Location of fluorine atoms and mechanism of improving superconducting properties with F-doped in YBaCuO series [①]

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Abstract : A series of $YBa_2Cu_3O_{6.5-0.5x+\delta}F_x$ ($x = 0 , 0.3 , 0.6 , 1.0 , 1.5 , 2.0$) samples were synthesized using state reaction method . The superconducting properties and microstructures of the samples were studied with AC susceptibility , DC resistivity , fluorine and oxygen content measurements , XRD , IR and XPS techniques . The results show that F-doping increases the T_C and decreases the transition width , and fluorine atoms have entered into the superconducting phase and substituted for the oxygen atoms at O(4) sites . The mechanism of improving superconducting properties is that fluorine-doping adjusts the hole carrier concentration in the Cu-O planes .

Key words : superconductor ; YBaCuO ; F-doped   **Document code : A**

1   INTRODUCTION

Since Ovshinsky et al[1] reported for the first time that a zero-resistance state at 155 K was observed in F-doped YBaCuO system , the effect of F-doping on superconducting properties has stimulated many scientists to further efforts . But various conflicting results were reported on whether the fluorine atoms have entered into the crystalline structure of the superconducting phase or not , and which sites the fluorine atoms occupy in the unit cell if they have been doped in . Perrin et al[2] thought that fluorine occupied O(1) sites at low fluorine content and O(5) sites at high fluorine content , respectively . Tyagi et al[3] thought that fluorine atoms only entered into O(4) sites , while La Graff et al[4] thought that fluorine entered into O(5) sites , and at the same time the possibility couldn't be ruled out that fluorine substituted O (4) sites . And it was also reported that fluorine did not enter into the superconducting phase at all , it existed only in the form of impurities[5] . The study on the mechanism of the effect of fluorine on superconducting properties is seldom , and on which the viewpoints are also different in Ref .[6 ~ 8] . So it is very important to study the substitution of fluorine for oxygen , whose size and electron states are close to oxygen , but whose valences and electronegativity are different . In this paper , the occupancy positions of fluorine substituting for oxygen and the mechanism of improving superconducting properties with fluorine - doping in YBaCuO system was studied .

2   EXPERIMENTAL

The samples examined during this study have nominal compositions of $YBa_2Cu_3O_{6.5-0.5x+\delta}F_x$ ($x = 0 , 0.3 , 0.6 , 1.0 , 1.5 , 2.0$) and were prepared by solid state reactions with appropriate amounts of high-purity powders Y_2O_3 , $BaCO_3$, CuF_2 and CuO . According to fluorine content the starting samples were labeled with 0($x = 0$) , 1($x = 0.3$) , 2($x = 0.6$) , 3 ($x = 1.0$) , 4($x = 1.5$) and 5($x = 2.0$) . The pre-sintered temperature was 945 ℃ , 930 ℃ , 925 ℃ , 920 ℃ , 915 ℃ , 905 ℃ , respectively . At first , the powders were mixed homogeneously and slowly heated to 450 ℃ , kept for 2 h , then further heated to 750 ℃ at a rate of 2 ℃·min^{-1} and kept for 1 h , and then further heated to the pre-sintered temperature as describing above and kept for 15 h before cooling naturally in the furnace down to room temperature . The pre-sintered samples were ground thoroughly and pressed into 18 mm × 6 mm × 2 mm bars . Then those bars were sintered in a furnace with identical heating steps described above . The samples were protected by nitrogen gas which contained a very small amount of oxygen impurity . At last , a part of the sintered samples were annealed for 12 h in purity oxygen atmosphere at 380 ℃ , and were re-labeled with $0'$, $1'$, $2'$, $3'$, $4'$, $5'$, respectively .

The superconducting properties of the samples were characterized by standard four-probe DC resistivity and by AC magnetic susceptibility measurements . The phase identifications were performed using powder X-ray diffractometer Simens D500 with Cu K_a radiation . The quantitative analysis of fluorine content was carried out with CSB-F-3 ion-chosen cathode . Oxygen content was measured with TC-436 nitrogen/ oxygen analysis apparatus . The Infrared absorption spectra were carried out with Nicolet 740-FTIR equipment . The XPS spectra were carried out

using a VG ESCA MK- II system with Mg K_a(h υ= 1 253 .6 e V) radiation at room temperature , under a pressure of 10^{-8} Pa .

