

# 졸-겔法으로 製造한 $YBa_2Cu_3O_{7-x}F_y$ 超傳導物質의 特性分析

## Characterization of $YBa_2Cu_3O_{7-x}F_y$ Superconducting Materials Made by a Sol-Gel Process

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**Abstract** - Fluorine - doped  $YBa_2Cu_3O_{7-x}F_y$  superconducting materials with  $y$  varying two orders of magnitude from 0.02 to 2.0 have been prepared by a sol-gel process by using metal nitrate salts, sodium hydroxide and sodium fluoride. Fluorine contents have been measured using an ion-selective electrode. All fluorine doped as reactant were found to be present in the resulted samples. From the observation of XRD it has been concluded that the samples with  $y \leq 0.2$  formed simply the single phase of perovskite structure, whereas those with  $y \geq 0.5$  yielded together some compounds such as  $BaF_2$ ,  $YF_3$  and  $CuO$  in the resulted samples. 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 fluorine incorporated into the lattice sites of  $YBa_2Cu_3O_{7-x}$  was approximately 0.2 per mole of the compound. Also electrical resistivity measurement indicated that onset transition temperature has the tendency to increase slightly with increasing  $y$  in the dilute region as  $y \leq 0.2$ .

**Key Words** : Fluorination of  $YBa_2Cu_3O_{7-x}$  by a sol-gel process  
(졸-겔 法으로  $YBa_2 Cu_3O_{7-x}$  에 弗素添加)  
Solid-state  $^{19}F$  NMR (固體  $^{19}F$  核磁氣公鳴)

### 1. Introduction

The mechanism for superconductivity in high  $-T_c$  oxide materials is a very important and highly interesting problem which is not yet entirely

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接受日字 : 1991年 10月 11日  
1次修正 : 1992年 4月 17日

understood. However, the means of doping systematics, in general, have provided useful insight to understand the conventional superconductivity and a number of results have already been obtained through this way for the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  superconductor. There have been several reports on the effect of cation substitution in different sublattices of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ . For instance, a complete substitution of yttrium ions by most other rare earth elements usually does not have a significant effect on the transition temperature [1~7] and a limited amount ( $\leq 40$  mole %) of Ba can be substituted by Sr without affecting the crystal structure, but it is reported that a gradual decrease in the transition temperature has been observed [1, 8]. Similarly, there has been observed that nickel [9] and silver [10] substitution in the copper sites may decrease the transition temperature. In the Cu-O regions, the replacement of  $\text{O}^{16}$  by  $\text{O}^{18}$  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 155K [13], and in another case to 148.5K [14]. A theoretical treatment within the framework of BCS theory [15] suggests that fluorine atoms in the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  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  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$

Fluorine-doped samples have been prepared 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 to increase doping effects. The resulted materials have been characterized by means of fluoride ion analysis, XRD,  $^{19}\text{F}$  NMR and electrical resistivity measurements.

## 2. Sample preparation and experiment

The fluorine-doped  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}\text{F}_y$  sample with the nominal contents of fluorine,  $y=0.02, 0.05, 0.2, 0.5$  and  $2.0$  have been prepared by a sol-gel

process [17] using high purity  $\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ,  $\text{Ba}(\text{NO}_3)_2$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{NaOH}$  (precipitation agent) and  $\text{NaF}$  (fluorination agent) as the starting materials.

