Effect of Fluorine Doping on the Synthesis of High-\(T_c\) Bi-Based Superconductors

Shigeo HORIZUCHI, Kaoru SHODA* and Yoshio MATSUI

National Institute for Research in Inorganic Materials, Tsukuba-shi, Ibaraki 305

* Ube Industries Ltd., Ube-shi, Yamaguchi 755

High-\(T_c\) Bi-based superconductive oxides are prepared by doping a small amount of fluorine. Starting materials including fluoride powders are heated in air. Under the optimum synthesis condition a superconductor with \(T_c=113\) K and \(T_{c\text{end}}=106\) K is obtained; the firing temperature is 860°C, which is lower by about 20°C as compared to the case without doping fluorines. During the heating process most fluorines are released from the crystal, while the grains with the \(243\) phase grow very large at the expense of the \(232\) grains. High-resolution transmission electron microscopy (HRTEM) reveals a frequent intergrowth of layers as well as a local deformation of the supercell from the orthorhombic to monoclinic system. Another series of synthesis in a closed reaction system resulted in a less favorable result.

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1. Introduction

It has been known for the high-\(T_c\) Bi-based superconductors that the transition from the \(232\) phase \((\text{Bi}_2(\text{Sr}, \text{Ca})_3\text{Cu}_2\text{O}_x)\) to the \(243\) phase \((\text{Bi}_2(\text{Sr}, \text{Ca})_4\text{Cu}_3\text{O}_x)\) causes the increase in the critical temperature from 80 K to 110 K. One of the efficient methods for promoting the transition is to slightly dope Pb into the Bi-Sr-Ca-Cu-O system. Since oxygens play an important role in the high-\(T_c\) superconducting mechanism, it seems worth replacing oxygens partly by other kinds of anions. We have examined the effect of fluorine doping and shortly reported that a superconductor with slightly higher \(T_c\) can be obtained.

Apart from the conventional synthesis method by sintering, the effect of fluorine on the Bi-based superconducting oxide was recently examined using the ion-implantation technique. It has also been observed that the \(T_c\) slightly increased. Although the volume of the implanted fluorines in the crystal has not been known, the existence of fluorines surely affect the electrical resistivity.

This paper presents detailed experimental data on the synthesis conditions of Bi-based superconductors doped with fluorines, based on a conventional solid-to-solid reaction.

2. Experimental

Starting powders of \(\text{Bi}_2\text{O}_3\), \(\text{SrCO}_3\), \(\text{CaCO}_3\), \(\text{CaF}_2\), and \(\text{CuO}\) were mixed with the nominal composition \(\text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 1 : 1 : 1 : 2\). The fraction of fluorine was controlled by changing the starting mixing ratio \(\text{CaCO}_3/\text{CaF}_2\) in the range between 19/1 and 1/1. The mixed powders were preliminarily heated at the temperature between 720° and 850°C for 12 h in air. It was noticed that the reaction temperature of the powders decreased with increase in the fraction of fluorine. For example, the powders with the mixing ratio \(\text{CaCO}_3/\text{CaF}_2 = 4/1\) started to coagulate at about 760°C. We have then set the calcination temperature at 780°C.

All the specimens were calcined for 12 h at the temperatures listed in Table 1. The products were pulverized, pressed into pellets (16 mm \(\phi \times 1\) mm) and then fired at the temperature between 810° and 880°C in air. It was noticed that the melting temperature decreased with the fluorine fraction. For example, a trace of melting was observed at

<table>
<thead>
<tr>
<th>Table 1. Temperatures for the calcination of specimens.</th>
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<td>(\text{CaCO}_3/\text{CaF}_2)</td>
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<tr>
<td>temperature (°C)</td>
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840°C for the specimen with the mixing ratio of CaCO₃/CaF₂ = 4/1.

