JOURNAL OF MATERIALS SCIENCE 25 (1990) 3551–3556

Preparation of Bi, Pb–Sr–Ca–Cu–O superconductor by the sol–gel method

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The high -T_c superconducting phase in the Bi, Pb–Sr–Ca–Cu–O system has been prepared by the sol–gel method. The formation process of the low-T_c phase as well as the high-T_c phase has been examined by thermal analysis, infra-red measurements and X-ray diffraction, and compared with the conventional solid-state reaction. At a low heat-treatment temperature of 400° C, Bi_2O_3, $CaCO_3$ and CuO are precipitated from the gel. These oxides react with each other to form several double oxides above 600° C and yield the low-T_c phase as a main product at 800° C. The heat treatment at higher temperatures effectively leads to the formation of the high-T_c phase. In particular, the high-T_c phase is most predominantly formed in the specimen heat treated at 845° C for 48 h after calcination at 800° C for 12 h, which is reflected in the critical temperature of 104 K. The temperature at which the low-T_c phase is formed is lower in the sol–gel-derived sample than in the specimen prepared by the solid-state reaction. Furthermore, the sol–gel method brought about a larger amount of the high-T_c phase than the solid-state reaction when the conditions for the heat treatment were identical. These facts clearly indicate the superiority of the sol–gel method for the formation of both high-T_c and low-T_c Bi, Pb–Sr–Ca–Cu–O superconducting phases.

1. Introduction

The copper-containing oxide superconductors with high critical temperature, first found by Bednorz and Müller [1], still attract attention from both fundamental and practical viewpoints. The recent discovery of the superconducting oxide phase with T_c over 100 K in the system Bi–Sr–Ca–Cu–O has led to subsequent vigorous studies on this system. Since the composition $BiSrCaCu_2O_y$, originally reported by Maeda *et al.* [2], includes two superconducting phases with high and low T_c, respectively, much attention has been paid to preparation of the pure high-T_c phase. Although the nominal composition of the high-T_c phase has been proposed to be $Bi_2Sr_2Ca_2Cu_3O_y$ [3], a single phase of this compound is difficult to prepare from the corresponding mixture of raw materials. Recently, Takano *et al.* [4] have found that the substitution of lead for bismuth effectively stabilizes the high-T_c phase. Endo *et al.* [5] have shown that the solid-state reaction of raw materials under low oxygen pressure, such as 1/13 atm, is effective for the formation of the pure high-T_c phase. They have also indicated the compositional range where no crystalline phases other than the high-T_c phase were observed [6].

As for the method of preparation, it is considered that the sol–gel method is superior to the conventional solid-state reaction method, because in the former it is possible to mix starting materials at molecular level and the resultant product is expected to be homogeneous [7]. In fact, the sol–gel method has been effectively applied to synthesize many functional ceramic materials so far. For example, fine particles prepared by this method give more homogeneous and denser sintered bodies at lower elevated temperatures than conventional ones [8–10]. Also, by utilizing this method ceramic fibres [11–14] and thin films [15–19] can be produced from sol-derived precursor gels with such shapes. Recently, $YBa_2Cu_3O_{7-\delta}$ superconductors in fibrous and thin-film forms have been prepared by the sol–gel method [20, 21].

In the present work, an attempt was made to prepare the high-T_c phase in the Bi, Pb–Sr–Ca–Cu–O system by the sol–gel method. The formation process of both low-T_c and high-T_c phases from gel was examined and compared with that through the conventional solid-state reaction. The effects of heat treatment temperature and duration on the formation of the high-T_c phase were also discussed briefly.

2. Experimental procedure

2.1. Preparation of gel

The gel preparation was performed by following the flow chart shown in Fig. 1. $Bi(NO_3)_3 \cdot 5H_2O$, $Sr(NO_3)_2 \cdot 0.5H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$, $Cu(CH_3COO)_2 \cdot H_2O$ and $Pb(CH_3COO)_2 \cdot 3H_2O$ were used as starting reagents. These reagents were weighed so that the molar ratio of lead, bismuth, strontium, calcium and copper was equal to 0.17 : 0.92 : 0.96 : 1.0 : 1.5, a composition inside the region which yields almost only the high-T_c phase as indicated by Koyama *et al.* [6]. First, 2.23 g of $Bi(NO_3)_3 \cdot 5H_2O$ was dissolved in 30 ml acetic acid (99.5%), and then 30 ml of