$\text{Y}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$  and  $\text{NaF}$  were dissolved in warm distilled water to obtain an aqueous solution containing yttrium cations and yttrium fluoride precipitates.  $\text{Ba}(\text{NO}_3)_2$  and  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  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  $\text{NaOH}$  simultaneously with vigorous motor stirring at the condition of solution basicities of pH 13 at room temperature. Blue white precipitates of the mixture of  $\text{Y}(\text{OH})_3$ ,  $\text{Ba}(\text{OH})_2$ ,  $\text{Cu}(\text{OH})_2$  and  $\text{YF}_3$  were formed from the clear transparent solution. The precipitates were isolated by filtration, washed with distilled water several times and dried overnight in drying oven at  $120^\circ\text{C}$ . Blue white gel-formed precipitates turned out to be black-tan. The black-tan precursors were thoroughly ground and calcined at  $850^\circ\text{C}$  for 12 hours in air, followed by slow cooling. The calcined powders were pressed into pellet form and these pellets were sintered at  $900^\circ\text{C}$  for 18 hours and then cooled down slowly to room temperature 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  $\text{NaOH}$  at  $700^\circ\text{C}$  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  $\text{CuK}_\alpha$  x-ray source. The diffraction patterns have been measured in the scanning range from  $2\theta=20^\circ$  to  $70^\circ$ .

Solid-state  $^{19}\text{F}$  NMR measurements have been made under a static magnetic field of 4.7 T and a modulation field of  $\sim 10$  gauss with a pulse FT (Fourier-Transform) spectrometer. The NMR

line shapes have been determined by Fourier transforming the free induction decay(FID) which occurs after the  $90^\circ$  pulses of  $1.7\mu\text{s}$  width and a spectral width of  $\pm 200\text{kHz}$  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 fluorine sensitive electrode that is an ion metal(Orion model 407A). 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 obtained by RIGAKU diffractometer. Samples with  $y \leq 0.2$  are monophasic and only contain the orthorhombic perovskite structure as the unique superconducting phase just as so in the undoped sample. However, compositions with  $y=0.5$  and  $2.0$  are multiphasic and consist of  $\text{BaF}_2$ ,  $\text{YF}_3$  and  $\text{CuO}$  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.

The replacement of oxygen by fluorine slightly decreases these parameters as expected from the difference in the ionic sizes.

Fig. 2 shows the decrease in the unit cell volume ( $V_m$ ) 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 responsible for superconductivity is almost unaffected by fluorine doping.

The fluorinated samples have been monitored by use of solid-state  $^{19}\text{F}$  NMR[18,19] in order to identify whether at least some of the fluorine is actually incorporated into the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  lattice sites.

Fig. 3(a) and(b) are  $^{19}\text{F}$  NMR spectra of the fluorinated samples with  $y=2.0$  and  $y=0.2$

