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Synthesis of bismuth-based high-T_c superconducting fibres by using sodium alginate as a polyelectrolyte

A. TAKADA, T. SHIMIZU*
*Department of Electrical Engineering and *Department of Material and Environmental Engineering, Hakodate National College of Technology, Hakodate 042 Japan*

The thermal pyrolysis processes and solid-state reactions in the synthesis of bismuth-based high-T_c superconducting fibre obtained by using sodium alginates are studied. This alginate is a polyelectrolyte and has not only an excellent ion-exchange property but also a gelation to synthesize long fibrous precursors. We first determined the optimum conditions to promote ion-exchange of this polyelectrolyte which yields high contents of metal ions in the precursor. The thermal pyrolysis of a precursor was studied by DTA and IR absorption. On the basis of the DTA and XRD, the solid-state reactions associated with the formation of the 2212 phase were revealed. Our method can be applied easily to synthesize Ag-sheathed fibre having an improved tensile strength.

1. Introduction

To date, much effort has been devoted to the preparation of good high-T_c superconducting material. Many studies have been made on specimen preparation in the form of wire, tape and fibre for high field magnets. Among the synthesis techniques utilized the "powder in tube" method is usually used, though many kinds of chemical techniques for the preparation of fibre specimens without powder material have also been developed. The simplicity of the chemical techniques is very advantageous to obtain fibrous specimens. For example, Zhuang *et al.* [1] prepared Bi–Pb–Sr–Ca–Cu–O fibres by using acetates and Nasu *et al.* [2] used naphtanetes. In these techniques, it is, however, difficult to prepare a fibre which has a uniform diameter. Moreover, there is a limit in specimen length which one can synthesize. Therefore the "hand drawing" method is impractical [2, 3]. Zheng *et al.* [4] improved on this by synthesizing a long Bi–Sr–Ca–Cu–O glass fibre with uniform diameter.

On the other hand, the superconductivity of specimens obtained by chemical techniques is generally poor and requires improvement. Though there is a report on the enhancement of the volume fraction of 2 2 2 3 phase in fibre preparation [5], the study focused only on the growth of the superconducting phases, and not on the formation of the intermediate compounds.

For the bulk specimen, detailed studies on the solild-state reactions were made. However it should be recognized that there is a distinct difference in the reactions between the bulk by the conventional solid-state reaction method and the fibre by the chemical method. This seems to result from the starting material or the synthesis process.

In the preparation of high-T_c superconductors, the formation of the superconducting phase depends on the solid-state reactions among intermediate compounds. However, the sintering process of the fibrous precursor itself has scarcely been studied.

We report on a framework for the synthesis of the bismuth-based high-T_c superconducting fibre by using sodium alginate [6] on the basis of the ion-exchange property of this polyelectrolyte. The alginate consists of a block-copolymer [6] which has the excellent property of accumulating cations in aqueous solutions and becomes a gel when soaked in nitrate solution. This gelation plays an important role in obtaining the fibre shape.

In this paper, the thermal pyrolysis of the precursor and the formation of superconducting phases are described. In our method, the length of the fibre is in principle unlimited and a uniform diameter is available. Furthermore our method can be applied easily to the synthesis of Ag-sheathed fibres having an improved tensile strength.

To our knowledge, Konishi *et al.* [7] first synthesized successfully a yttrium-based superconducting fibre by using sodium alginate. Their study is interesting from the viewpoint of not only the preparation technique but also the use of a polyelectrolyte.

2. Synthesis and thermal analysis of precursor

2.1. Synthesis procedure

The fabrication process for Bi–Pb–Sr–Ca–Cu–O (BPSCCO) fibre is shown in Fig. 1. This process enables the synthesis of a long precursor with uniform diameter. First we prepared a nitrate solution with Bi, Pb, Sr, Ca and Cu ions by using pure nitrates; $Bi(NO_3)_3{\cdot}5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2{\cdot}4H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$. The PH value of this solution is