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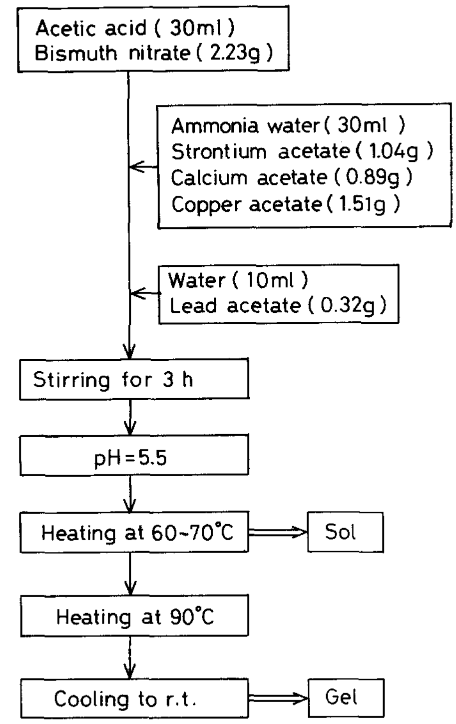

Figure 1 Flow chart for the preparation of gel in the Pb, Bi–Sr–Ca–Cu–O system.

ammonia water (28%) dissolving $Sr(NO_3)_2 \cdot 0.5H_2O$, $Ca(CH_3COO)_2 \cdot H_2O$ and $Cu(CH_3COO)_2 \cdot H_2O$ was added to this solution. Further, 0.32 g of $Pb(CH_3COO)_2 \cdot 3H_2O$ dissolved in 10 ml of water was added, and the resultant solution stirred for 3 h. Ammonia water was then added to the solution to adjust the pH value to 5.5. The pH value was critical, because precipitation occurred in the solution if pH was either lower or higher than 5.5. The sol became viscous during heating at 60 to 70° C. By heating at 90° C and cooling to room temperature, the sol was set to a transparent wet gel.

2.2. Thermal analysis and heat treatment of gels

The gel thus obtained was subjected to thermogravimetric and differential thermal analyses (TG-DTA) with a heating rate of 10° C min^{-1} up to 800° C in air. The heat treatment of the gel was carried out as follows. On the basis of the results of TG-DTA and IR measurements, as described below, the gel was first heat treated at 250° C for 5 h in air to eliminate water, ammonia and nitrate groups. Then the resultant sample, which was brittle and several millimetres in size, was heat treated at several temperatures from 250 to 800° C for 5 h in air.

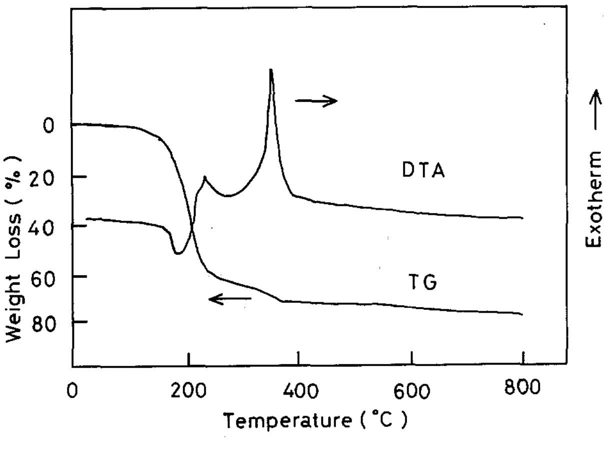

Figure 2 TG and DTA curves of the gel.

Since the heat treatment at 800° C was incomplete for formation of the high-T_c phase as indicated by X-ray diffraction analysis, as shown below, further heat treatment at higher temperatures was carried out. After the sample obtained by heating the gel at 250° C was calcined at 800° C for 12 h in air, the resultant specimen was pulverized and pressed into a pellet 1 cm in diameter and 1 mm thick, and reheated at 830 to 855° C for 12 to 72 h in air.