3   RESULTS AND DISCUSSION

3 .1   Experimental results

Fig .1 shows the measuring results of AC magnetic susceptibility for the samples without being annealed , and the critical temperature of the susceptibility , T_C , are listed in Table 1 . The samples for x = 1 .0 have the maximum value $T_{C,max}$ = 93 K , while the Meissner effect of the samples without fluorine is very poor at 87 K , which shows that F- doping enhances the T_C for the F- doped samples . The T_C enhances with fluorine increasing while it drops with fluorine further increasing from 1 .0 to 2 .0 . The resistivity- temperature curves are shown in Fig .2 , which are normalized at 150 K . The detailed data are also listed in Table 1 . Here $T_{C,0}$ is zero- resistance temperature , ΔT_C is the superconducting transition width , and $T_{C, onset}$ is the onset transition temperature of resistivity . It is shown that the curve for the F- undoped samples begins to deviate from the linearity at 89 K , while the resistivity is not zero at 77 K , and ΔT_C is greater than 20 K by estimating . But for the F- doped
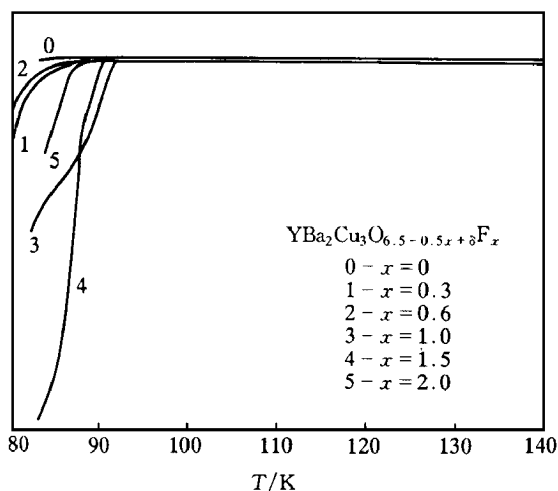

Fig .1   Susceptibility vs temperature characteristics of sintered samples

Table 1   Measurements of superconducting properties   (K)

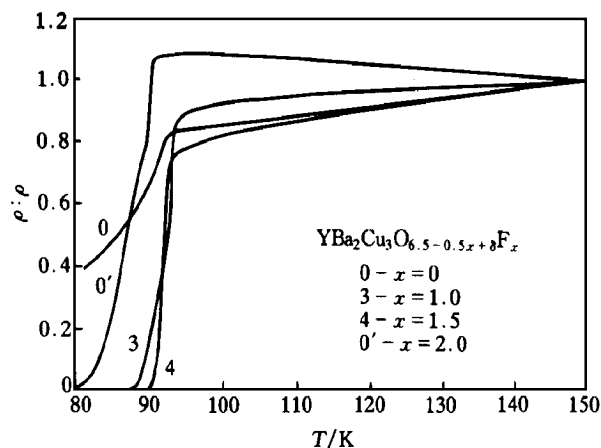| Samples No.	DC resistivity			AC susceptibility
	$T_{C, onset}$	$T_{C,0}$	ΔT_C	T_C/ K
0	89 .0	< 77 .0	> 20 .0	87 .0
1	92 .0	86 .0	3 .5	90 .0
2	91 .0	85 .0	4 .5	88 .5
3	94 .5	88 .0	3 .0	93 .0
4	94 .0	90 .0	2 .0	91 .5
5	93 .0	88 .0	3 .0	89 .0

Fig .2   Resistivity vs temperature characteristics of samples

$0'$ —F- undoped sample annealed at 380 ℃ for 12 h in oxygen ; ρ(150 K) —Resistance value of samples at 150 K

samples 3 and 4 , the $T_{C,onset}$ is 94 .5 K and 94 K , the $T_{C,0}$ is 88 K and 90 K , ΔT_C is 3 .5 K and 2 K , respectively .

After being annealed for 12 h in pure oxygen atmosphere at 380 ℃ , the resistivity and susceptibility curves of the F- undoped samples change a lot . Curve $0'$ in Fig .2 is the resistivity curve for sample $0'$, the $T_{C,onset}$ is 89 K and $T_{C,0}$ is 79 K , while the T_C , $T_{C,onset}$ and $T_{C,0}$ values of the F- doped samples keep almost unchanged . As seen from Fig .2 , the samples without doped fluorine have transformed from metals- like to semiconductors- like after being annealed . Why this happened is still unknown and further work is under way . When the sintered samples are annealed for 1 h in high- purity nitrogen atmosphere at 400 ℃ , the T_C of the samples for x = 1 .0 and x = 1 .5 is 85 K and 84 K , respectively , while that of the samples for x = 0 is below liquid nitrogen temperature . We also measured the T_C of the samples annealed in different atmospheres and found that the samples for x = 1 .0 have the maximum T_C value , the samples for x = 1 .5 have the second maximum T_C value .

