전기전자재료학회지 제4권 제4호 1991년 12월

졸-겔法으로 $YBa_2Cu_3O_{7-x}$에 弗素添加

(Fluorination of $YBa_2Cu_3O_{7-x}$ by a Sol-Gel process)

김봉흡*, 강형부**, 김현택***
(Kim Bong-Heup, Kang Hyung-Boo, Kim Hyun-Taek)

요 약

y의 크기가 0.02에서부터 2.0까지의 두 次數만큼 變하게 弗素가 添加된 $YBa_2Cu_3O_{7-x}F_y$ 超傳導物質을, 金屬窒酸鹽과 水酸化나트륨 및 弗化나트륨을 써서 졸-겔法으로 製造하였다. 弗素含有量들을 이온-선택 電極을 使用하여 測定하였다. 反應物質로 添加된 弗素全部가 最終試料속에 存在한다는 것을 알았다. XRD 觀測으로부터 $y \leq 0.2$인 試料들은 단지 單相 페로브스카이트 構造로 되었고, 反面 $y \geq 0.5$인 것들은 最終試料속에 BaF_2 YF_3 및 CuO와 같은 化合物들과 함께 生成되어져 있다고, 結論지을 수가 있다. 더구나 固體 ^{19}F 核磁氣共鳴觀測이, 弗素가 정말로 格子位置들 속에 混入되어 있는지 여부를 確認하기 위하여 行해졌는데, 實驗結果로부터 $YBa_2Cu_3O_{7-x}$ 格子位置속에 混入된 弗素의 몰比는 化合物 1 몰 當 約 0.2라는 것을 보여주었다. 또한 電氣抵抗率의 測定은 開始監界溫度가 $y \leq 0.2$와 같이, 指定된 添加率이 적은 領域에서는 y의 增加에 따라 약간씩 增加하는 傾向이 있음을 보여주고 있다.

ABSTRACT

Fluorine-doped $YBa_2Cu_3O_{7-x}Fy$ superconducting materials with y varing two orders of magnitude from 0.02 to 2.0 have been prepared by a sol-gel process using metal nitrate salts, sodium hydroxide and sodium fluoride. Fluorine contents have been measured using an ion-selective electrode. All fluorine introduced as reactant was found to be present in the resulted samples. From the observation of XRD it has been concluded that the samples with $y \leq 0.2$were single phase of perovskite structure, whereas those with $y \geq 0.5$

yielded compounds such as BaF_2, YF_3 and CuO. The observation of solid state ^{19}F NMR has been carried out in order to check whether fluorine was actually incorporated into the lattice sites. and the experimental results revealed that the mole ratio of fluouine incorporated into the lattice sites of $YBa_2Cu_3O_{7-x}$ was approximately 0.2 per mole of the compound when saturated. Also electrical resistivity measurement indicated that onset transition temperature has the tendency to increase slightly with increasing y in the pointed dilute region $y \leq 0.2$.

*한양대학교 전기공학과

1. Introduction

The mechanism for superconductivity in high-Tc oxide materials is a very important and highly interesting problem which is not yet understood. However, the means of doping systematics, in general, have provided useful insight to understand the convensional superconductivity and a number of result have already been obtained through this way for the $YBa_2Cu_3O_{7-x}$ superconductor. There have been several reports on the effect of cation srbstitution in different srblattices of $YBa_2Cu_3O_{7-x}$. A complete substitution of yittrum ions by most other rare earth elementts usually does not have a significant effect on the transition temperature [1-7]. A limited amount($\leq$40 mole %) of Ba can be substituted by Sr without affecting the crystal structure, but a gradual decrease in the transition temperature have been reported [1, 8]. Similary, there has been reported that nickel [9] and silver [10] substitutuon in the copper sites may decrease the transition temperature. In the Cu-O regions themselves, replacement of O^{16} O^{18} appears to indicate that isotope effect is either absent [11] or very small [12]. By contrast with these null effects or Small changes, it has recently been reported that the introduction of fluorine into the oxygen sublattice yielded the new prospective materials with onset transition temperature of 155 K [13], and in another case to 148.5K [14]. A theoretical treatment within the frame-work of BCS theory [15] suggests that fluorine atoms in the $YBa_2Cu_3O_{7-x}$ lattice may be related to changes of electronic density of states at the Fermi-level [16]. Therefore, a systematic substitution of oxygen by fluorine have been carried out in this experiment to $YBa_2Cu_3O_{7-x}$.

