Effect of Fluorine on Decrease of Synthesis Temperature in Binary Superconductors

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Abstract- The validity of fluorine for decreasing the synthesis temperature in binary (Nd, Sm)-Ba-Cu-O superconductor has been investigated. The synthesis temperature of the sample doped fluorine decreased than that in the sample undoped. In addition, the void size in the microstructure in NSBCO superconductors were larger than those in YBCO superconductors despite decrease of the synthesis temperature. For getting finer voids and/or larger grains, the cooling rate in the binary NSBCO superconductors should decrease at a slow speed in comparison with that in YBCO superconductors. This is explained from the difference of atomic mass of the elements of Y, Sm, and Nd.

Keywords – fluorine, (Nd, Sm)-Ba-Cu-O superconductor, thermal analysis, synthesis temperature, microstructure

I. INTORODUCTION

The critical current density, J_c, in superconductors is a very important parameter for their power applications, and usually decreases with increasing temperature and/or magnetic field. However, the anomalous phenomenon on the critical current density was reported as the increase in the critical current density with increasing temperature and/or magnetic field. This is called as the peak effect. If we intentionally can reproduce the peak effect in the superconducting materials, the critical current characteristic will be greatly improved. For achieving the material design using the peak effect, we have large two problems. Problem 1, synthesis temperatures in high temperature superconductors are higher than those in metal superconductors. Problem 2, we assume the peak effect occurs by a pinning mechanism. It is not easy to control the pinning strength on the each pinning centers in the sample. Therefore, we try to use a binary superconducting material in order to appear the peak effect [1]. That is, one superconductor with low Ginzburg-Landau parameter, κ, changes to a normal conductor at a certain magnetic field and acts as the pinning centers, an another superconductor with high Ginzburg-Landau parameter, κ, will have a condition of superconductivity in more higher magnetic fields than the former superconductor. This will be improved the characteristic of the critical current density in high temperature superconductors. In this paper, we simply present the progress only about the Problem1, i.e., the validity of fluorine concerning the synthesis temperature in binary superconductor with different Ginzburg-Landau parameters has been studied.

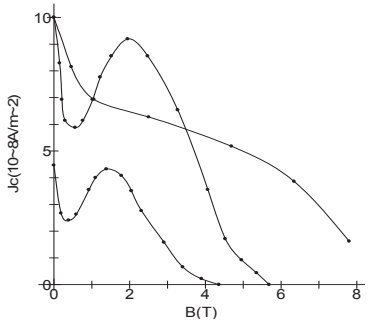
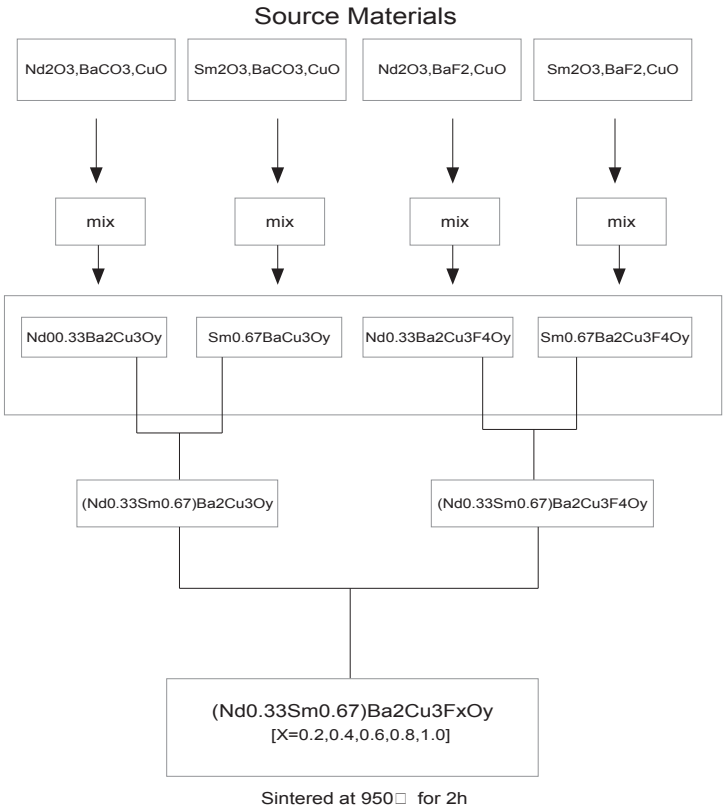


Figure1. Critical Current Density, J_c, generally decreases with increasing magnetic field. The samples with and without the peak effect are compared. Peaks of the critical current density are appeared [2].