Table 2 lists the measuring results of oxygen and fluorine content , which shows that about 60 % fluorine still exists in the samples . The measured oxygen content decreases with increasing nominal fluorine content , while the sum of the measured oxygen and fluorine content changes slightly .

The XRD patterns for the samples $0'$, $3'$, $4'$ are shown in Fig .3 and the lattice parameters are listed in Table 3 . For the sample $0'$, the superconducting phase is a single orthorhombic 123 phase . The major phases for the samples $3'$ and $4'$ are still orthorhombic 123 phase , while there are a small amount of impurity phases such as BaF_2 and Y_2BaCuO_5 (denoted with " * " in Fig .3) . And the impurity phase volumes are about 11 % and 13 % for samples $3'$ and $4'$, respectively . The unit cell volumes (V) and orthorhombic

**Table 2**　Measurements of oxygen and fluorine content　　　　　(mole fraction)

Samples No.	Nominal F-content	Measured F-content	Ratio of measured F and nominal F-content	Measured O-content	Sum of measured F and O-content
0′	0	0	—	6.909	6.909
1′	0.3	0.182	60.6 %	6.713	6.895
2′	0.6	0.357	59.5 %	6.530	6.887
3′	1.0	0.607	60.7 %	6.332	6.929
4′	1.5	0.895	59.7 %	6.001	6.896
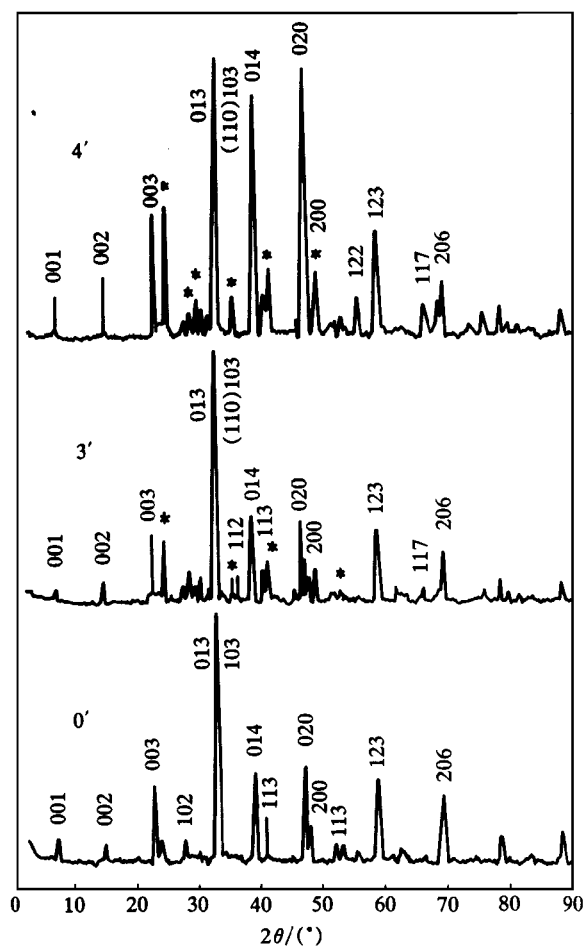
Fig.3　Powder XRD patterns of YBaCuO(F) samples
*　—Denotes impurity peaks for BaF₂ and Y₂BaCuO₅

Table 3　Lattice parameters

Samples No.	Lattice parameters/Å			Volume(V) /Å³	Distortion e
	a	b	c		
0′	3.8127	3.8741	11.6779	172.4898	0.01598
3′	3.8186	3.8830	11.6690	173.0230	0.01672
4′	3.8224	3.8964	11.6319	173.2392	0.01917

distortions of the lattice ($e = 2(b - a)/(b + a)$) are also listed in Table 3. The lattice parameters a and b increase, while c decreases with increasing fluorine content. The volumes and distortions also increase.