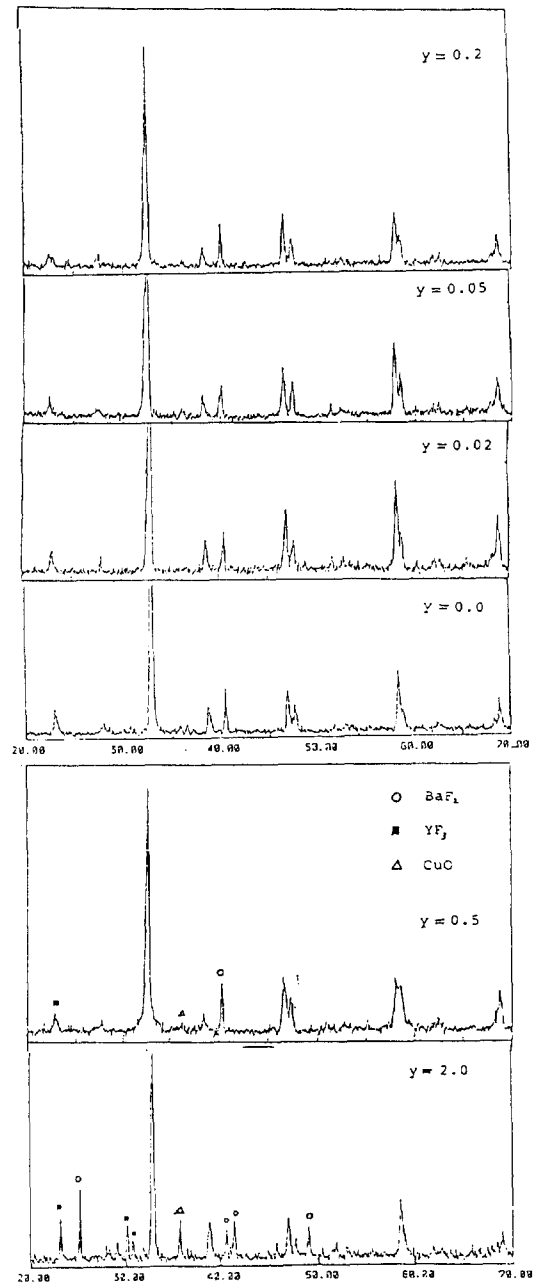


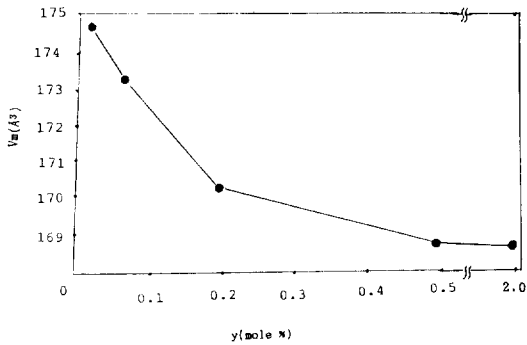
Fig. 1 X-ray powder diffraction patterns of the fluorinated samples.

respectively, and those are obtained by Fourier transforming the FID signals averaged 1024 traces and 612 traces respectively, following the  $90^\circ$  pulses of repetition time of 200ms. The measured spin-lattice relaxation times, as shown afterward

**Table 1** Orthorhombic unit cell parameters of the fluorinated samples.

Value of $y$	Lattice parameters ( $\text{\AA}$ )			Unit cell volume ( $\text{\AA}^3$ )	$\frac{(b-a)}{(b+a)}$
	a	b	c		
0.02	3.84	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

[ $\ast$ ], of fluorine in the lattice sites,  $\text{YF}_3$  and  $\text{BaF}_2$  are approximately 0.2, 10 and 200 seconds. Therefore, the spectra can be thought of as resonance spectra from fluorine in the lattice sites

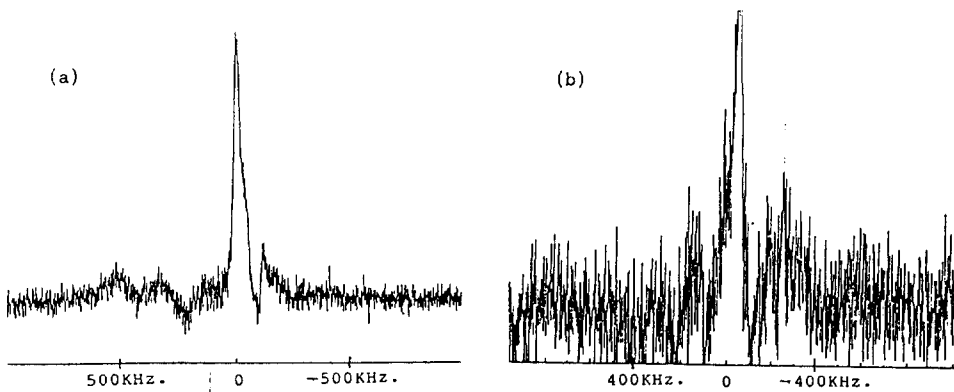
**Fig. 2** The unit cell volume vs fluorine content for the fluorinated samples.

only, because the repetition time is too short than the spin-lattice relaxation times of fluorine in  $\text{YF}_3$  and  $\text{BaF}_2$  to contain the resonance component from fluorine of those compounds in the spectra.

Fig. 4 shows the plots of  $\log[M(\infty) - M(T)]$  against  $T$  (repetition time) of the samples with  $y=2.0$  and  $0.2$ , where  $M(\infty)$  is the saturated magnetization and  $M(T)$  is the relaxed magnetizations in time  $T$  following the  $90^\circ$  pulse.