Fluorine-doped samples have been pre-

pared by a sol-gel process, since a sol-gel process has such important advantages in the field of doping study as to permit the mixing of reactants at a molecular level. The resulted materials have been characterized by means of fluoride ion analysis, XRD, ^{19}F NMR and electrecal resistivity measurements.

2. Sample preparation and experiment

The Fluorine-doped $YBa_2Cu_3O_{7-x}F_y$ samples with the nominal contents of fluorine, $y=0.02$, 0.05, 0.2, 0.5 and 2.0 have prepared by a sol-gel process [17] using high purity $Y(NO_3)_3 \cdot 5H_2O$, $Ba(No_3)_2$, $Cu(NO_3)_2 3H_2O$, NaOH (precipitation agent) and NaF(fluorination agent)as the starting materials.

$Y(NO_3)_3 \cdot 5H_2O$, $Ba(No_3)_2$, $Cu(NO_3)_2 \cdot 3H_2O$,and NaF were weighted to get Y : Ba : Cu : F ratios to be the aimed nominal composition.

$Y(NO_3)_3 \cdot 5H_2O$ and NaF were dissolved in warm distilled water to obtain an aqueous solution containing yittrium cations and yittrium fluoride precipitates. $Ba(No_3)_2$ and $Cu(NO_3)_2 \cdot 3H_2O$ were dissolved in warm distilled water to obtain an aqueous solution containing barium and copper cations. These two sorts of solution were slowly poured into an aqueous solution of NaOH simultaneously with vigorous motor stirring at the condition of solution basicities of pH 13 at room temperature. Blue white precipetates of the mixture of $Y(OH)_3$, $Ba(OH)_2$ and YF_2 were formed from the clear transparent solution. The precipitates were isolated by filltration, washed with destilled water several times and dried overnight in drying oven at 120℃. Blue white gel formed precipitates turned out to be black-tan. The black-tan precursors were thoroughly ground and calcined at 850℃ for 12 hours in air, followed by slow cooling. The calcined powders were pressed into pellet form and these pellets were sintered at 900℃ for 18 hours and then cooled down slowly to room tenperature in the flow of oxygen.

The fluorine analysis of the resulting materials has been carried out by the following manner. The fluorinated samples were decomposed by an alkaline flux fusion technique and fluoride contents were determined by a fluoride ion-selective electrode. The samples were fused with NaOH at 700℃ in a nickel crucible. The fused melts were digested in water, adjusting pH value up to 8. Tisab Ⅱ solution (buffer solution of pH 5~5.5) was added in the melts, adjusting the total ionic strength with buffer.

X-ray powder diffraction analysis has been carried out using a computer controlled diffractometer with CuKα X-ray source. The diffraction patterns have

been measured in the scanning range from $2\theta = 20℃$ to $70℃$.

Solid-state ^{19}F NMR measurements have been made under a static magietic field of 4.7 T and a modulation field of ~ 10 gauss with pulse FT(Fourier-Transform)spectrometer. The NMR line shapes have been determined by Fourier transforming the free inductuon decay(FID) which occurs after the 90℃ pulses of 1.7 μs width and a spectral width of $\pm$ 200 kHz are applied.

Electrical resistivity measurements of the sintered pellets have been performed using the standard four-probe method.

3. Results and discussion

The fluoride contents of the resulting materials have been measured using a fluorine sensitive electrode (Orion model 407 A). The result of the fluorine analysis revealed that all fluorine introduced as reactant was found to be present in the resulting samples, indicating that none was lost as fluoride ion during the preparative procedure.

X-ray diffraction analysis have been performed on the characteristics by a RIGAKU diffractometer. Fig. 1 shows the X-ray powder diffraction patterns of the samples. Samples with $y \leq 0.2$ are monophasic and only contain the orthorhombic perovskite phase as in the undoped sample. However, compositions with $y = 0.5$ and 2.0 are multiphasic consisting of BaF_2, YF_3 and CuO in addition to the perovskite superconducting phase. Orthorhombic unit cell parameters have been calculated by least-square refinement of the X-ray diffraction data. These parameters are listed in Table I.