2.3. The solid-state reaction

Commercially available reagent-grade Bi_2O_3, Pb_3O_4, $SrCO_3$, $CaCO_3$ and CuO were used as raw materials. They were weighed in the same composition as the sol–gel-derived specimen so that the total weight was 3 g, and mixed thoroughly in a porcelain mortar for 10 min. The mixture was put on a platinum plate and heat treated at 300 to 800° C for 5 h in air. Furthermore, the mixture of the raw materials was calcined at 800° C for 12 h in air, cast into a pellet, and heat treated at 830 to 855° C for 12 h in air in order to compare the formation process of the high-T_c phase with that in the sol–gel method.

2.4. Measurements

The gel and the mixture of oxides heat treated using the above heating schedule were subjected to X-ray diffraction analysis and IR measurements. The nickel-filtered CuK_α radiation was used as an X-ray source. The IR measurements were performed by the KBr pellet method in the wave-number range of 400 to 4000 cm^{-1}. Some specimens containing the high-T_c phase were subjected to resistivity measurements. The measurements were carried out at 300 to 50 K using a four-probe method with an electric current of 5 mA.

3. Results

3.1. Formation of high- and low-T_c phases from gel

TG-DTA curves of the gel are shown in Fig. 2. One endothermic peak and two exothermic peaks appear at about 160, 230 and 350° C, respectively, in the DTA curve. The last peak in particular is very intense. A drastic drop in weight is seen around 200° C and a slight weight loss is observed at 230 to 370° C in the TG curve. No evident changes are observable above 400° C in both TG and DTA curves.

IR spectra of the gel and the heat-treated specimens are shown in Fig. 3. For the gel, absorption peaks attributed to H_2O (3430 and 1620 cm^{-1}), NH_4^+ (3170 cm^{-1}), NO_3^- (1385 cm^{-1}) and CH_3COO^- (1560, 1410, 1050, 1020, 660 and 615 cm^{-1}) are clearly observed. For the assignment of these peaks see Nakamoto [22] and Kozuka *et al.* [23]. The spectrum of the specimen heat treated at 250° C is similar to that of the gel, but does not include a peak due to NH_4^+. Also, the peaks due to H_2O and NO_3^- become weak and an additional peak appears at 880 cm^{-1}, which is

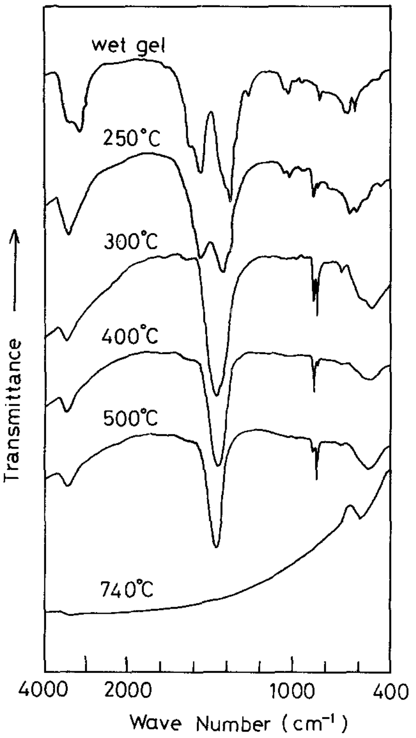

Figure 3 IR spectra of the gel and the heat-treated specimens. Temperature indicated above the spectrum denotes the heat-treatment temperature.

ascribed to out-of-plane bending vibration of CO_3^{2-} [22]. The intensity of the peaks due to CH_3COO^- still remains unchanged. At 300° C, the peaks ascribed to CH_3COO^- as well as NO_3^- disappear. Instead, a new absorption peak due to stretching vibration of the C–O bond in CO_3^{2-} appears at 1460 cm^{-1} [22] accompanied by an increase in intensity of the peaks at 860 and 880 cm^{-1}. Further, a new peak is observable around 530 cm^{-1}, which is ascribed to the metal–oxygen–metal bond [23]. The IR spectra of the specimens heat treated at 400 and 500° C are not so different from that of the specimen heat treated at 300° C. All of the peaks due to CO_3^{2-} disappear at 740° C. Moreover, the peak at 3430 cm^{-1} due to H_2O almost disappears at this temperature.

and the specimens heat treated at several temperatures. The gel is found to be X-ray amorphous. Heat treatment of the gel at 250° C gives rise to precipitation of an unidentified compound. At 400° C, $CaCO_3$ is precipitated in accordance with the results of the IR measurements. Moreover, diffraction peaks attributed to Bi_2O_3 and CuO are observed. Namely, the starting reagents of bismuth, calcium and copper do not react with each other and/or the starting reagents of lead and strontium, but are converted to their stable oxide forms at this temperature. Some double oxides such as $(Sr, Ca)_3Cu_5O_x$, Ca_2PbO_4 and $CuBi_2O_4$, along with $SrCO_3$, precipitate at 600° C, and a significant amount of the low-T_c phase appears at 740° C. The specimen heat treated at 800° C consists of the low-T_c phase with a small amount of Ca_2PbO_4.