For the samples with  $y=2.0$ ,  $[M(\infty) - M(T)]$  can be fitted with the sum of three exponentials, such as  $M_{10}\exp(-T/T_{11}) + M_{20}\exp(-T/T_{12}) + M_{30}\exp(-T/T_{13})$ .

The spin-lattice relaxation times and the ratios of fluorine in the lattice sites,  $\text{YF}_3$  and  $\text{BaF}_2$  can be obtained from the plots. Where,  $T_{11}$ ,  $T_{12}$  and  $T_{13}$  are the spin-lattice relaxation times in the lattice sites,  $\text{YF}_3$  and  $\text{BaF}_2$  respectively and  $M_{10} : M_{20} : M_{30}$  is the ratio of the amount of fluorine in the

**Fig. 3**  $^{19}\text{F}$  NMR spectra from fluorine in the lattice sites of the fluorinated samples with  $y=2.0$  (a) and  $0.2$  (b).

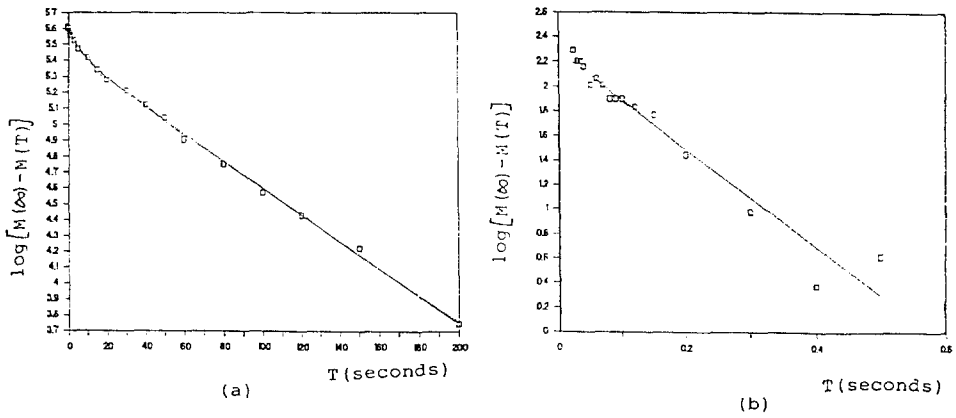


Fig. 4 The plots of  $\log[M(\infty) - M(T)]$  against  $T$  of the samples with  $y=2.0$ (a) and  $0.2$ (b).