The electrical resistivity of the fired specimens was measured in the temperature range over the boiling point of the liquid nitrogen by means of conventional four-probe method, using the dc current mostly at 10 mA. The powder X-ray diffraction (XRD) was measured to identify the phase species of the products, using Rigaku D-9C. A scanning electron microscope (SEM), Akashi DS 130, was used to observe the morphology of grains. The microstructures of the specimens were observed by a transmission electron microscope (TEM), using HU-9000 type one operated at the accelerating voltage of 300 kV. Differential thermal analysis (DTA) was measured in order to examine the phase relation, using Rigaku TAS-100 and TG 8110.

3. Results
3.1 Electrical resistivity
The effect of fluorine doping on electrical resistivity appears differently for each composition. Table 2 shows the firing temperature, at which the resistivity drop occurs at maximal temperature for each composition. Here the firing period is kept constant for 50 h. For example, for the specimen with the mixing ratio CaCO₃/CaF₂ = 19/1 the highest Tc is obtained from the specimen fired at 870°C (Fig. 1(a)). The firing temperature is almost coincident with the melting temperature of the specimens.

The best effect of fluorine doping is obtained for the specimen heated at 860°C with the mixing ratio 9/1 (Fig. 1(b)), in which Tc = 113 K. The drop of the resistivity starts at about 120 K (Tc onset) and it reaches the zero value at 106 K (Tc end).

Table 2. Firing temperatures to get the maximal Tc for different specimen compositions. The firing duration is 50 h. Superconductive phases clarified by X-ray diffraction are also listed.

<table>
<thead>
<tr>
<th>CaCO₃ / CaF₂</th>
<th>19/1</th>
<th>9/1</th>
<th>4/1</th>
<th>1/1</th>
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</thead>
<tbody>
<tr>
<td>temperature (°C)</td>
<td>870</td>
<td>860</td>
<td>850</td>
<td>840</td>
</tr>
<tr>
<td>Tc onset (K)</td>
<td>120</td>
<td>120</td>
<td>120</td>
<td>90</td>
</tr>
<tr>
<td>Tc end (K)</td>
<td>81*</td>
<td>106</td>
<td>&lt;77*</td>
<td>&lt;77</td>
</tr>
<tr>
<td>phases, major</td>
<td>(243)</td>
<td>(245)</td>
<td>(232)</td>
<td>(232)</td>
</tr>
<tr>
<td>minor</td>
<td>(232)</td>
<td>(232)</td>
<td>(232)</td>
<td>-</td>
</tr>
<tr>
<td>impurity</td>
<td>(221)</td>
<td>(221)</td>
<td>CaO</td>
<td>CaO. Bi₂O₃</td>
</tr>
</tbody>
</table>

Fig. 1. Temperature dependence of the electrical resistivity. The fired temperature and period, together with the starting mixing ratio CaCO₃/CaF₂ are indicated in the figure.

The resistivity does not approach zero even at 77 K (Fig. 1(c)). For the mixing ratio 1/1 Tc onset is nearly 90 K (Fig. 1(d)).

3.2 XRD
Figure 2 represents the powder X-ray diffraction charts taken from the specimens fired under the same conditions as those in Fig. 1. The results are summarized in Table 2. We notice that the major phase for the mixing ratio 19/1 or 9/1 is the (243) phase (Figs. 2(a) and (b)), which is necessary for getting higher Tc, while the (232) phase becomes a major one for the mixing ratio 4/1 or 1/1 (Figs. 2(c) and (d)). CaO. Bi₂O₃ increases in volume as an impurity phase in the latter composition.

3.3 SEM
Figure 3(a) shows the SEM image of the specimen with the highest Tc (Fig. 1(b)), fired at 860°C with the mixing ratio 9/1. The fractured surface is observed. As a comparison, Fig. 3(b) is an image of the specimen fired at 878°C (near melting point) without doping any fluorine. The grain growth rate is quite different so that the grain size of the former is more than ten times
larger than that of the latter. It is interesting to note that there are a lot of pores in the former. It is known by the NMR measurement that most fluorines are released from the specimen on heating in the open system. Therefore, the pores must have been formed relating to the release of fluorines from the inside of the crystal.