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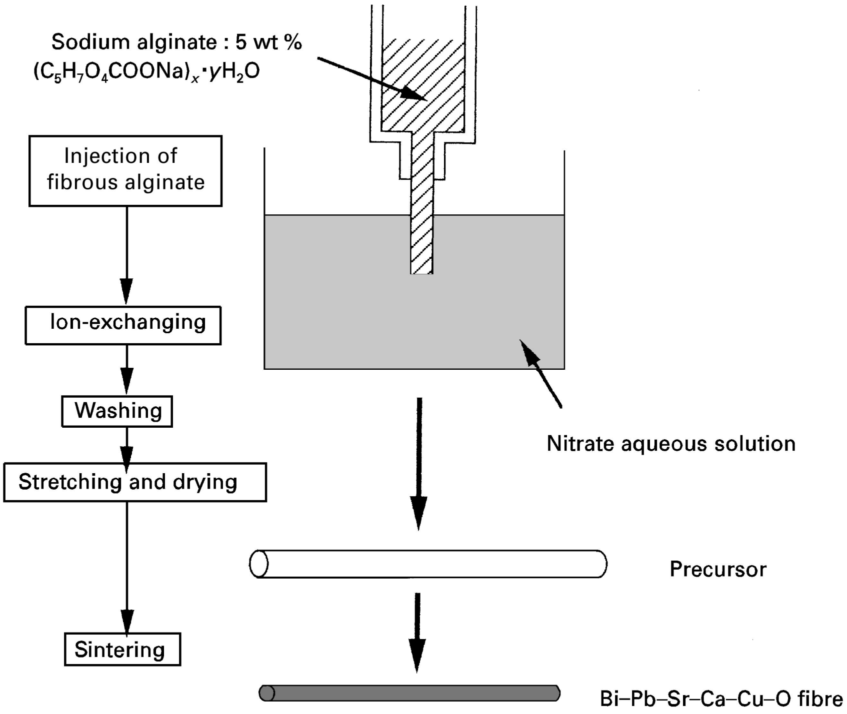

Figure 1 Experimental procedure for the preparation of Bi–Pb–Sr–Ca–Cu–O fibre.

about 3. This relatively high acidity is reasonable due to the slight solubility of bismuth in an acid solution. Then 5 wt % viscous aqueous solution of the sodium alginate was injected as a fibre into the nitrate solution from a nozzle (2 mm in diameter) and soaked in the solution for 1 h. Then Bi, Pb, Sr, Ca, Cu cations in the nitrate solution were incorporated into the sodium alginate, instead of excretion of sodium ions from this alginate. Then the alginate instantaneously became a gel. For a precise control of the cation ratio in this gel, i.e. to avoid additional accumulation of cations in the gel, the gel was rinsed using distillate water. Consequently, the fibrous precursor with more than 1.5 m in length and ~0.6 mm in diameter was easily synthesized by stretching and drying this wet gel, even using our small scale equipment. The maximum length of the precursor is only restricted by the capacity of the implements used such as the nozzle and beaker.

The alginate also has an individual selectivity in the ion exchange for accumulation of the various cations. This selectivity has been studied for individual Pb, Sr, Ca, Cu ions, but not for either the bismuth ion or a mixture of various cations. Furthermore, the cation ratio in the alginate gel is also affected by the ion-exchange time which is fixed at 1 h in our study. Preliminary experiments revealed that the content of bismuth ion in the alginate gel gradually increases with time in comparison with decreasing contents for the other metal ions used here. This tendency remained unchanged for at least 4 h.

Taking into account these quantitative properties of the alginate, we determined a composition for these multivalent cations in the nitrate solution based on the atomic absorbent spectrum analysis of the resultant precursor, so as to obtain the precursor with the nominal composition of high-T_c phase, i.e. (Bi,Pb):Sr:Ca:Cu = 2:2:2:3 which was exactly modified to be Bi:Pb:Sr:Ca:Cu = 1.84:0.34:1.91:2.03:3.06 for the starting composition [8]. Consequently we obtained Bi:Pb:Sr:Ca:Cu = 0.43:0.22:2.05:3.14:2.91 as the composition of the nitrate solution before the injection of the fibrous alginate.

After sintering the precursor in air at 810–860 °C, a Bi–Pb–Sr–Ca–Cu–O superconducting fibre with approximately 200 μm in diameter was obtained.