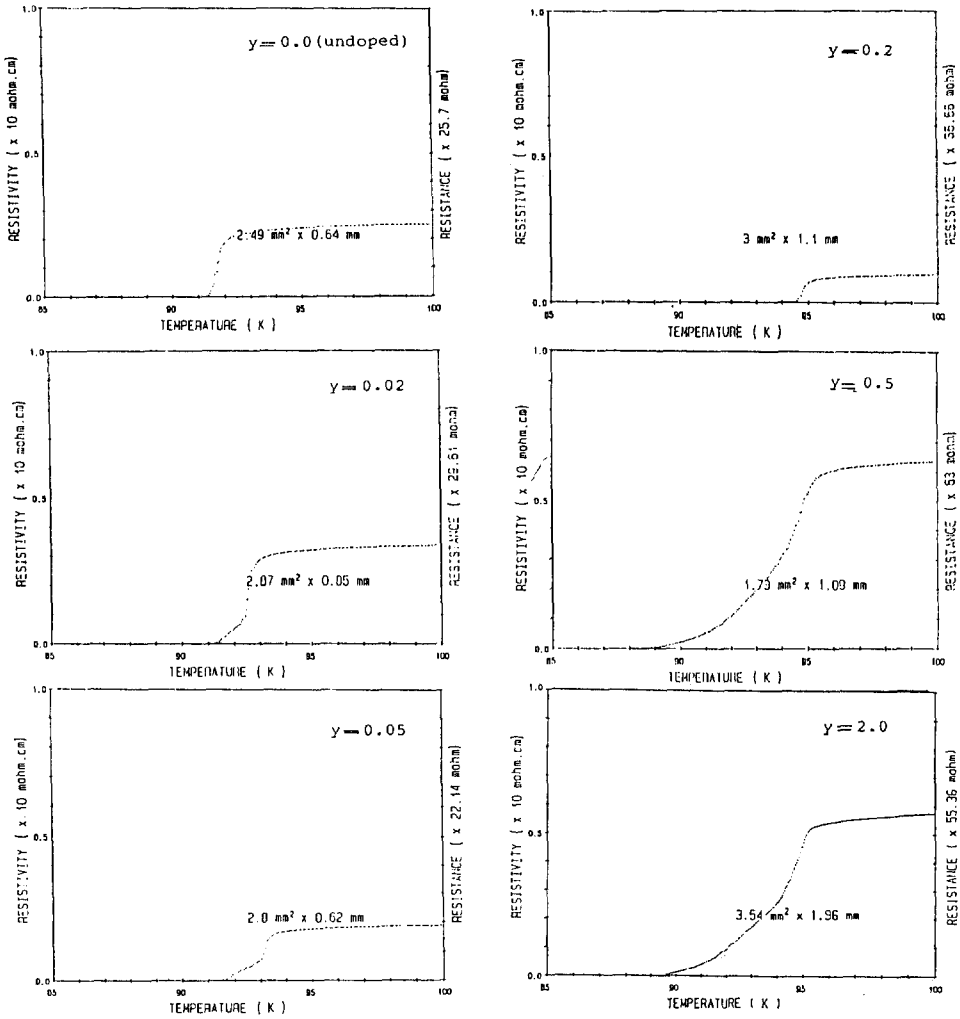


Fig. 5 Temperature dependence of resistivity.

**Table 2** Resistive transition temperatures and transition widths of the fluorinated samples.

Value of $y$	$T_c(\text{onset})$ ( $k$ )	$\Delta T_c$ ( $k$ )
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

lattice site,  $YF_3$  and  $BaF_2$ . Therefore, the value of  $M_{10}/(M_{10}+M_{20}+M_{30})$  is the ratio of fluorine 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 in a single exponential[\*], because the plot of  $\log[M(\infty)-M(T)]$  is linear against  $T$ . This means that the spin-lattice relaxation time of this sample has a single value and all of the added fluorine into the lattice sites in the samples with  $y=2.0$  and  $0.2$  are approximately 9.4 and 100% respectively. Therefore, it is found that the ratio of incorporated fluorine into the lattice sites is approximately 0.2 mole per mole of compound.

Standard four-probe method was used to measure the electrical resistivity of the sintered pellets. Fig. 5 shows the obtained curves for the temperature dependence of resistivity close of  $T_c$  of the samples with  $y=0.0, 0.02, 0.05, 0.2, 0.5$  and  $2.0$ . The values of the onset transition temperatures ( $T_c$ ) and transition widths ( $\Delta T_c$ ) are listed in Table II.

The onset transition temperature increased slightly with increasing  $y$  and reached a maximum of approximately 95K for  $y \geq 0.2$ . According to the BCS theory on the transition temperature that can be expressed in the form appropriate to the electronic density of states at the Fermi-level  $N(E_F)$ [15] —i.e. —  $T_c \propto \exp[-1/N(E_F)]$ , 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  $N(E_F)$  related to this valence difference[20].

#### 4. Conclusion

- (1) XRD measurements indicate that the unit cell parameters slightly decrease with increasing mole % of fluorine. This fact appears 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.
- (3) Electrical measurements exhibit that the onset transition temperatures of the fluorinated samples with  $y \geq 0.2$  slightly increase (approximately  $\sim 3K$ ) than that of the undoped sample. This fact suggests that the experimental results are consistent with limited incorporation of fluorine, on the order of approximately 0.2 mole, in the fluorination process.

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