3.4 TEM

Small blocks of the specimen with the highest $T_c$ (Fig. 1(b)) were crushed. The crystal fragments obtained were mounted on a microgrid and observed in a transmission electron microscope. Superstructure spots are observed in the electron diffraction patterns. The lattice parameters of the subcell measured from fundamental reflections are $a=b=5.4$ Å and $c=30.8$ Å (pseudotetragonal) for the (232) phase and $a=b=5.4$ Å and $c=36.0$ Å (pseudotetragonal) for the (243) phase. The superstructure reflections are located along the $b$ direction in the so-called nonintegral positions, indicating the formation of an incommensurately modulated structure. The size of the supercell in the $b$ direction is about $4.8 \times b$ for both phases.

**Figure 4(a)** is a high-resolution lattice image taken with the incident beam along the $a$ axis. The photograph shows that the crystal is composed of layers. The large spots with darkest contrast represent the positions of Bi atoms, which serve to outline the so-called Bi sheets running horizontally. We may then distinguish the (232) phase, marked by $L$, from the (243) phase, marked by $H$. At the center of the photograph both phases are adjoinning so that a local interface is created. The situation in the outlined area in Fig. 4(a) can be schematically drawn like in Fig. 4(b), where the curved lines indicate the $(020)$ lattice planes. Small ellipses represent the Bi-concentrated bands. An interesting feature is that the crystal system is different at the both sides of the interface; the system of outlined supercells is orthorhombic at the upper left part, while monoclinic at the lower right part.

A diffraction pattern in Fig. 5 was taken from the area including that of Fig. 4. Strong spots are from the (232) phase, while weak ones from the (243) one. There are weak but clear, diffuse streaks along the $c$ axis, which must be due to the frequent intergrowth of layers with different thick-
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This was proved true by a HRTEM image in Fig. 4. Moreover, it is interesting to note that the direction of diffraction spots are slightly tilted with the angle $\theta$, which is estimated to be in the range less than 10°, from the horizontal line. This indicates that the lowering of the crystal symmetry, as has been schematically shown in Fig. 4(b), occurs in a rather wide range in the specimen.

4. Discussion

4.1 Synthesis in a closed system

So far the specimens were heated in air, i.e. in an open system. In order to further examine the effect of fluorine doping, another series of experiments was carried out in a closed system; starting powders without CaF$_2$ were calcined. The products were pulverized and mixed with CaF$_2$. The shaped pellet (3x1x15 mm) was set in a Pt capsule, which was sealed by a silica tube, and then heated. The melting point of the products further decreased, as compared to the case heated in the open system. On heating at 840°C, for example, a trace of melting was observed in the specimen with the mixing ratio of CaCO$_3$/CaF$_2$ = 9/1. Here, the first drop of the resistivity started at about 120 K but it did not reach zero. The second drop occurred at about 80 K. Similar drops in two steps appeared even after heating for a longer period. Figure 6 shows the results, which gives the resistivity drop at the highest temperature for each mixing ratio. Any specimens do not allow a clear drop of resistivity in one step over 100 K. This is because of the strong retardation of the transition from the (232) phase to the (243) one, which has been confirmed by the XRD analysis.
4.2 Microstructures

The microstructures in Fig. 4 must represent the local reconstruction of the structure, relating to the rapid crystal growth. We may assume that the reconstruction has been initiated in response to the release of fluorine from the crystal.

It seems probable at such local interfaces as those found in Fig. 4 that some of Cu-O planes at the both sides are directly linked. This could be related to the slight increase in $T_c$ of the specimen.

4.3 DTA

The measurement of DTA was performed for the specimens, which were prepared by heating mixed powders, pulverizing and shaping into pellets, with a heating rate of 10°C/min in air (Fig. 7). No clear peaks were detected up to the temperatures of melting point, which decreased with the fraction of fluorine, for the specimens with the mixing ratio of CaCO$_3$/CaF$_2$=19/1 and 9/1. This supports the above-mentioned results that small amounts of fluorines are still left in the specimen crystals, in spite of their release into air during heating. The origin of extra peaks for the specimens CaCO$_3$/CaF$_2$=4/1 and 1/1 is not known. Further measurement is now going on.

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