The X-ray diffraction patterns of the specimens heat treated at 830 to 855° C for 12 h are shown in Fig. 5. All of the diffraction peaks observed for each specimen are attributed to either the low-T_c or the high-T_c phase. A close look at this figure reveals that the ratio of the amount of the high-T_c phase to that of the low-T_c phase is larger in the specimens heat treated at 845 or 850° C than those heat treated at other temperatures. Thus heat treatment at around 845° C for periods longer than 12 h was carried out to promote the conversion of the low-T_c to the high-T_c phase. The results of X-ray diffraction analysis on the specimens thus obtained are shown in Fig. 6. It is found that the high-T_c phase preferentially grows at the expense of low-T_c phase in all of the specimens.

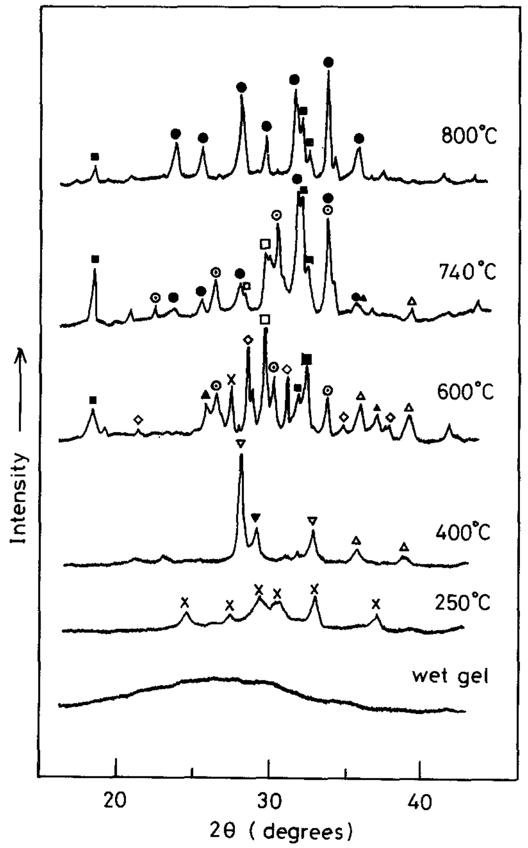

Figure 4 X-ray diffraction patterns of the gel and the heat-treated specimens obtained by the sol–gel method. ●, Low-T_c phase ($Bi_2(Sr, Ca)_3Cu_2O_x$); ⊙, Bi-Sr-Ca-Cu-O with c-dimension of ~24 Å; □, $(Sr, Ca)_3Cu_5O_x$; ■, Ca_2PbO_4; △, CuO; ▲, $SrCO_3$; ▽, Bi_2O_3; ▼, $CaCO_3$; ◇, $CuBi_2O_4$; x, unknown.

The resistivity of these specimens as a function of temperature is shown in Fig. 7. The superconducting transition around 100 K is evidently seen for all the specimens. The T_c values of the specimens evaluated from this figure are summarized in Table I. These values are somewhat lower than those reported by Takano *et al.* [4] and Koyama *et al.* [6], but are all over 100 K. Table I also indicates that the result obtained in the heat treatment for 72 h is rather inferior to that for 48 h from the standpoint of increasing the critical temperature.

