

# Polymer–metal chelate precursor reduced its firing temperature and time for preparing yttrium barium cuprate powder

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Bulk  $\text{YBa}_2\text{Cu}_3\text{O}_x$  was prepared by a polymer chelate precursor method using poly[(*N,N*-dicarboxymethyl)allylamine] as a chelating polymer of which molecular weights were  $3 \times 10^4$  (PDAA-L) and  $3 \times 10^5$  (PDAA-H), respectively. X-ray diffraction (XRD) analysis of the precursor from PDAA-H shows that  $\text{YBa}_2\text{Cu}_3\text{O}_x$  (Y123) phase appeared after being calcined at 750 °C for 5 h and the mixture was completely converted to tetragonal Y123 phase after being calcined at 800 °C for 5 h. The phase evolution of the precursor from PDAA-H during isothermal experiment at 800 °C showed that pure tetragonal Y123 was produced even after the polymer chelate precursor was heated for 2 h in air, although a very small amount of  $\text{BaCO}_3$  was recognized. This  $\text{BaCO}_3$  phase was hardly recognized after 4 h calcination. The precursor prepared from PDAA-L was fully converted to pure tetragonal Y123 after 3 h calcining at 800 °C. On the other hand, the sample prepared from metal nitrate solution without PDAA was not fully transferred to Y123 phase after heating at 800 °C for 10 h. Large amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$  and CuO were observed. These results indicated that the greater homogeneity in the polymer chelate precursor leads to reduced firing times and temperature compared with the metal nitrate precursor.

## 1. Introduction

After the discovery of high temperature superconducting oxides many attempts have been made to develop an efficient technique for preparing homogeneous superconducting products. Traditional solid synthesis of bulk superconducting ceramics needs high-temperature processing; repeated calcination, grinding, and sintering for many hours are required. High processing temperature promotes grain growth and often produces non-uniform large sintered particles. To suppress the grain growth and to limit the particle size, a low-temperature processing is an alternative to the traditional high-temperature processing, and can achieve sufficient superconducting properties. One major obstacle to processing at lower temperatures, however, is the decomposition of barium carbonate in air for preparing  $\text{YBa}_2\text{Cu}_3\text{O}_x$ . It has been reported that a complete elimination of carbonate during calcination cannot be achieved under 800 °C, even for fine particle precursors [1]. Another observation showed that a high percentage of the  $\text{BaCO}_3$  can be decomposed at 780 °C, if calcined for a long enough time in air (60 h) [2]. To achieve an efficient low-temperature and short-time processing, precursors of great homogeneity would be required.

Macromolecules containing inorganic elements are of considerable interest as precursors to ceramics [3, 4]. It has been shown that the direct transformation of polymeric shapes into silicon-based ceramic

parts comprised of silicon carbide without the addition of sintering aids, can be performed at an unusually low temperature. On the contrary, the use of polymers as precursors to transition metal-containing solid state materials, which are known to possess a wide range of interesting electrical, magnetic and optical properties, is virtually unexplored [5]. Previously we introduced a novel concept of polymer–metal chelate precursor technique that utilizes organic polymers possessing strong chelating ligands for metal ions [6, 7]. Poly[(*N,N*-dicarboxymethyl)allylamine] of molecular weight  $3 \times 10^4$  (PDAA-L) was synthesized and used as a chelating polymer for Y, Ba and Cu. The polymer–metal chelate precursor was calcined at 880 °C for 10 h and sintered at 920 °C for 10 h to develop the pure superconductor Y123 phase. The sintered sample showed superconductivities of  $T_c$  (onset) at 92 K and  $T_c$  (end) at 88 K and critical current density ( $J_c$ ) of  $165.9 \text{ A cm}^{-2}$ .

In this paper, we show that polymer chelate precursors prepared from poly[(*N,N*-dicarboxymethyl)allylamine] of molecular weights  $3 \times 10^5$  (PDAA-H) and  $3 \times 10^5$  (PDAA-H), respectively, reduced its firing temperature and time to produce highly pure tetragonal Y123 phase compared with a sample prepared from metal nitrate solution without PDAA. Although barium carbonate was formed during calcination of the polymer–metal chelate precursor from PDAA-H, barium carbonate can start to decompose at 750 °C

and fully decomposed to tetragonal Y123 at 800 °C within 4 h.