The IR vibration peaks for the annealed samples mainly appear in the range of $300 \sim 1200 \, cm^{-1}$, as shown in Fig.4. The number of IR peaks for the F-
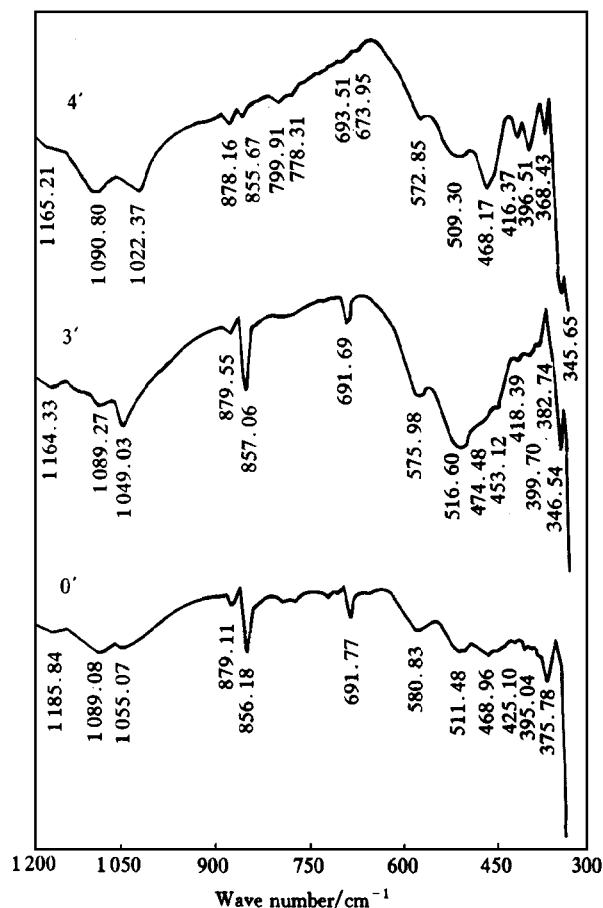
Fig.4　Infrared absorption spectra for sample 0′, 3′ and 4′

doped samples increases, and in samples 3′ and 4′ the Cu-F peaks appear clearly at 346.54 and 345.65 cm^{-1}, respectively. XPS spectra are shown in Fig.5 and Fig.6. The binding energy of $Cu2p_{3/2}$ in sample 0′ is 933.2 eV, while it increases 0.4 eV for the F-doped samples. As for F1s peaks, the binding energy in sample 3′ is 685.6 eV and 686.4 eV, respectively. But for sample 4′, the main peak of F1s is at about 685.2 eV, and the spectrum broadens towards low binding energy.

3.2　Discussion
3.2.1　Effect of fluorine on superconducting properties of YBaCuO series
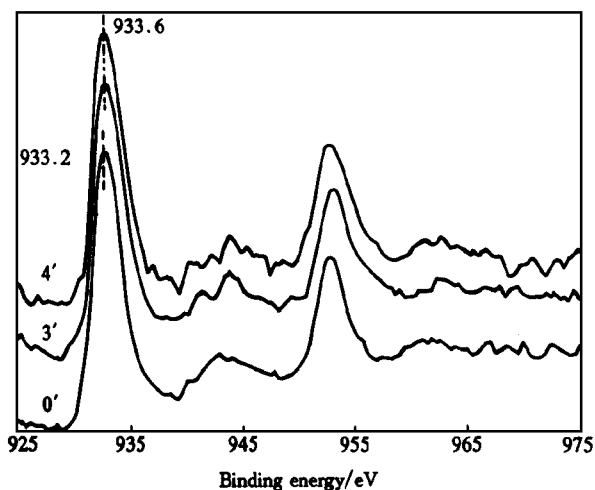The results of resistivity and susceptibility for the

Fig .5   XPS spectra of $Cu2p_{3/2}$ for sample $0'$, $3'$ and $4'$
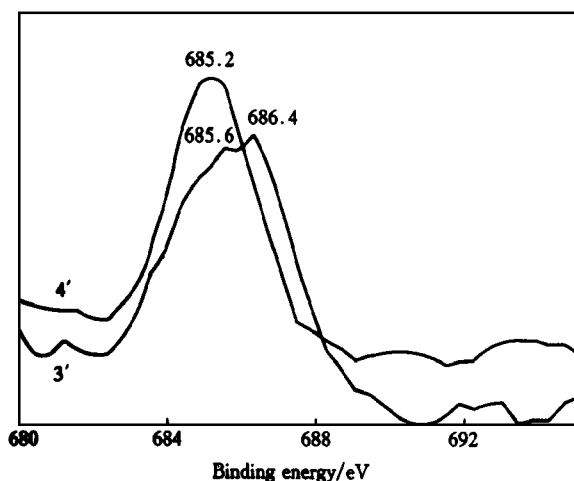

