Synthesis of High- T_c 2223 Phase in Bi-Pb-Sr-Ca-Cu-O System by Short-Term Firing

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短時間焼成による Bi 系2223相の合成

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The high- T_c 2223 phase in the Bi-Pb-Sr-Ca-Cu-O system has been synthesized by solid-state reaction. The processing parameters which give the largest volume fraction of the 2223 phase were found as follows. A mixture of Bi_2O_3 , PbO, SrCO_3 , CaCO_3 and CuO was pressed into a bar-shape and calcined at 1133 K for 5h, then cooled to 873 K with a cooling rate of 0.5 K/min. After being pulverized and pressed, the specimen was fired again at 1133 K for 5h and cooled to 873 K with a cooling rate of 0.5 K/min. With these simple synthesizing procedures, a superconducting sample which has a high T_c -2223 phase volume fraction as high as 91%, was successfully obtained. Our synthesizing method results in a much greater volume fraction of the 2223 phase than do conventional methods. The zero-resistance temperature of our sample was 102 K.

Key-words: Superconductor, Bi-Pb-Sr-Ca-Cu-O, 2223 phase, Solid-state reaction

1. Introduction

There are three superconducting phases in the Bi-Sr-Ca-Cu-O system: $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (so-called 2201^(1,2)), $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_x$ (2212⁽³⁾) and $\text{Bi}_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}_x$ (2223⁽³⁾). Among them, the 2223 phase has the highest critical temperature ($T_c=110$ K). Practical applications at liquid-nitrogen temperature are expected for this superconductor. However, formation of the 2223 phase is so slow that it is very difficult to synthesize a specimen having a high 2223 phase volume fraction.

From previous reports,⁽⁴⁻⁷⁾ the following can be listed as effective procedures in accelerating 2223 phase production:

- (1) substitution of Pb (30 to 40%) for Bi,⁽⁴⁾
- (2) selection of proper compositions of metals in starting mixtures, which are generally different from the stoichiometric 2223 composition,⁽⁵⁾
- (3) synthesis of precursor powders having high homogeneity through chemical routes,⁽⁴⁻⁶⁾
- (4) long-term (about 100h) firing just below the melting point,⁽⁷⁾ and

- (5) firing under low oxygen partial pressure ($P_{\text{O}_2}=1/13$ atm).⁽⁶⁾

Procedures (1) and (5) decrease the temperature at which the sample starts to partially melt, and this can be a reason for the acceleration of 2223 phase production.^(6,8) However, it still takes a long time, about 100h, to synthesize a good 2223 sample even when the steps shown above are adopted. It is hoped that 2223 samples will be synthesized more quickly even in air. It is also very important to clarify the formation mechanism of the 2223 phase from the material-science point of view.

In the present work, we examined the early stage of 2223 phase formation in the conventional solid-state reaction process by using X-ray diffraction (XRD) measurement and scanning electron microscopy (SEM). We found that the specimen starts to partially melt at around 1073 K. The processing conditions for attaining the largest amount of the 2223 phase are reported.

2. Experiment

Reagent-grade Bi_2O_3 , PbO, SrCO_3 , CaCO_3 and CuO were used as raw materials. The nominal molar ratio was Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.92 : 2.02 : 3.06.⁽⁵⁾ Mixed powders were pressed into bar-shaped specimens of $3 \times 3 \times 15$ mm³ under a pressure of 100 MPa.

Some of the specimens were heated on a silver sheet⁽⁹⁾ in air up to 1073 K or 1133 K with a heating rate of 5 K/min, and then quenched in water.

In order to synthesize a good 2223 phase, these compact-body specimens were calcined on a silver sheet at 1073 K which is a conventional calcining temperature,⁽³⁻⁷⁾ or at 1133 K, which was reported in our previous paper for the citrate method,⁽⁹⁾ for 5h in air with a heating rate of 5 K/min. The cooling rate was 0.5 K/min down to 873 K.^(9,10) These calcined specimens were pulverized in an agate mortar and then pressed into similarly bar-shaped specimens under the same pressure as mentioned above.

These specimens were fired on a silver sheet at 1133 K for 5h in air with a heating rate of 5 K/min. The cooling rate was 0.5 K/min down to 873 K. We call the specimen calcined at 1073 K and then fired at 1133 K specimen (a), and the specimen calcined at 1133 K and then fired at 1133 K specimen (b).

The phases produced in the specimens were identified by XRD measurement using Cu K α radiation. The fracture surfaces of the water-quenched specimens were observed with SEM.

Magnetic susceptibility of the specimens was measured with a SQUID at a magnetic field of 1.0 Oe at temperatures down to 5 K. For the magnetic measurement, the sample was pulverized in an agate mortar and then solidified into a bar-shape of 3 $\times$ 5 $\times$ 5 mm³ with GE7031 varnish. Resistivity of 3 $\times$ 3 $\times$ 10 mm³ bar-shaped specimens was measured using a conventional DC four-probe technique at a current density of about 100 mA/cm² upon cooling to 78 K.