II. EXPERIMENTAL PROCEDURE

The nominal $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3F_xO_y$ [x=0, 0.2, 0.4, 0.6, 0.8, and 1.0] compositions used in this study were prepared from the four master compositions, $Nd_{0.33}Ba_2Cu_3O_y$, $Sm_{0.67}Ba_2Cu_3O_y$, $Nd_{0.33}Ba_2Cu_3F_4O_y$, and $Sm_{0.67}Ba_2Cu_3F_4O_y$. Each master composition was synthesized as follows: $Nd_{0.33}Ba_2Cu_3O_y$ was synthesized from Nd_2O, $BaCO_3$, and CuO. $Sm_{0.67}Ba_2Cu_3O_y$ was synthesized in same manner, but Nd_2O was changed to Sm_2O_3. $Nd_{0.33}Ba_2Cu_3F_4O_y$ was synthesized from Nd_2O, BaF_2, and CuO. $Sm_{0.67}Ba_2Cu_3F_4O_y$ was synthesized in same manner, but Nd_2O was changed to Sm_2O_3. The starting materials were mixed, and the four master compositions were calcined at 900℃ for 8 h in air. Each master composition then cooled to room temperature and was ground again in a mortar. From the obtained powders, we prepared the nominal composition, $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3O_y$, from the master compositions of $Nd_{0.33}Ba_2Cu_3O_y$, and $Sm_{0.67}Ba_2Cu_3O_y$. In addition, the nominal composition, $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3F_4O_y$, was prepared from the two master compositions of $Nd_{0.33}Ba_2Cu_3F_4O_y$, and $Sm_{0.67}Ba_2Cu_3F_4O_y$,. The obtained two nominal compositions of $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3O_y$, and $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3F_4O_y$ were mixed to change the fluorine rates as $(Nd_{0.33}Sm_{0.67})Ba_2Cu_3F_{0.4}O_y$. The compounds with several fluorine are sintered at 950 for 8h in air. This flow chart of sample preparation is shown in Fig. 2. The applied techniques are mainly differential thermal analysis (DTA), X-ray diffractometer (XRD), and an optical microscope. DTA measurements were carried out from room temperature to 1000 . The experimental conditions were as follows: sampling rate 1.0s, increasing temperature rate 10 min^{-1} and used a platinum thermocouple. The microstructure observations were used specimens with their surfaces polished like mirrors.



. Figure2. Flow chart of sample preparation

III. RESALTS AND DISCUSSIONS

3.1. DTA curves in NSBCO doped fluorine with several quantities –

An effect of fluorine for decreasing synthesis temperature was reported by the present authors [3], e.g., the result for YBCO has been shown in Fig. 3. A sample doped fluorine has four endothermic peaks in the DTA curves, the