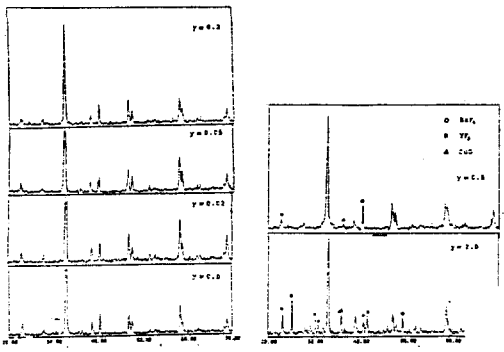

Fig. 1. X-ray powder diffraction patterns of the fluorinated samples.

Table I : Orthorhombic unit cell parameters of the fluorinated samples.

y	Lattice parameters(A)			Unit cell	$\frac{(b-a)}{(b+a)}$
	a	b	c	Volume(A^3)	
0.02	3.8 4	3.88	11.73	174.77	0.005
0.05	3.83	3.87	11.70	173.30	0.005
0.2	3.81	3.84	11.64	170.30	0.004
0.5	3.80	3.83	11.62	169.12	0.004
2.0	3.80	3.83	11.61	168.97	0.004

The replacement of oxygen by fluorine slightly decreases these parameters as expected from difference in the ionic sizes. Fig. 2 shows the decrease in the unit cell volume(Vm)with increasing mole % of fluorine in the fluorinated samples. The orthorhombic strain (b−a)/(b+a) is approximately constant, suggesting that the ordered vacancy structure is almost unaffected by fluorine doping.

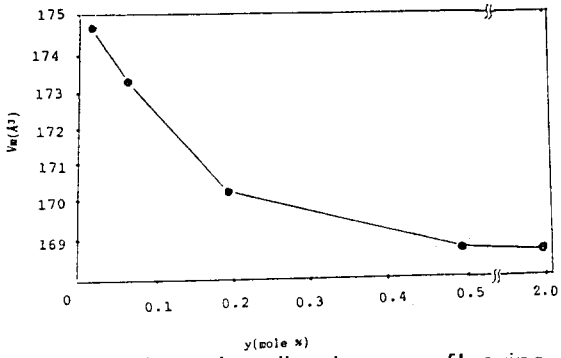

Fig. 2 The unit cell volume vs fluorine content for the fluorinated samples.

The fluorinated samples have monitored with use of solid-state ^{19}F NMR [18, 19] in order to identify whether at least some of the fluorine is actually incorporated into the $YBa_2Cu_3O_{7-x}$ lattice sites.

Fig. 3(a) and (b) are ^{19}F NMR spectra of the fluorinated samples with y=2.0 and y=0.2 respectively, and those are obtained by Fourier transforming the FID signals averaged 1024 traces following the 90° pulses of repetition time of 200ms.

The measured spin-lattice relaxation times of fluorine in the lattice sites, YF_3 and BaF_2 are approximately 0.2, 10 and 200 seconds, respectively as shown afterward.[※] Therefore, the spectra can be thought of as resonance spectra from fluorine in the lattice sites only, because the repe tition time is too shorter than the spin-lattice relaxation times of fluorine in YF_3 and BaF_2 to contain the resonance component from fluorine of those compounds in the spectra.

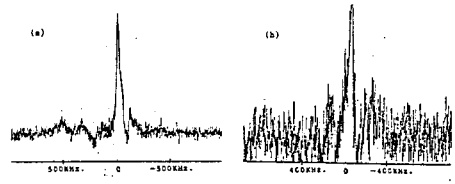

Fig. 3 ^{19}F NMR spectra from fluorine in the fluorinated samples with y=2.0(a) and 0.2(b)

Fig.4. shows the plots of log[M(∞)-M(T)] againt T(repetition time) of the sam ples with y=2.0 and 0.2, where M(∞) is the saturated magnetization and M(T) is the relaxed magnetizations in time T follow ing the 90° pulse.