TABLE I The critical temperature (T_c) of the specimens obtained by the sol–gel method

Conditions for heat treatment		
Temperature (° C)	Time (h)	T_c (K)
845	48	104
845	72	103
848	48	101

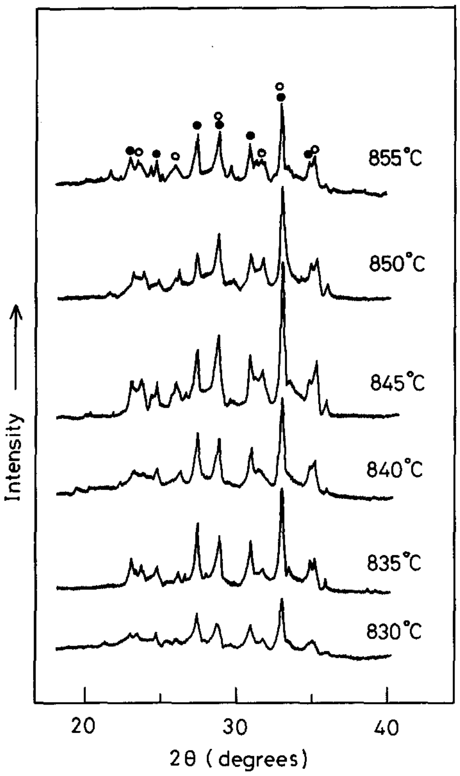

Figure 5 X-ray diffraction patterns of the sol–gel-derived specimens heat treated above 830° C for 12 h after calcination at 800° C for 12 h. Open and closed circles denote high-T_c and low-T_c phases, respectively.

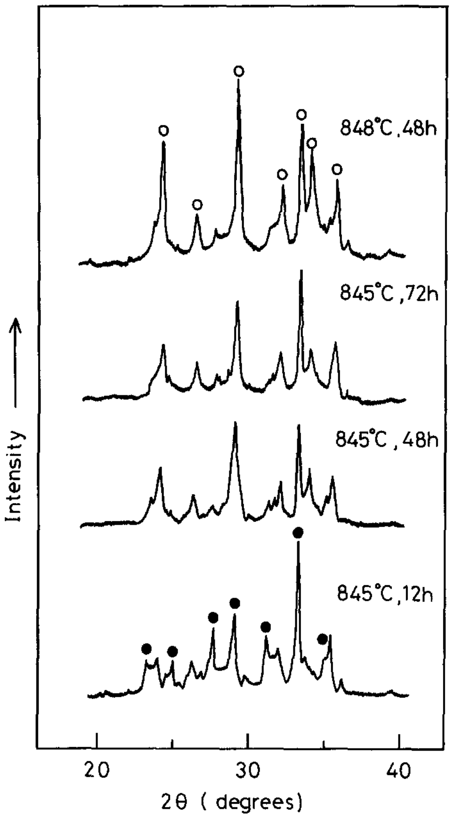

Figure 6 X-ray diffraction patterns of the sol–gel-derived specimens heat treated around 845° C for several periods. The meaning of the symbols is identical with that in Fig. 5.

3.2. Formation of high- and low-T_c phases through the solid-state reaction

Results of the X-ray diffraction analysis on the specimens prepared by the solid-state reaction are shown in Fig. 8. The diffraction pattern shown in the bottom of the figure is for the mixture of starting oxides. The same diffraction pattern as this was observed for specimens heat treated up to 400° C. This means that the solid-state reaction of the starting oxides cannot happen without heat treatment above 400° C. At 600° C, the solid-state reaction proceeds and several oxides which are observed in the gel-derived specimens are formed. The low-T_c phase does not form even though the heat-treatment temperature is raised up to 750° C. In the specimen heat treated at 800° C, the Bi–Sr–Ca–Cu–O phase with a c-dimension of ~24 A, the proposed composition of which is $Bi_2(Ca, Sr)_{2-x}CuO_{6-y}$ [24], is predominantly formed, accompanying a small amount of the low-T_c phase. Fig. 9 shows X-ray diffraction patterns of the specimens heat treated at 830 to 855° C for 12 h. The high-T_c phase as well as the low-T_c phase is observed in all of the specimens except for one heat treated at 830° C. However, the ratio of the amount of high-T_c phase to that of low-T_c phase is small compared to the specimens prepared from the gel.