largest one is observed at 938℃. On the other hand, the DTA curve in the sample un-doped fluorine has three endothermic peaks at 850, 940, and 1024℃. The largest peak appears at 1024℃. This differs from the result of the sample doped fluorine, i.e., the effort of fluorine can be fairly understood. Then, we also applied the effect of decreasing the synthesis temperature for NSBCO superconductors. The DTA measurement results are shown in Fig 4. The heat treatment temperature was changed from the room temperature to 1000℃, here the DTA measurement curves displayed only between the temperatures from 500℃ to 1000℃. The quantity of fluorine changed from 0 to 1.0 mol at intervals of 0.2 mol to the samples. DTA curves include two or three large endothermic peaks in the all. A DTA curve for a sample which does not include fluorine is shown as $(Nd,Sm)Ba_2Cu_3F_xO_y$, x=0. Here two large endothermic peaks can be observed. We shall compare the endothermic peak on the lower temperature side with those in other DTA curves. On a DTA curve in a sample with fluorine rate x=0.2 mol, the remarked endothermic peak appears at 762℃. The temperature difference in comparison with that in the sample without fluorine is too large. The tendency that the temperature of the endothermic peak appears at lower temperature side by doping fluorine continues with increasing the quantities of fluorine. It can see in the DTA curves of fluorine rates x=0.2, 0.6, 0.8, and 1.0 in comparison with the fluorine rate x=0. However, the temperature decrease by doping fluorine is saturated in the vicinity of 750℃. This temperature is too lower than the melting point of silver to be used as silver sheath. That is, it is found that fluorine doped in NSBCO superconductors works effectively to decrease the synthesis temperature as similarly decreasing that in the YBCO superconductors. It is noticed that the temperatures of endothermic peak on the higher temperature side for all figures are hardly changed. However, the state of each figures is not same, the DTA curves in the samples included fluorine show complex changes at temperature around 950℃ and upward. The behaviour of fluorine in the sample of YBCO superconductors has been reported as that the fluorine evaporates in air in the vicinity of 950℃[4]. Since the DTA curves in NSBCO superconductors also included fluorine, it will show a similar situation to that in fluorine-doped YBCO superconductors. The complex changes in the DTA curves should be affected by the fluorine.

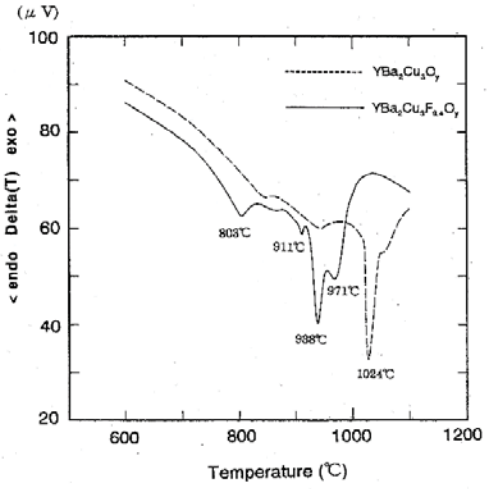


Figure3. Comparison with DTA curves of YBCO superconductors with doping and un-doping fluorine .

3.2 X-ray diffraction patterns for NSBCO samples doped fluorine –

A method which determines a quality of materials has been often used in X-ray diffraction measurement. We examined the mentioned above NSBCO samples on the diffraction peaks in the range of between 20 and 70 degrees for 2θ. Intensity in the each diffraction peaks has 2000cps. The results are shown in Fig. 5. In the two Figures, the diffraction peaks of NS123, Nd422, and Sm211 are indicated by following symbols of ◆, , and ▼. It is found that the diffraction peaks of NS123 for the sample un-doped fluorine, x=0, appear clearly in the diffraction pattern. The diffraction peaks of NS123 grow with increasing the doping rate of fluorine. As a result, the crystalline of NS123 is improved by addition of fluorine. However, other diffraction peaks in Nd422 and Sm211 also appear in the diffraction pattern of x=0.4. In general, melt-textured crystal in $(Nd_{1-x}Sm_x)Ba_2Cu_3O_{7-y}$ has been known to have main and minor second phases, which are the phases of Nd422 and Sm211, respectively. Though the heat treatment temperature arises up to the temperature of 950 , the diffraction peaks in Nd422 and Sm211 are saliently observed in the samples doped fluorine in comparison with the sample un-doped. The tendency lasts for the samples with fluorine X=1.0. It can be conceived that fluorine in the samples acts as the compound to melt them at a lower

temperature than usual. That is, by melting or partially melting the sample, the elements composed the sample can easily move for the synthesis of NSBCO superconductor. If not melting, the moving of the elements will not be easy.