2.2. Thermal analysis for the precursor

In order to reveal the thermal reactions in the precursor in the heat-treatment, DTA and IR absorbent analysis were made. Fig. 2 shows differential thermal analysis (DTA) and thermal gravimetric (TG) data for the precursor at temperatures below 600 °C, using a RIGAKU thermoflex 8100. In this figure, exothermic and endothermic reactions accompanied by weight losses, defined as W_1, W_2 and W_3, were monitored for the three distinct temperature regions, defined as T_{w1}, T_{w2} and T_{w3}, respectively. From this figure, the following considerations are available. First, up to about 150 °C, an endothermic reaction with small weight loss (W_1) occurs, which results from evaporation of moisture from the precursor. In the upper temperature region (T_{w2}:150–380 °C) in which the loss (W_2) occurred, the structure of the alginate was decomposed and organic matter was evaporated as a gas. Lastly, at temperatures above 375 °C (T_{w3}:375–600 °C), the organic compound formed in the previous region (T_{w2}) was burned resulting in the loss W_3. These considerations were consistent with the IR absorbent spectra for the precursor as shown in Fig. 3 obtained for various temperatures up to 550 °C. In this figure, (a) represents the spectrum for

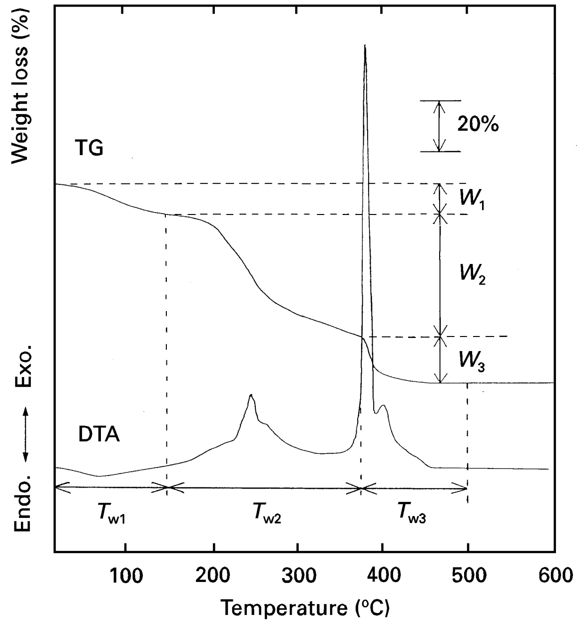

Figure 2 DTA–TG curves of precursor for temperatures below 600 °C.

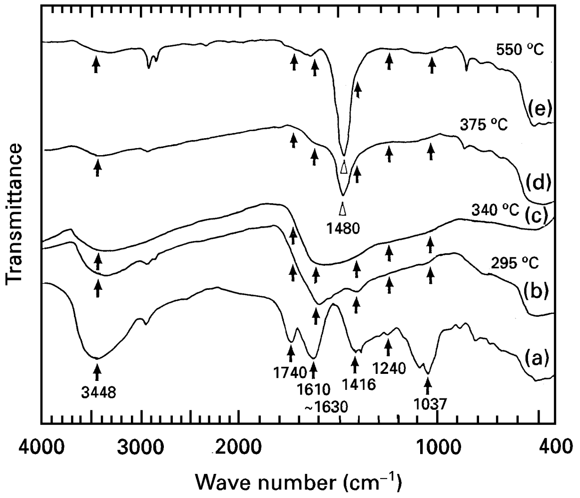

Figure 3 Typical IR spectra (4000–400 cm^{-1}) of the precursor heat treated at various temperatures.

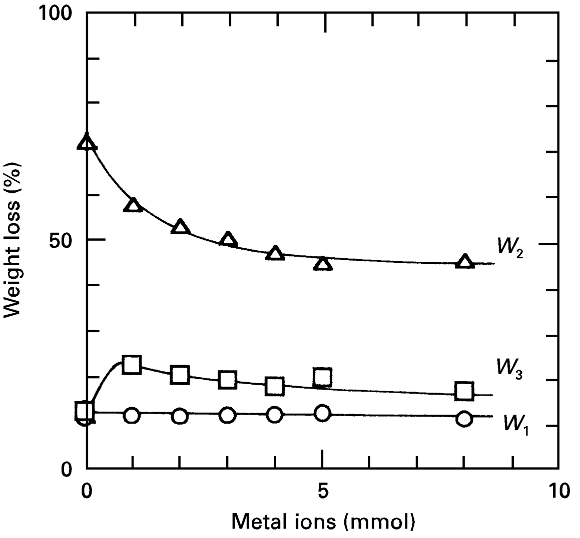

Figure 4 Dependence of the concentration of solution on the weight loss of the precursor. Composition of solution was 200 ml, Bi:Pb:Sr:Ca:Cu = 0.43:0.22:2.05:3.14:2.91 and sodium alginate was 1.5 g.