## 2. Experimental procedure

Unless stated otherwise, all reagents and chemicals were obtained from Wako Pure Chemical Co. and used without further purification. Poly(allylamine) (PAA) of average molecular weight  $1 \times 10^4$  (PAA-L) and  $1 \times 10^5$  (PAA-H) were obtained from Nittobo Co. Poly[(*N,N*-dicarboxymethyl)allylamine] (PDAA) was prepared from PAA according to a previous report [10]. Powder X-ray diffraction (XRD) was performed with a Rigaku No. 2013 using Ni-filtered  $\text{CuK}\alpha$  X-ray beam excited at 30 kV and 15 mA. Thermolysis of polymer chelate was performed with Shimadzu TGA-30 to obtain a thermogravimetric analysis (TG) curve at a heating rate of  $5^\circ\text{C min}^{-1}$ .

### 2.1. Preparation of polymer chelate precursor

The mixture consisted of 25 ml of  $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (0.1 M), 50 ml of  $\text{Ba}(\text{NO}_3)_2$  (0.1 M), and 75 ml of  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  (0.1 M) was added to 300 ml of the polymer solution (0.03 mol by repeating unit) with the addition of 25%  $\text{NH}_3$  solution to maintain the solution's pH at 8 to give the metal chelate in the same molar ratio. Then the solution was concentrated to 300 ml, and was poured into 3 l of ethanol to precipitate the polymer-metal chelate. The resulting solid was collected, washed with 50 ml of ethanol, and dried at 110 °C for 12 h in air. The metal nitrate precursor was prepared by removal of water from the solution containing each metal nitrate (the cation mole ratio of Y:Ba:Cu = 1:2:3).

### 2.2. Bulk YBCO preparation

The precursor was ground to a powder, and placed in a high purity alumina boat, heated from room temperature to 800 °C at a heating rate of  $3^\circ\text{C min}^{-1}$ , calcined for the desired times, and cooled to room temperature at a rate of  $3^\circ\text{C min}^{-1}$ . The calcined powder was milled and pressed at  $500 \text{ kg cm}^{-2}$  into pellet form (10 mm diameter, and 1 mm thick). The pellet was sintered at 920 °C for 10 h in air, and annealed at 600 °C for 5 h under flowing oxygen ( $0.3 \text{ l min}^{-1}$ ).

## 3. Results and discussion

### 3.1. Polymer chelate precursor synthesis

The poly[(*N,N*-dicarboxymethyl)allylamine]s of molecular weights  $3 \times 10^4$  (PDAA-L) and  $3 \times 10^5$  (PDAA-H) were dissolved in deionized water, and the 0.4 equivalent molar amount of metal nitrates having the cation mole ratio of Y:Ba:Cu = 1:2:3 were added to form a homogeneous dark blue solution with the pH adjusted to 8 by  $\text{NH}_4\text{OH}$ . Then the solution was concentrated, and poured into ethanol to precipitate the polymer-metal chelate precursor. If the metal ions existed in the filtrate, the deviation of metal

compositions could occur. Removal of the solvent from the filtrate under reduced pressure caused a white residue in which the polymer was not found by  $^1\text{H}$ -nuclear magnetic resonance (NMR). More than 98% of the amount of the residue was lost after heating at 880 °C for 10 h, which indicated that the metal ions were rarely found in the filtrate. These results suggested that the polymer chelate having the cation mole ratio of Y:Ba:Cu = 1:2:3 was obtained without any deviation of the metal compositions. The chelate formations of each metal in the polymer chelate precursors were confirmed by C=O stretching bonds. It is clear that the absorption band for the C=O in  $>\text{HN}^+ - \text{CH}_2\text{COO}^-$  group shifted to lower frequencies, i.e.  $1610\text{--}1620 \text{ cm}^{-1}$ , compared with that of metal-free polymer isolated from the pH 8.0 solution [7]. The X-ray diffraction pattern of the polymer-metal precursor has no crystal structure peak, which means that no metal nitrates remained unreacted in the polymer-metal precursor.