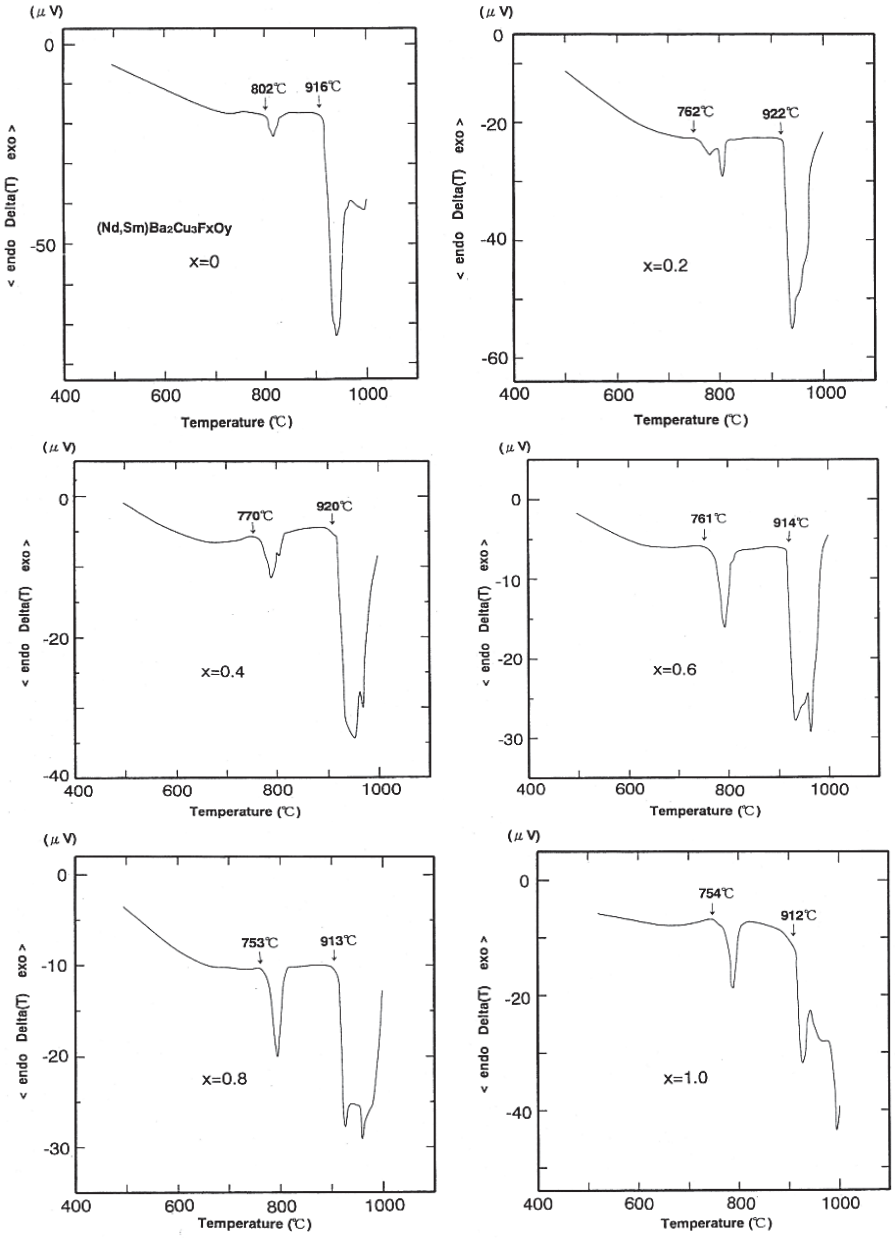


Figure4. DTA curves for NSBCO superconductor with some fluorine rates.

Therefore, the samples doped fluorine have strong diffraction peaks than that in the sample un-doped fluorine.