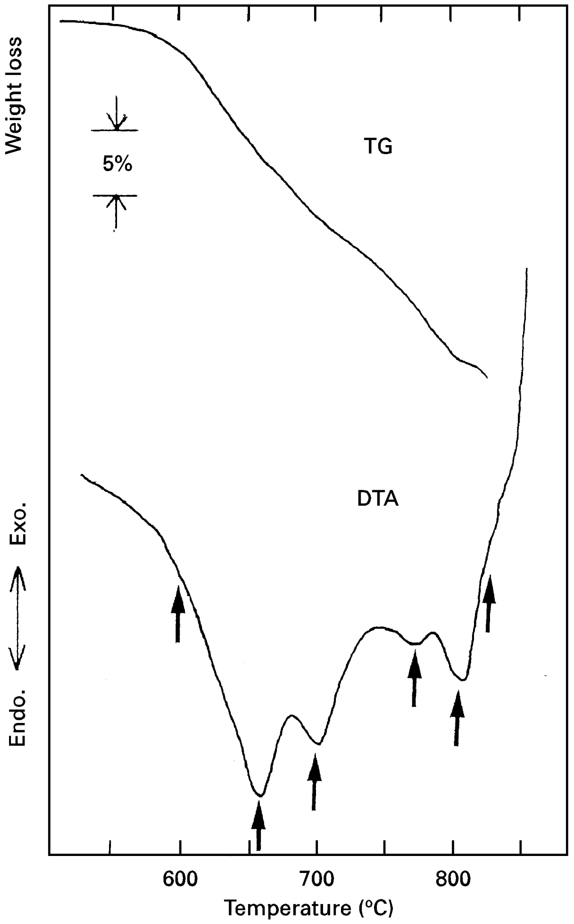

Figure 5 DTA–TG curves of precursor for temperatures above 500 °C.

the original precursor without heat treatment. The absorption of the IR at the wave number marked by solid arrows show the characteristic spectra for the alginate reported by Kuyucak and Volesky [9] and Iwasaki and Hayashi [10]. It is obvious that these spectra apparently disappear above 375 °C as shown in (b) and (c). This represents the decomposition of the molecular structure of the alginate. Above this temperature, the other IR-absorption appears at 1480 cm^{-1} as shown in (d) and (e). This absorption seems to result from the formation of carbonates such as $SrCO_3$ or $CaCO_3$ which is closely compatible with that of commercial powders.

As shown in Fig. 4, W_1, W_2 and W_3 are replotted against total content of the mixed cations (metal ions) in the nitrate solution. These results were obtained under fixed conditions, i.e. 1.5 g of sodium alginate, 200 ml of the nitrate solution and Bi:Pb:Sr:Ca:Cu = 0.43:0.22:2.05:3.14:2.91 as the atomic ratio in the nitrate solution. It is evident that there is a relatively strong dependence of W_2 on content compared with W_1 or W_3 below 4 mmol. Hence we considered that W_2 is closely related to the content of the cations in the precursor. As cation