### 3.2. Thermal decomposition of polymer chelate precursor

The TG curve for pure polymer of PDAA-L is shown in Fig. 1a. More than 97% of the polymer was decomposed over 500 °C and completely decomposed over 850 °C. The thermolysis results of the polymer-metal chelate precursor prepared from PDAA-L took place between 200 and 500 °C and the plateau observed above 750 °C. Weight loss at 930 °C indicated a decomposition of the resulting ceramics sample. To consider the thermolysis behaviour of polymer-metal chelate precursor, each polymer chelate (Y-PDAA, Ba-PDAA, and Cu-PDAA) was prepared from the homogeneous solution having 0.5 equivalent molar amount of each metal nitrate and their thermal decomposition were examined (Fig. 1b). The thermolysis results of Ba-PDAA and Cu-PDAA took place between 200 and 400 °C and the plateau observed above 400 °C. The TG curve for Y-PDAA shows the main weight loss appeared at 400 °C and complete decomposition at 580 °C. The final weight remained for Ba-PDAA, Cu-PDAA, and Y-PDAA were 45, 26 and 25%, respectively. These values agree fairly well with the theoretical values when Ba-PDAA, Cu-PDAA, and Y-PDAA are converted to  $\text{BaCO}_3$ , CuO, and  $\text{Y}_2\text{O}_3$  in air, respectively; the residue calculated for  $\text{BaCO}_3$  is 41%, for CuO 19%, and for  $\text{Y}_2\text{O}_3$  26%.

### 3.3. Phase evolution during Y123 formation

The precursor from PDAA-H was ground to a powder, placed in a high purity alumina boat, heated from room temperature to desired temperature at a heating rate of  $3^\circ\text{C min}^{-1}$  and kept for 5 h at this temperature. XRD analysis shows that the sample was almost amorphous up to 300 °C (Fig. 2). At this temperature weak reflections at  $43.48^\circ$  and  $50.52^\circ$  indicated the presence of metallic copper. The large amount of the precursor transformed to crystalline  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and CuO at 350 °C. Crystalline  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and CuO were not decomposed up to 700 °C. A Y123

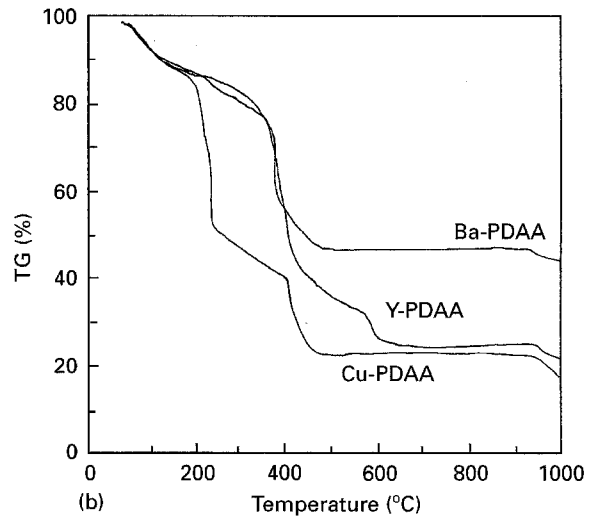
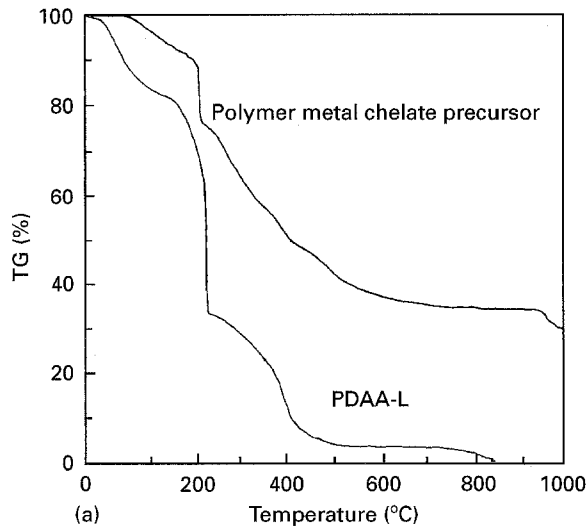


Figure 1 TG curves for PDAA-L and polymer-metal chelate precursor (a), Y-PDAA, Ba-PDAA, and Cu-PDAA (b).