Fig .6   XPS spectra of F1s for sample $3'$ and $4'$

sintered samples in nitrogen atmosphere show that the T_C increases with more fluorine being doped. Sample 3 and 4 have the maximum $T_{C,onset}$, 94 .5 K and 94 .0 K, respectively. The $T_{C,0}$ for F-doped samples is 12 K higher than that for F-undoped samples. Even if the samples were annealed for 12 h in pure oxygen, the $T_{C,onset}$ for the F-doped samples is about 5 K higher than that for the F-undoped samples. Comparison of the F-doped and F-undoped samples which were annealed in different atmosphere, the T_C values for the former are always higher than that of the latter, and the transition widths for the former are narrower. Thus F-doping not only promotes the formation of the superconducting phase but also enhances the T_C of the samples.

In the experiments, it was found that the melting points of the F-doped samples decreased with increasing fluorine. The F-doped samples melt partly when the sintered temperature was higher than 930 ℃. When fluorine content was 2 .0 and the sin-

tered temperature was 905 ℃, the samples with $T_{C,onset}$ = 92 K and $T_{C,0}$ = 88 K were synthesized; while the $T_{C,0}$ for the F-undoped sample was below 77 K with the sintered temperature at 945 ℃. From these facts it can be said that F-doping can decrease the sintered temperature, accelerate the reaction and reduce the sintered time. In YBaCuO series it is known that the superconducting properties have direct relation with oxygen content[9], high quality superconductors can be obtained only in abundant oxygen atmosphere. While the bulk T_C for the F-doped samples sintered in nitrogen atmosphere is about 94 K in the experiments, which shows the important effect of fluorine on improving superconducting properties. All the above show that, even if oxygen is not enough, fluorine can improve the superconducting properties relying on its own properties after substituting for oxygen. And F-doping can also control the necessary oxygen content to make the superconducting properties improved. Therefore, the F-doping can be used as an efficient method of controlling oxygen, which make us synthesize this kind of superconductors more easily.

3 .2 .2   Possibility of fluorine entering into superconducting phase

The powder XRD experiment has been used widely to study the relationship between the structure parameters and fluorine content in YBa_2Cu_3-$O_{6.5-0.5x+\delta}F_x$ series. It was reported that a axis expanded and c axis contracted with increasing fluorine content, while the length change of b axis was not related with fluorine content[10]. In the XRD patterns, a and b axes expand, c axis contracts with increasing fluorine content, while the major phase is still orthorhombic 123 phase. And it is also found that about 60 % fluorine still exists in the samples, while few fluorine exists in the form of impurity BaF_2. It can thus be concluded from these facts that fluorine have possibly incorporated into the superconducting phase lattice.

The infrared intrinsic vibration peaks of 123 phase appear distinctly in the IR spectra as shown in Fig .4 . The number of IR peaks increases for the samples with fluorine and some IR peaks shift to larger wave-numbers, which shows that F-dopant make the chemical circumstance change and the symmetry thus decreases. It is also found that the Cu-F peaks for F-doped samples appear clearly at 345 . 65 cm^{-1} and 346 .54 cm^{-1}, respectively. The binding energies of the F1s double-peaks for sample $3'$ are 685 .6 eV and 686 .4 eV, respectively. The low-energy component is similar to that obtained for Cu-F bonds in CuF_2[11]. As for sample $4'$, the F1s main peak appears at 685 .2 eV, and there is a shoulder at low binding energy. Thus F1s peak can be resolved to two peaks around 685 .2 eV. The peak ～685 .6 eV is attributed to the

F1s peak of Cu-F bonds . The results in Fig .5 display that the binding energy of $Cu2p_{3/2}$ shifts 0 .4 e V towards higher energy in F-doping samples , which should be corresponded to the interaction of Cu-F bonds . In addition , the radii of O^{2-} and F^- are 1 .40 Å and 1 . 33 Å , respectively , and their electronic structures are almost the same . From the viewpoint of structural chemistry , fluorine can substitute for oxygen successfully . Based on the above discussion , it can be concluded that the fluorine atoms have surely entered into the superconducting phase .