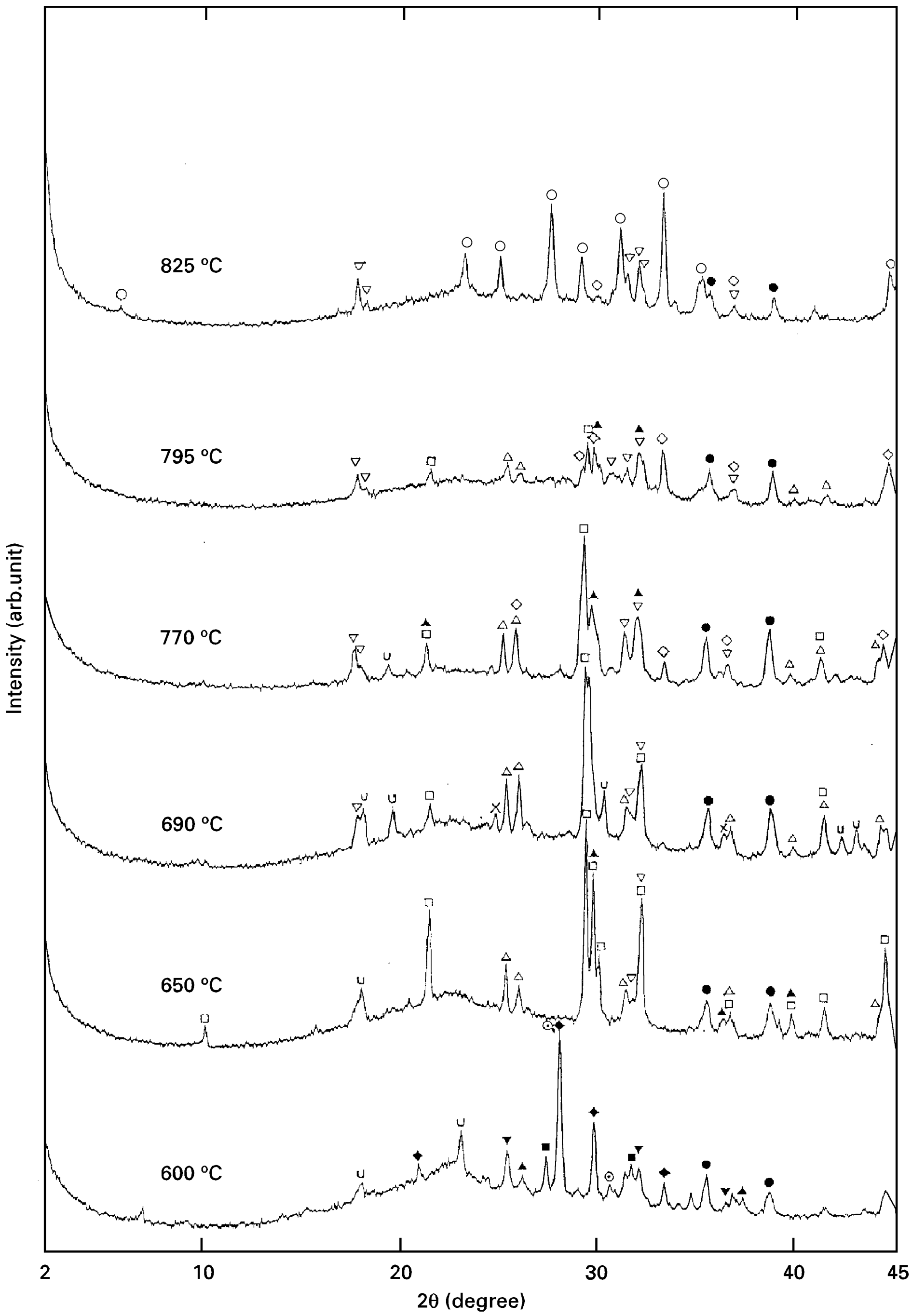

Figure 6 XRD patterns for precursors sintered for 1 h at various temperatures. Key: ○ $(Bi,Pb)_2Sr_2Ca_1Ca_2O_x$; ◇ $Bi_2Sr_2CuO_y$; ▽ Ca_2PbO_4; □ $Bi_{10}Ca_7O_{22}$; ● CuO; △ $SrCO_3$; ▲ $CaCO_3$; × Ca_2CuO_3; ⊙ Cu_4O_3; ◆ $CuBi_2O_4$; ▼ PbO_2; ■ Bi_2O_3; u unknown.

content increases, W_2 decreases gradually and approaches a constant value. This situation suggests a saturation of the accumulation of the cations in the alginate greater than 4 mmol which is comparable to $\sim 0.165\ \mathrm{mol}^{-1}$ in concentration. We adopted this value as the optimized concentration of the nitrate solution. However, if a solution with a much higher concentration is used, the gel of the alginic acid can not sink under the surface of the solution due to the relatively light specific gravity of the solution.