4. Discussion

Preparation of the gel from metal acetates has been reported by several authors. Mosset *et al.* [25] prepared gel for $BaTiO_3$ by using $Ti(OC_2H_5)_4$ and $Ba(CH_3COO)_2$ as raw materials, and examined its structure by the large-angle X-ray scattering method. They concluded that the gel consists of $Ba_4(CH_3COO)_8$ and a titanium hexanuclear molecule, that is $Ti_6(\mu_3\text{-}O)_2(\mu_2\text{-}O)_2(\mu_2\text{-}OC_2H_5)_2(\mu\text{-}CH_3COO)_8(OC_2H_5)_6$, being

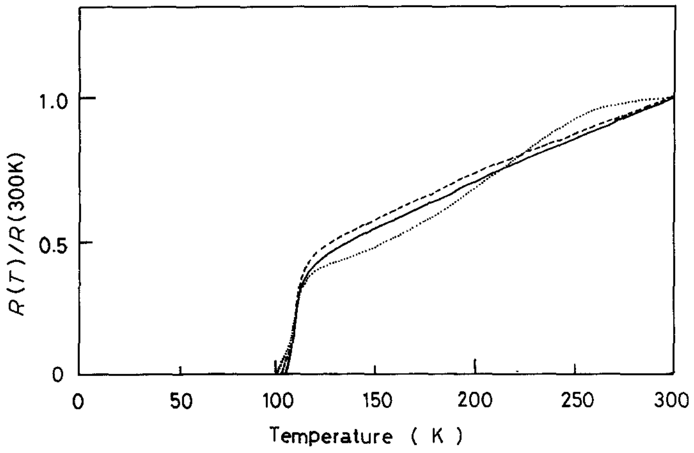

Figure 7 Temperature dependence of resistivity normalized by the value at 300 K. Three curves correspond to the specimens heat treated at different temperatures and times: 845° C, 48 h (solid curve); 845° C, 72 h (broken curve); 848° C, 48 h (dotted curve).

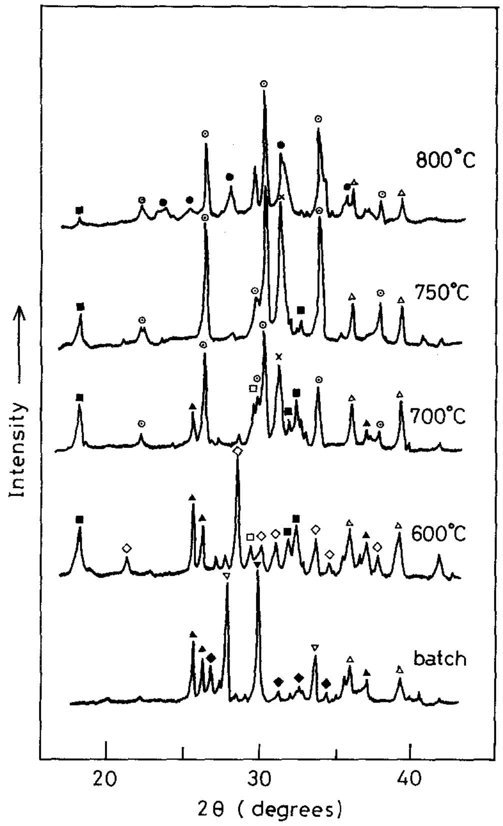

Figure 8 X-ray diffraction patterns of the heat-treated specimens obtained by the solid-state reaction of oxide powders. The meaning of the symbols is identical with that in Fig. 4 except for ◆, Pb_3O_4.

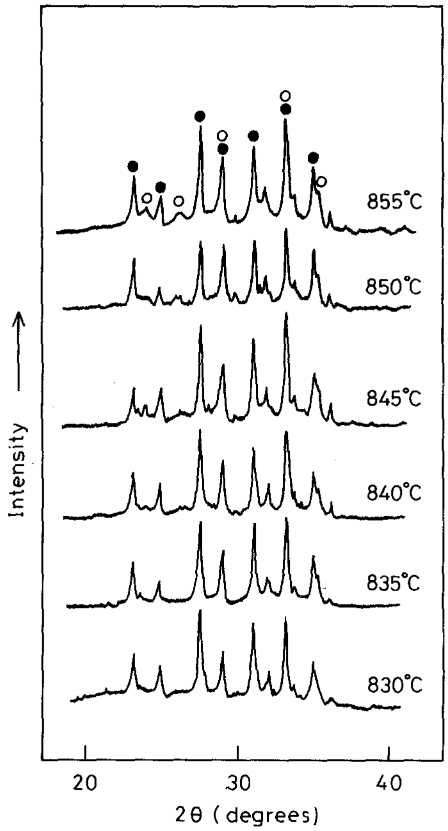

Figure 9 X-ray diffraction patterns of the specimens obtained by the solid-state reaction and heat treated above 830° C for 12 h. The meaning of the symbols is identical with that in Fig. 5.