3.3 Microstructure observation for samples in NSBCO doped fluorine

The crystalline in those also increases in comparison with that in the sample un-doped fluorine. We suppose that some changes for the samples doped fluorine are in comparison with the sample un-doped fluorine. Then we investigated the microstructural change on the samples. The results are shown in Fig.6. The microstructure in the sample un-doped fluorine is a typical cinder like the YBCO superconductor. However, the appearance of microstructure of the sample included fluorine 0.2 mol is severely changed in comparison with that in the sample un-doped fluorine. There are some small grains and only a little void on the polished surface. However, the appearance of microstructures in the samples with fluorine 0.6, 0.8 and 1.0 mol are changed in comparison with

others in Fig.6. The size of grain in the each samples is larger in accordance with increasing doping rate in comparison with doping rate x=0.2 mol. That is, endothermic peak in the DTA curves the above mentioned moved

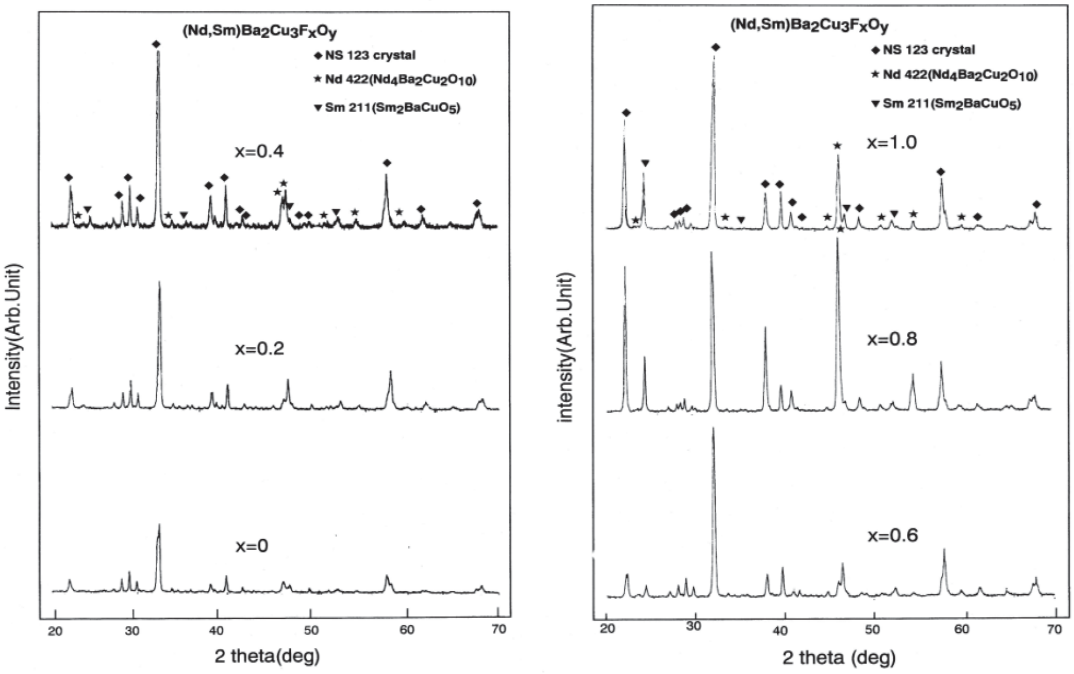


Figure5. X-ray diffraction patterns for NSBCO superconductors.

toward the low temperature side with increasing doping rates in comparison with the sample un-doped fluorine [5]. In addition, strong diffraction peaks appeared with increasing doping rate. From these facts, it has been supported that the source materials included fluorine melt or partially melt at a lower temperature than usual. Then the elements move and are synthesized the grains, so the grain in the sample x=1.0 is larger than those in the other samples. However, these microstructures observed in this study include large voids and grain in comparison with that in YBCO doped fluorine. This can be explained from the atomic mass for each element. The lightest atomic mass among the three elements is the Y element, i.e., this describes that the Y element can be easily moved in comparison with the other elements. Then it may be necessary to decreasing the voids and grains in the microstructures of the binary NSBCO superconductors by decreasing the cooling rate than that used in this study, 2 h^{-1}.