3. Solid-state reaction and formation of superconducting phase

Fig. 5 shows a DTA–TG trace for the precursor above 500 °C. It is suggested that several endothermic reactions, as marked by arrows, appear below the melting temperature. As an attempt to clarify the formation process of the superconducting phase via intermediate compounds, X-ray diffraction patterns for the specimens obtained at various temperatures, marked by arrows in Fig. 5, were studied as shown in Fig. 6. These specimens were prepared by the following process. Raising the temperature of the specimen up to one of those marked by an arrow, the specimen was prepared after sintering at the temperature for 1 h. From this analysis, it is revealed that $SrCO_3$ and $CaCO_3$ were present up to a temperature near 800 °C and a portion of CuO seemed to be present up to 825 °C. In the conventional solid-state reaction method, these carbonates seem to disappear at 800 °C. $Bi_2Sr_2CuO_x$, which is called the "2201 phase", was

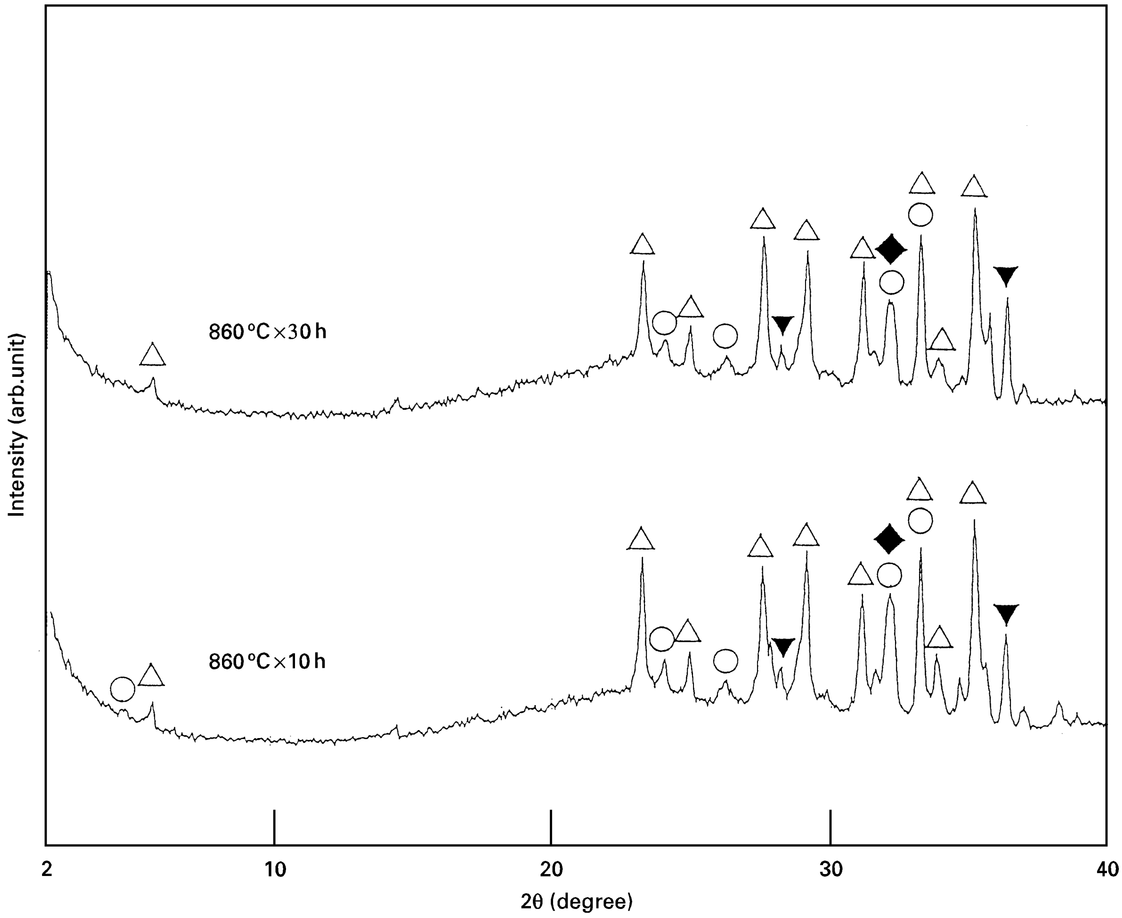

Figure 7 XRD patterns for precursors sintered at 860 °C for 10 h and 30 h, respectively. Key: ○ 2 2 2 3 phase; △ 2 2 1 2 phase; ▼ Ca_2CuO_3; ◇ (Sr, Ca)$_3Cu_5O_x$.