3. Results and discussion

The authors have reported a citrate method⁹⁾ in which specimens having a high 2223 phase volume fraction can be synthesized by short-term firing in air. In our citrate method, partial melting of the specimens was found to start at a lower temperature than in the conventional solid-state reaction. This partial melt at the lower temperature may be crucial in attaining a high 2223 phase volume fraction by short-term firing in air. It is inferred that the 2223 phase grows more easily in the system when a melt phase is included. The phases existing just below the partial melt temperature were identified as Bi(Sr_{0.5}Ca_{0.5})O₂, Ca₂PbO₄, SrCO₃ and CuO.¹¹⁾ Based on this finding, a mixture of these phases, each prepared by solid-state reaction in advance, was heated under an appropriate condition. The sample thus obtained showed a 2223 phase volume fraction almost equal to that of the specimen synthesized by the citrate method.¹²⁾ From these results, it was found to be important to produce these phases and to promote partial melting through the reaction between these phases, for synthesizing the 2223 phase in air with short-term firing.

Figure 1 shows the SEM photographs for the fracture surface of the specimens quenched from 1073 K and 1133 K. As seen in the photograph of the specimen quenched from 1073 K, the liquid phase is observed; this implies that the specimen started to partially melt at around 1073 K. On the other hand, platelike crystallites are observed in the specimen quenched from 1133 K.

Figure 2 shows XRD patterns of the specimen quenched from 1073 K and 1133 K. As seen in the pattern of the specimen quenched from 1073 K, the 2201 phase, Bi(Sr_{0.5}Ca_{0.5})O₂, Ca₂PbO₄, SrCO₃ and CuO are produced in the specimen heat-treated through solid-state reaction, as well as in the specimen synthesized by the citrate method. In the speci-

men quenched from 1133 K, the 2212 phase, 2201 phase, Ca₂PbO₄, CuO and CaO are identified. Consequently, the platelike crystallites can be assumed as the 2212 phase.

Figure 3 shows XRD patterns for specimens (a) and (b). In the XRD pattern of specimen (a), strong

Fig. 1. SEM photographs for the fracture surface of the specimens quenched from 1073 K and 1133 K.

Fig. 2. XRD patterns measured with Cu K α radiation of the specimens quenched from 1073 K and 1133 K.

● 2212, $\triangle$ 2201, $\blacktriangle$ Ca₂PbO₄, $\diamond$ CuO, $\blacklozenge$ SrCO₃, $\blacksquare$ Bi(Sr_{0.5}Ca_{0.5})O₂, ∇ CaO

Fig. 3. XRD patterns measured with Cu K α radiation of specimen (a) and specimen (b).

○ 2223, ● 2212, $\triangle$ 2201, $\blacktriangle$ Ca₂PbO₄, $\square$ Ca₂CuO₃, $\blacktriangledown$ 3321

diffraction peaks for the 2212 phase appear. In specimen (a), the 2223 phase, Ca_2CuO_3 and Ca_2PbO_4 were minor phases. Specimen (b) had a large volume fraction of the 2223 phase, while those of the 2212 phase, Ca_2PbO_4 and the 3321 phase ($\text{Pb} : \text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 3.0 : 0.5 : 2.5 : 2.0 : 1.0$)¹³⁻¹⁵ were small. In order to estimate the volume fraction of the 2223 phase, a method using the intensity of reflected X-rays of the 2223 and 2212 phases⁹ was used. In specimen (a), the volume fraction of the 2223 phase is only 6 %, while in specimen (b), the volume fraction reached a high value of 91%.

The temperature dependence of susceptibility of specimens (a) and (b) showed two-step changes, as seen in Fig. 4. Specimen (a) exhibited large diamagnetic susceptibility below 80 K. On the other hand, specimen (b) exhibited a large change in susceptibility around 110 K and showed a small change around 70 K.

Figure 5 shows the temperature dependence of electrical resistivity of specimens (a) and (b). The

Fig. 4. Temperature dependences of susceptibilities for specimen (a) and specimen (b).

Fig. 5. Temperature dependences of electrical resistivities for specimen (a) and specimen (b).

temperature dependence of resistivity of specimen (a) showed a two-step change. The zero-resistance temperature was as low as 78 K. On the other hand, resistivity of specimen (b) began to decrease around 120 K and became zero at 102 K.

These results were reproducible within experimental error. More detailed studies on the formation mechanism of the 2223 phase are now in progress.

4. Conclusions

In conclusion, a simple synthesis method was found which is effective in the preparation of the high- T_c 2223 phase in the Bi-Pb-Sr-Ca-Cu-O system. With this method, even a short-term firing of 5h in air yields a high volume fraction of the 2223 phase of more than 90%.

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