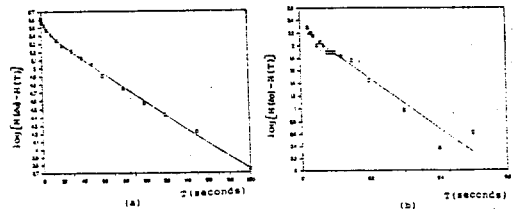

Fig. 4. The plots of log [M(∞) − M(T)] against T of the samples with y=2.0(a) and 0.2(b)

For the samples with y=2.0, [M (∞) − M(T)] can be fitted with the sum of three exponentials, $M_{10}\exp(-$

$T/T_{11}) + M_{20}\exp(-T/T_{12}) + M_{30}\exp(-T/T_{13})$

The spin-lattice relaxation times and the ratios of fluorine contents in the lattice sites, YF_3 and BaF_2 can be obtained from the plots. Here, T_{11}, T_{12}, and T_{13} are the spin-lattice relaxation times in the lattice sites, YF_3 and BaF_2, respectively, and $M_{10} : M_{20} : M_{30}$ is the ratio of the amount of fluorine in the lattice site, YF_3 and BaF_2. Therefore, the value of $M_{10}/(M_{10}+M_{20}+M_{30})$ is the ratio of flusorine in the lattice sites. The obtained value is approximately 9.4%.

For the sample with $y=0.2$, $[M(\infty) - M(T)]$ can be fitted to a single exponential, because the plot of $\log[M(\infty) - M(T)]$ is linear againt T[※] This means that the spin-lattice relaxation time of this sample has a single value and all of the added fluorine was incorporated into the lattice sites. The determined ratios of fluorine contents incorporated into the lattice sites in the samples with $y=2.0$ and 0.2 are approximately 9.4 and 100% respectively. Therefore, it is concluded that the ratio of inconporated fluorine into the lattice sites is approximately 0.2 mole per mole of compound when saturated.

Standard four-probe method was used to measure as a function of temperature the electrical resistivity of the sintered pellets. Fig. 5 shows the results in the proximity for four samples with $y=0.0$, 0.02. 0.05, 0.2, 0.5 and 2.0. The valuse of the onset transition temperatures(Tc) and transition widths(ΔTc)are listed in Table Ⅱ.

The onset transition temperature increased slightly with increasing y and reached a maximum of approximately 95 K for $y \geq 0.2$. According to the BCS theory on the transition temperature that is expressed in terms of the electronic density of states at the

y	T_c(onset) (K)	ΔT_c (K)
0.0	92.2	0.8
0.02	92.8	1.4
0.05	93.4	1.6
0.2	95.0	0.5
0.5	95.3	6.3
2.0	95.2	5.7

Table Ⅱ ; Resistive transition temperatures and transition widths of the fluorinated samples.

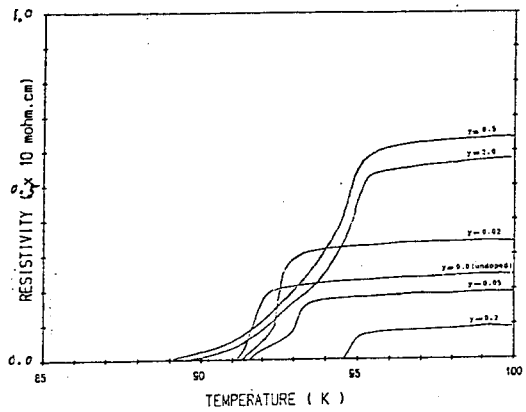

Fig. 5 Temperature dependence of resistivity.

Fermi-level $N(E_F)$[15], or $T_c \propto \exp[-1/N(E_F)]$, an increase in T_c reflects an increase in $N(E_F)$.

Fluorine is monovalent in contrast to the divalent oxygen, so that incorporated fluorine in the $YBa_2Cu_3O_{7-x}$ lattice sites certainly increases $N(E_F)$ due to this valence difference.[20]

4. Conclusion

(1) XRD measurements indicate that the cell parameters slightly decrease with increasing mole % of fluorine. This fact appears to be due to the difference of ionic sizes between oxygen and fluorine. The orthorhombic strain is approximately constant, suggesting that the ordered vacancy structure is unaffected by fluorine doping.