formed after a reaction near 770 °C. The consistent decrease in the weight loss in Fig. 5 can be explained by the decomposition of the carbonates. Since there is a remarkable change from the pattern for 795 °C to that for 825 °C, it can therefore be presumed that the low-T_c phase (2 2 1 2 phase) was formed via a reaction among the 2 2 0 1 phase, CuO and $CaCO_3$, as indicated by the following equation

$$Bi_2Sr_2CuO_6 + CaCO_3 + CuO \rightarrow Bi_2Sr_2CaCu_2O_8 + CO_2\uparrow$$

In the above equation, $CaCO_3$ should be replaced with Ca_2CuO for the reaction in the conventional method using powder material [11]. This difference may be due to the relatively high content of organic compound in our precursor. In fact, it is possible to say that this is a common feature in chemical techniques for the preparation of high-T_c superconducting fibre. This suggests that individual sintering conduction should be developed. The main product obtained at 825 °C is 2 2 1 2 phase and the residual impurities were Ca_2PbO_4, CuO and 2 2 0 1 phase.

Fig. 7 shows the XRD patterns for the specimens obtained at 860 °C for 10 and 30 h, respectively. The principal products formed in the specimen were 2 2 1 2 and 2 2 2 3 phases except for Ca_2CuO_3 and (Sr, Ca)$_3Cu_5O_x$. In addition, partial melting was observed in the bulk specimen. There have been many reports on enhancement of the volume fraction of 2 2 2 3 phase in the BPSCCO system. However, the reported conditions depend upon the individual synthesis process.

In spite of this situation, it has been shown that either a liquid phase associated with the formation of 2 2 2 3 phase is present or 2 2 1 2 phase converts to 2 2 2 3 phase. Chen *et al.* [11] proposed that the liquid phase results in a higher internal diffusion of Ca_2CuO_3 or CuO exceeds solid-state diffusion. Also the catalytic reaction of Ca_2PbO_4 helps to form and stabilize the structure of the 2 2 2 3 phase. If this can be applied to our study, it is expected that the quantity of Pb ion in the nitrate solution was not enough to enhance the catalytic reaction. Possibly this is due to the decomposition of Pb compounds or evaporation of Pb. This explanation can also be used to explain the poor growth of the superconducting phase for long sintering times as described later. Although our result is inconsistent with their consideration of the formation of Ca_2CuO_3, Ca_2PbO_4 and 2 2 1 2 phase at above 800 °C.

A d.c. four terminal measurement for the sample obtained by sintering at 860 °C for 30 h was made to trace the temperature dependence of the electrical resistance as shown in Fig. 8. Decreasing temperature, the resistance decreased rapidly at temperatures of 108 and 81 K (zero resistance), corresponding to the superconducting transition of 2 2 2 3 and 2 2 1 2 phases, respectively. In the case of sintering for 10 h at this temperature, the sample had a residual resistance

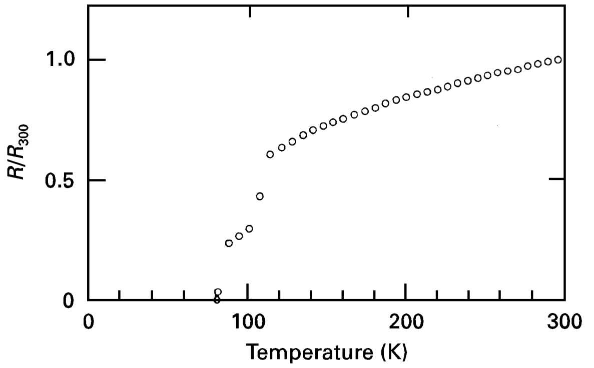

Figure 8 Temperature dependence on normalized resistance of the fibre obtained for sintering at 860 °C for 30 h.