connected with each other through acetate bridges. Kozuka *et al.* [23] prepared the gel precursor for the $YBa_2Cu_3O_{7-\delta}$ superconductor from yttrium, barium and copper acetates. They revealed, on the basis of IR measurements, that the gel contains some complex-like species weakly bonded with each other, instead of strong metal–oxygen–metal bond. The gel prepared in the present study may have a similar structure: it is thought that each metal cation is surrounded by any ligands such as CH_3COO^- to form a complex, and probably connected with each other through the acetate groups. The chemical bonds between metal ions via oxygen ions are not formed, as revealed by the absence of peaks below 600 cm^{-1} in the IR spectrum of the gel [23].

On the basis of the results of IR measurements and X-ray diffraction analysis, along with the TG-DTA curves of the gel, the formation process of the low- and high-T_c phases from the gel is summarized as follows. At 160 to 200° C, H_2O and NH_3 involved in the gel are lost, which causes the endothermic peak around these temperatures in the DTA curve. Considering that the relatively weak endothermic peak appears in spite of the considerable weight loss observed in the TG curve, it is found that the water molecule lost in this temperature region is physically adsorbed in the gel. The acetate groups decompose at around 300° C, leading to the intense exothermic peak in the DTA curve. Simultaneously, $CaCO_3$ and $SrCO_3$ are formed. The same phenomenon was observed by Kozuka *et al.* [23]. They found that decomposition of acetate ions in the $YBa_2Cu_3O_{7-\delta}$ gel accompanies the formation of $BaCO_3$, and suggested that carbonate ions are supplied by oxidation of acetate ions. This idea may also apply to the present case. The solid-state reaction between carbonates thus formed and other oxides precipitated in the gel at about 400° C begins above 600° C. The decarbonation is completely accomplished at 740° C, and finally the low-T_c phase is formed as a main product at 800° C. The low-T_c phase is converted to the high-T_c phase when the temperature is raised to around 845° C.

A comparison of Figs 4 and 8 reveals that the sol–gel method requires a lower temperature for the formation of the low-T_c phase than the conventional solid-state reaction method. Also, it is found from Figs 5 and 9 that the amount of the high-T_c phase is larger in the sol–gel-derived specimen than in the specimen prepared through the solid-state reaction. These facts imply that the formation of superconductor consisting predominantly of a high-T_c phase with a critical temperature of 104 K is realized by heat treatment for a relatively short period even in air, without any limited atmosphere such as low oxygen pressure, if gel is used. Thus the sol–gel method is superior to the conventional solid-state reaction method for the preparation of both high-T_c and low-T_c phases. This may be ascribed to the fact that crystalline particles precipitated in the gel are small and homogeneously mixed with each other, leading to a decrease of the temperature at which the low-T_c phase is formed and an increase of the amount of high-T_c phase under the relatively mild heat-treatment conditions.

5. Conclusions

A superconductor consisting of the high-T_c phase in the Bi, Pb–Sr–Ca–Cu–O system was successfully prepared by the sol–gel method. As for the formation process from the gel, oxides and carbonates of the constituent metal cations were precipitated at low heat-treatment temperature, and reacted with each other to form the low-T_c phase at 800° C. Further, heat treatment at 830 to 855° C in air effectively led to the high-T_c phase. In particular, the specimen heat treated at 845° C for 48 h contained a large amount of high-T_c phase and exhibited zero resistivity at 104 K.

From the comparison of the formation process in the sol–gel method with that in the conventional solid-state reaction method, it was found that the temperature for the formation of low-T_c phase via the former is lower than that through the latter. Furthermore, the amount of the high-T_c phase formed through the sol–gel method was larger than that prepared by the solid-state reaction when the same heat treatment was applied. These effects may be attributed to the fact that the sol–gel method gives homogeneous and small oxide or carbonate particles, which are reactive and intimately mixed.

6. Acknowledgements

The present authors would like to thank Professor O. Yamamoto and Dr Y. Takeda of the Chemistry Department of Resources, Mie University, for the electrical measurements. This work was financially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science and Culture (63550579).

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Received 13 March
and accepted 30 August 1989