(2) ^{19}F NMR experiments reveal that the ratio of the amount of fluorine entering into the lattice sites is approximately 0.2 mole per mole of compound when saturated.

(3) T_C(onset)appears to increase with F-content up to $y=0.2$ and then saturates, indicating that the solubility limit of F is reached.

References

1) D.W. Murphy. S. Sunshine. R.B. van Dover, R.J. Cava, b.Batlogg, S. M.Xahurak, and L.F. Schneemeyer ; Phys. Rev. Lett. 58, 1988(1987)

2) S.Tsurumi, M.Hikita, T.Iwata. K. Semba, and S.Kurihara, jpn.J. Appl. Phys. 26, L856(1987).

3) S.Ohshima and T.Wakiyama, Jpn. J. Appl. Phys. 26, L704(1987).

4) S.Tsurumi, M.Hikita, T.IWata, and K.Semba, Jpn. J. Appl. Phys, 26, L704(1987)

5) K.Takita, H.Akinaga, H.Katah, T. Ipposhi. and K.Masida, Jpn. J. Appl. Phys. 26, L633(1987).

6) T.Yamada, K.Kinoshita, A.Matsuda,T. Watanabe, and Y.Asano, Jpn. J. Appl. Phys. 26, L633(1987).

7) J.M.Tarascon, W.R. Mckinnon, L.H. Greene, G.W. Hull, and E.M. Vogel. Phys. Rev. B36, 226(1987).

8) T.Wakda S Adachi, T.Mihara, and R. Inaba, Jpn. J. Appl. Phys. 26, L706 (1987).

9) Y.Maeno, T.Nojima, Y.Aoki, M.Kato, K.Hoshino, A.Minami, and T.Fujita, Jpn. J. Appl. Phys. 26, L774(1987).

10) Y.Saito, T.Noji, A.Endo, N.Higuchi, K. Fujimoto, T.Oikawa, A.Hattori and K. Furuse. Jpn. J. Appl. Phys.26, L832 (1987).

11) B.Batlogg, R.J. Cava, A.Jayaraman, R. B. van Dover, A.Kourouklis, S.Sunshine, D.W. Murphy, L.W.Rupp. H.S. Chen. A. White, K.T.Short, A.N. Mujsce, and E.A. Rietman, Phys. Rev. Lett 58, 2333(1987) : also L.C. Bourne, M.F. Crommie, A.Zettl. H.C. Love, S.W. Keller, K.L.Leary, A.M. Stacy, K.J.Chang, M.L.Cohen, and D. E.Morris : Phys. Rev. Lett. 58, 2337 (1987)

12) K.J. Leary, H.C.Love, S.W.Keller, T.A. Faltens, W.K.Ham, J.N.Michaels, and A.M.Stacy, Phys. Rev. Lett. 59, 1236 (1987).

13) S.R.Ovshinsky, R.T.Young, D.D.Allred, G.De ,Maggio, and G.A. Van Der Leeden, Phys. Rev. Lett.58, 2579 (1987).

14) M.Xian Ren. R.Yan Ru, L.Ming Zhn, T.Qing Yun, L.Zhen Jin, S.Li Hua, D. Wel Qing, F.Min Hua, M.Qing Yuan, L.Chang Jiang, L.Xiu-Hua, Q. Guan Ling and C.Mon Yuan, Solid State Commun, 64, 325(1987).

15) F.Herman, R.V.Kasowski, and W.Y. Hen, Phys. Rev. B.36, 6904(1987)

16) William Y.Hsu and Robert V. Kasowski, Frank Herman : Phys, Rev. Vol.37, No.10, April, 1988(5824 -5827)

17) B.H.Kim, H.B.Kang, and H.T.Kim, Trans. KIEE, Vol.40, No.3, MAR. 1991(275-281)

18) Fukushima Experimental pulse NMR (1989).

19) C.P.Poole Theory of magnetic resonance(1972).

20) G.J.Hyland Jph.J.Appl.Phys.27, (pp. L598~L599)1988.

(1991년 10월 16일 접수)