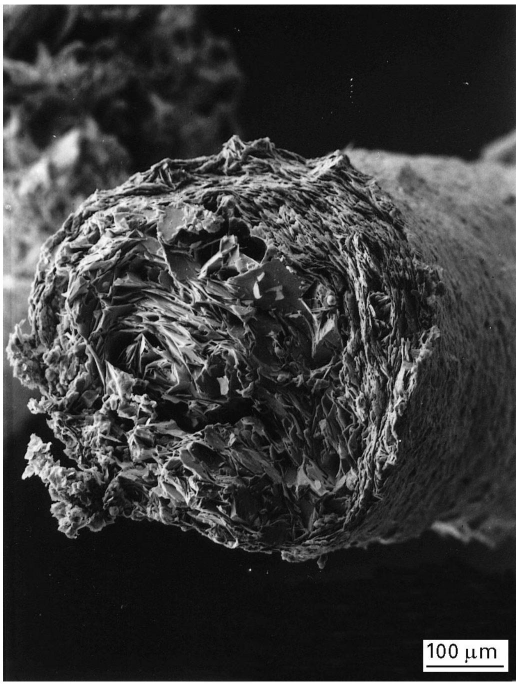

Figure 9 SEM cross-sectional view of a broken fibre.

at 77 K, though there is no significant difference in either the XRD pattern shown in Fig. 7 or SEM observations of the crystal growth between 30 and 10 h. This difference seemed to be related to the microstructure, especially, to the grain boundary.

Fig. 9 shows the cross-sectional view of the sintered fibre. In this figure, it is observed that the grains at outside surface of the fibre were oriented in the direction of length. At the centre of the fibre, the grains were oriented comparatively randomly. We consider that the orientation of the grains is obtained by the contraction in radius of the precursor during sintering. In fact, the radius of the specimen decreased to one third of the original precursor on sintering. On the other hand, it is well known that grains in the BPSCCO system easily grow on the *ab*-plane and become plate-like. Therefore it is concluded that the grain growth was affected by the contraction of the radius in the specimen. This effect is similar to that of the "rolling process" described by Ullrich *et al.* [12] who attained a high packing density by aligning all plate-like grains parallel to each other and perpendicular to the direction of the external forces. The orientation of the grain is preferable from the view point of a high-current conductor, because the critical current density of BPSCCO in the absence of an external magnetic field at 4.2 K is $\sim 10^5$ A cm^{-2} for a *c*-axis textured oriented sample in comparison with the poor current density of $\sim 10^4$ A cm^{-2} for a random-grained sample [13].

In this study the sintering time of 30 h seems to be preferable over sintering for a longer period. For example, sintering for more than 50 h resulted in poor growth of the superconducting phase. This may be due to the decomposition of the superconducting phase possibly caused by the evaporation of a small amount of Pb during the long sintering period [3]. One should note that this situation is the opposite of the remarkable improvement of the superconducting property in the bulk sample for long sintering time using the conventional solid-state reaction method [14]. We consider that this decomposition of the superconducting phase occurs easily due to the porous structure of our fibre.

For the preparation of a high-T_c superconducting wire, the Ag-sheathed fibre is preferred as a practical material. Preliminary experiments revealed that it can be carried out easily using our method. The Ag-sheathed BPSCCO fibre was synthesized successfully by sintering a precursor which was already coated with Ag paste on its surface. A preliminary experiment showed that the fibre obtained from sintering at 830 °C mostly consisted of 2 2 1 2 phase and the tensile strength of the fibre was quite improved. The details will be published elsewhere.

4. Conclusions

We synthesized a bismuth-based superconducting fibre by using sodium alginate on the basis of the ion-exchange property of the alginate. The solid-state reaction for sintering of the precursor was studied by X-ray diffraction analysis and DTA. Consequently, the formation of Ca_2CuO_3, Ca_2PbO_4 and 2 2 1 2 phase above 800 °C is inconsistent with the results for the conventional method using powder material. Also it is confirmed that partial melting is closely related to the growth 2 2 2 3 phase. The sintering conditions of 860 °C for 30 h seem to be preferable to sintering for longer periods. Detailed studies such as measurement of the critical current density of the specimen, especially for the Ag-sheathed fibre, are in progress.

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