3 .2 .3 Crystallographic position of fluorine in superconducting phase

There are five kinds of crystallographic positions for oxygen atoms in YBaCuO series , and the positions replaced by fluorine atoms are reported differently in Ref .[2 ~ 5] . The bond length (~ 1 .93 Å) of Cu-O bonds in the Cu-O planes is shorter than that (~ 2 .30 Å) of Cu-O bonds along the c axis , and the bond energy of the former is also higher , the substitution of fluorine atoms for the oxygen atoms at O(2) and O (3) sites is thus very difficult . Fluorine atoms maybe have occupied the O(4) and O(5) sites when c axis contracts . While in 123 series , the more the O(5) sites are occupied , the less the orthorhombic distortion of the lattice is , and the crystalline structure will tend to be tetragonal . In the XRD experiments , the orthorhombic distortions change from 0 .016 72 to 0 .019 17 , which shows that fluorine can' t occupy O (5) sites . If it is assumed that fluorine atoms occupy the apical O(4) sites , F and Cu will bond to ion binding . The electronegativity of fluorine is higher than that of oxygen , and the ion radii of fluorine is smaller than that of oxygen , then the bond length of Cu-F bonds is shorter than that of Cu-O bonds , the interaction between F and Cu will thus become stronger , which will cause c axis contracting .

In the IR spectra for the samples without fluorine , the peak at 580 .85 cm^{-1} to the stretching vibration modes of Cu-O bonds along c axis is assigned , which is in agreement with other researchers' results[12 ,13] . The peaks for F-doped samples shift to 575 cm^{-1} and 572 cm^{-1} , respectively , which shows that fluorine disturbed slightly the vibration of apical oxygen atoms . LaGraff et al[4] found that c axis decreased and Cu(1)- O(4) bond lengths increased with increasing nominal fluorine content . It can also be deduced from the XRD patterns that fluorine has occupied O(4) sites , and the Cu(1)- F bond length is thus longer than the Cu(1)- O(4) bond length . According to the empirical rule $\nu R^3 =$ constant (where ν , R are wave number and bond length , respectively) , the IR spectra will shift to long wave , which is consistent with the IR experiments . At the same time , the atomic mass of fluorine is larger than that of oxygen , which also make the IR vibration frequency lower . In

the IR spectra of F-doped (Bi ,Pb)- Sr-Ca-Cu-O superconductors the Cu-F bond vibration peak at 345 .95 cm^{-1} is also found and attributed to the fluorine substituting for apical oxygen[14] . It is known that there is a similar CuO_5 pyramidal structure in both Bi- series and Y- series , and only the chemical environment around the apical oxygen is the same . Hence it can be concluded that fluorine also substitutes for the apical O(4) sites , and the peak at 346 cm^{-1} is the stretching vibration modes of fluorine atoms along c axis .

The increase of the binding energy of $Cu2p_{3/2}$ electron for the F- doped samples can be attributed to the highly electronegative characteristic of fluorine atoms which are occupying the positions in the CuO_2 planes and thus increase the copper effective nuclear charge on the Cu atoms[3] . To decrease the charge effect , the difference of the binding energy among different elements is calculated , and it is found that the binding energy difference between $Cu2p_{3/2}$ and F1s is 248 e V , which is less than that between Cu and F in copper fluoride . And in the XRD patterns no compound CuF_2 is found . These show that fluorine can' t occupy O(5) sites , but only occupy O(4) sites . La-Graff et al[4] thought fluorine possibly substituted for O(4) sites and caused the oxygen at O(4) sites transferring to other sites . The Raman spectrum experiments of Guo et al[16] also obtained the same results .

From the viewpoint of coordination chemistry , both F and O can exist in binary and quadri coordination . However F exists usually in binary coordination while the oxygen at O(4) sites just exists in binary coordination . The replacement of oxygen at O(4) sites by fluorine is therefore reasonable . The Cu-F bonds are polar bonds , which are ionic bonds partly with some kinds of covalent bonds . Seen from structural chemistry , the compound structure formed from polar bonds will be more loose , which is in agreement with our XRD results .

