



1 Ruby edge
2 Rod
3 Copper sample holder
4 Liquid nitrogen
5 Sm-Co magnet
6 Sample
7 Thermo-couple

Fig 7 Schema of MEED

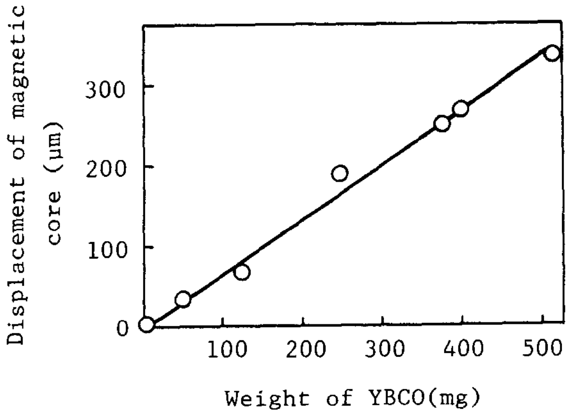


Fig.8. Calibration line of MEED (measured at 84.5 K).

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