Further investigation is necessary for the NSBCO samples doped fluorine to measure the critical current density in high temperature regions. However, the critical current density may not be expected enough values. Because as far

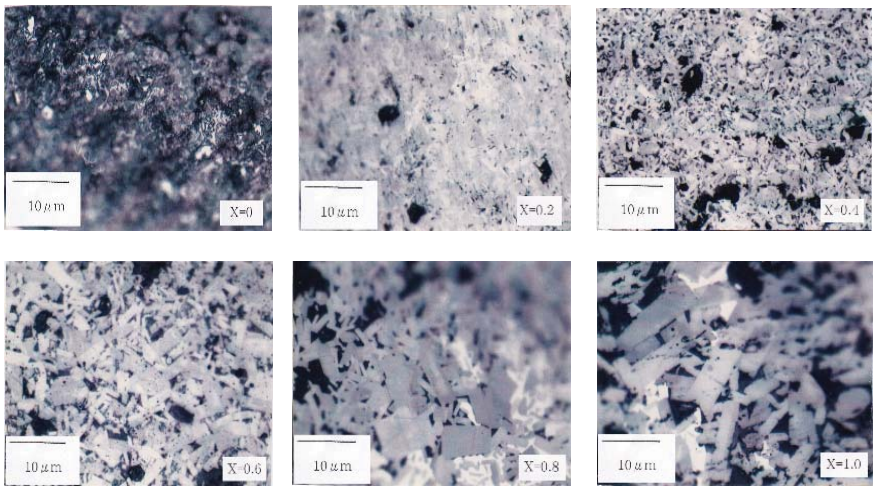


Figure6. Microstructure observation.

as we investigated the microstructure of the each samples, the included voids which acted as a pinning center were too larger size than those in YBCO superconductors doped fluorine. So we are necessary to obtain finer voids in the microstructure of NSBCO samples for increasing the critical current density. In addition, it is important for NSBCO (NBCO and SBCO) superconducting tape-wires with different Ginzburg-Landau parameters to establish the fabrication techniques so as to work as the pinning center for the superconductor with higher, κ, by the superconductor with lower, κ,.

IV.CONCLUSION

The validity of fluorine for decreasing the synthesis temperature by doping fluorine has been investigated for the binary NSBCO superconductor. The following results were obtained:

1. The endothermic peaks on the lower temperature side in DTA curves were moved toward the low temperature side with increasing the doping rate of fluorine.
2. The diffraction peaks of NSBCO superconductor were improved on the crystalline by addition of fluorine. That is, by melting or partially melting the sample, the atomic elements in the sample composed could move easily on the synthesis of NSBCO superconductor.
3. The grain size became larger in accordance with increasing doping rates. The samples included larger grains with increasing fluorine as the fluorine worked as melting or partially melting the samples.

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REFERENCES

[1] T.Hamada, Y.Ozono, T.Akune, and N. Sakamoto, "Effect of Platinum on the critical current density of fluorine-doped YBa2Cu3Ox superconductors"*J. Mate. Scie.. vol.32 3469-3473 , 1997*

[2] Yu.F.Bychkov, V.G.Vereshchagin, V.R.Karasik, G.B.Kurganov, Sov. Phys. JETP. *vol.29, 276-279, 1969.*

[3] T. Hamada, and R.Morimo, "Thermal Analysis on Fluorine-Doped and Non-Doped $Y_1Ba_2Cu_3O_x$ Superconductors" *phys. Stat. sol. (a) vol.45, 61-67, 1994.*

[4] T.Hamada, K.Iida,, and K. Mitsuda, "Effect of BaF_2 in Formation of Y_2BaCuO_5 Particles in Y-Ba-Cu-O Superconductor "*J. Thermal Analysis . vol.48. 981-988 , 1997*

[5] Yuki Sakamoto, Tsugio Hamada, Koki Otokata, and Yusuke Hisamatsu, "Effect of Fluorine on Decrease of Synthesis Temperature in Binary (Nd, Sm)-Ba-Cu-O Superconductors " *Proc. of Int. Workshop on Fundamental Research for Sci. and Tech. 2015, 64-69 , 2015*