Using CNDO/ 2 method , some associative double-atoms energy E_{AB} and the total energy E_T of the YBaCuO systems are calculated , in which fluorine atoms substituted for oxygen atoms at different sites[17] . The magnitudes of E_T were in the order $E_{T(3)} > E_{T(2)} > E_{T(1)} > E_{T(4)}$. From the viewpoint of thermodynamics , there is a close relation between the stable phase and the lowest energy state . The calculated results show that the total energy of the system becomes lowest and it is energetically favorable when fluorine replacing O(4) sites . It can be concluded that there is a possibility of the substitution of fluorine for O(4) sites . Other calculated results also show that the substitution of fluorine for O(4) sites is more reasonable[18 ,19] . All references provide us with the theoretical foundation when we consider , from the experimental results , that fluorine atoms replace the apical oxygen atoms . In short , various results and discussion

show that fluorine occupies the apical O(4) sites.

3.2.4　Mechanism of improving superconducting properties with F-doped

In the p-type high-T_C cuprate superconductors, the T_C value is related with many factors besides the relation with structure parameters. Hole carrier concentration is one of the crucial factors. There is a maximum T_C at a characteristic hole concentration p_h in each family[20]. ZHANG et al[21] found that there exists a universal relationship between $T_C/T_{C, max}$ and hole concentration, and the variation of $T_C/T_{C, max}$ with the hole concentration is independent of the compound considered. From the analyses of the above sections, it is known that fluorine atom entered into the superconducting phase and occupied O(4) sites. The fluorine-dopant undoubtedly changes the electronic properties between the Cu-O planes and Cu-O chains, then adjusts the hole carrier concentration in the Cu-O planes, which make the superconducting properties changed accordingly.

Fluorine has higher electronegativity and smaller ion radius than oxygen, and thus has greater ability to attract electron cloud. The electron cloud will intensively lean to O(4) sites when the apical oxygen is replaced by fluorine, so fluorine has greater ability to transfer the charges, and thus increases the positive valences of some Cu ions and shifts the core energy levels of Cu. The intensity ratios of I_{sat}/I_{main} of the Cu2$p_{3/2}$ satellite peaks and main peaks for samples 0', 3' and 4' are calculated to be 0.166, 0.130, 0.111, respectively. For the XPS spectra of Cu atoms with a valence of 1 or 0 have no satellite peaks at higher binding energy[23], the decrease of the intensity ratios shows that F-doping increases the number of mono-valence Cu ions. The outermost layer of fluorine has more electrons than that of oxygen. When a fluorine atom substitutes an oxygen atom, it will trap an electron and make the system in the lowest energy state, and reduce the hole carrier concentration of Cu-O planes and the valences of some Cu ions. In a word, two-sided reactions have adjusted the carrier concentration to the near-optimum hole doping levels, which help to improve the superconducting properties.

The strong coupling of Cu-O plane and Cu-O chain is essential to the superconducting mechanism[22]. Therefore, the contraction along c axis, which is caused by the addition of fluorine into the crystal, is similar to the strengthening of the coupling between Cu-O plane and Cu-O chain. And the substitution of fluorine for O(4) will make Cu(1)-O(4) bonds lengthen and Cu(2)-O(4) bonds shorten[4], then the O(4) sites will be closer to the middle situation between Cu(1) and Cu(2), which helps to control the transportation of the carriers. The Cu(2)-O(4) distance is also a crucial parameter, which is involved in the charge-transfer process (to or from the

CuO$_2$). Whangbo et al[24] reported distinct (Cu-O) — T_C relations, and Rao et al[25] obtained a more meaningful relation between the normalized values of T_C and r(Cu-O), which showed that in each family the T_C value increases linearly with decreasing the length of Cu(2)-O(4) bonds. The substitution of fluorine for the O(4) sites increases the Cu(1)-O(4) bonds length and decreases Cu(2)-O(4) bonds length. Hence, F-doping helps to enhance the T_C value.

4　CONCLUSION

A series of YBa$_2$Cu$_3$O$_{6.5-0.5x+\delta}$F$_x$ samples with nominal fluorine contents $x = 0$, 0.3, 0.6, 1.0, 1.5, 2.0 have been synthesized using state reaction method. The superconducting properties of the samples annealed under various atmosphere conditions are studied. It is found that F-doping can increase the T_C value and narrow the transitional width. Various experimental results show that fluorine atoms have entered into the superconducting phase and occupied O(4) sites. Fluorine-doping decreases the Cu(2)-O(4) bonds length and adjusts the hole carrier concentration in the Cu-O planes to the optimum hole doping levels, which helps to increase T_C value and improve the superconducting properties.

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