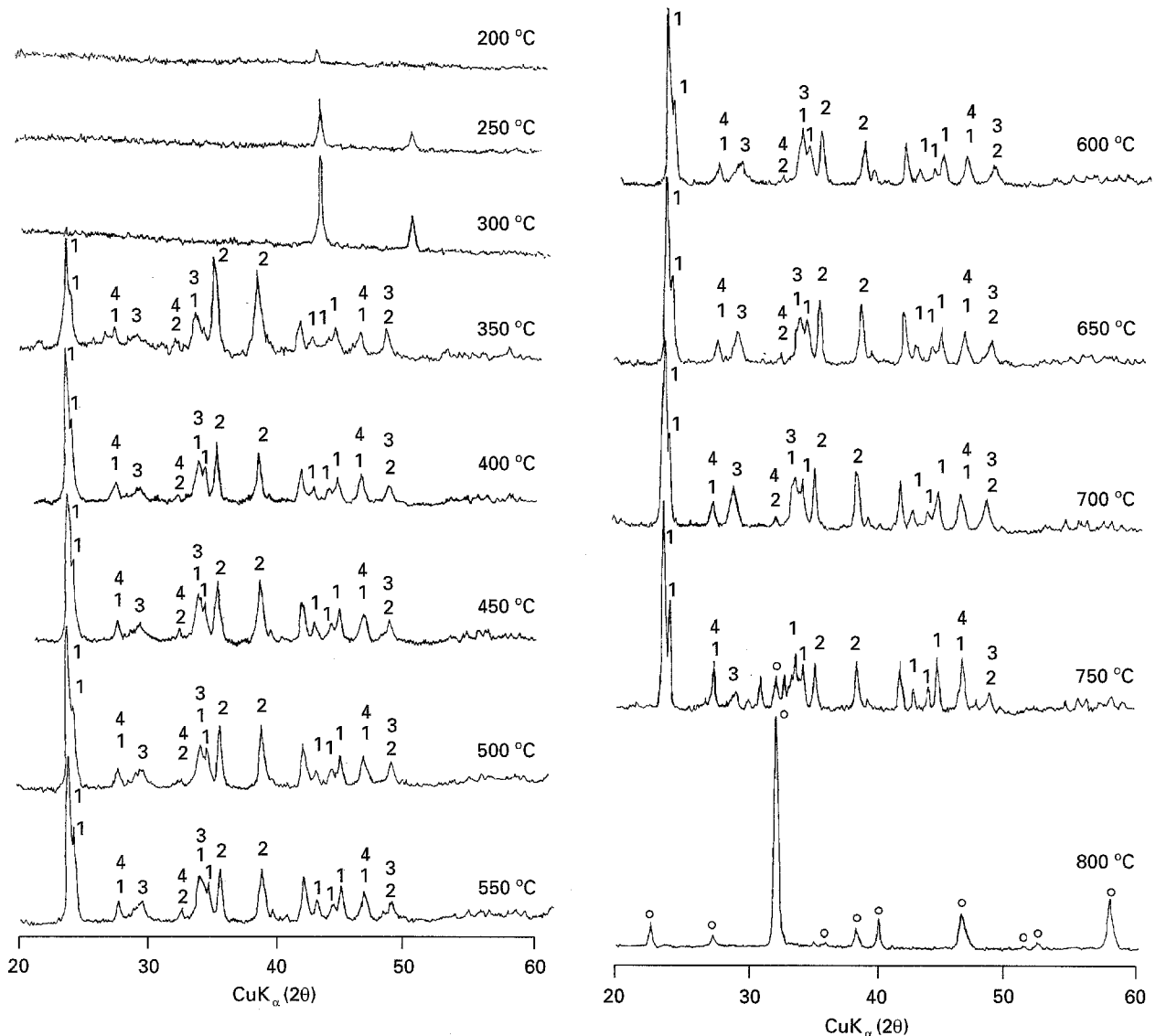


Figure 2 The X-ray diffraction patterns for the samples from polymer chelate precursor prepared from PDAA-H as a function of calcined temperature from 200 °C to 800 °C. (○):  $\text{YBa}_2\text{Cu}_3\text{O}_x$  1:  $\text{BaCO}_3$ , 2:  $\text{CuO}$ , 3:  $\text{Y}_2\text{O}_3$ , 4:  $\text{BaO}$ .

phase appeared at 750 °C and the mixture was completely converted to a tetragonal Y123 phase at 800 °C. On the other hand, the sample prepared from metal nitrate solution without PDAA had each metal nitrate remaining up to 450 °C (Fig. 3). Although

crystalline  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  were apparent at 500 °C, some amount of metal nitrates still remained. The nitrate precursor was not fully transferred to a Y123 phase after heating at 800 °C for 5 h. Large amounts of  $\text{Y}_2\text{O}_3$ ,  $\text{BaCO}_3$ , and  $\text{CuO}$  were

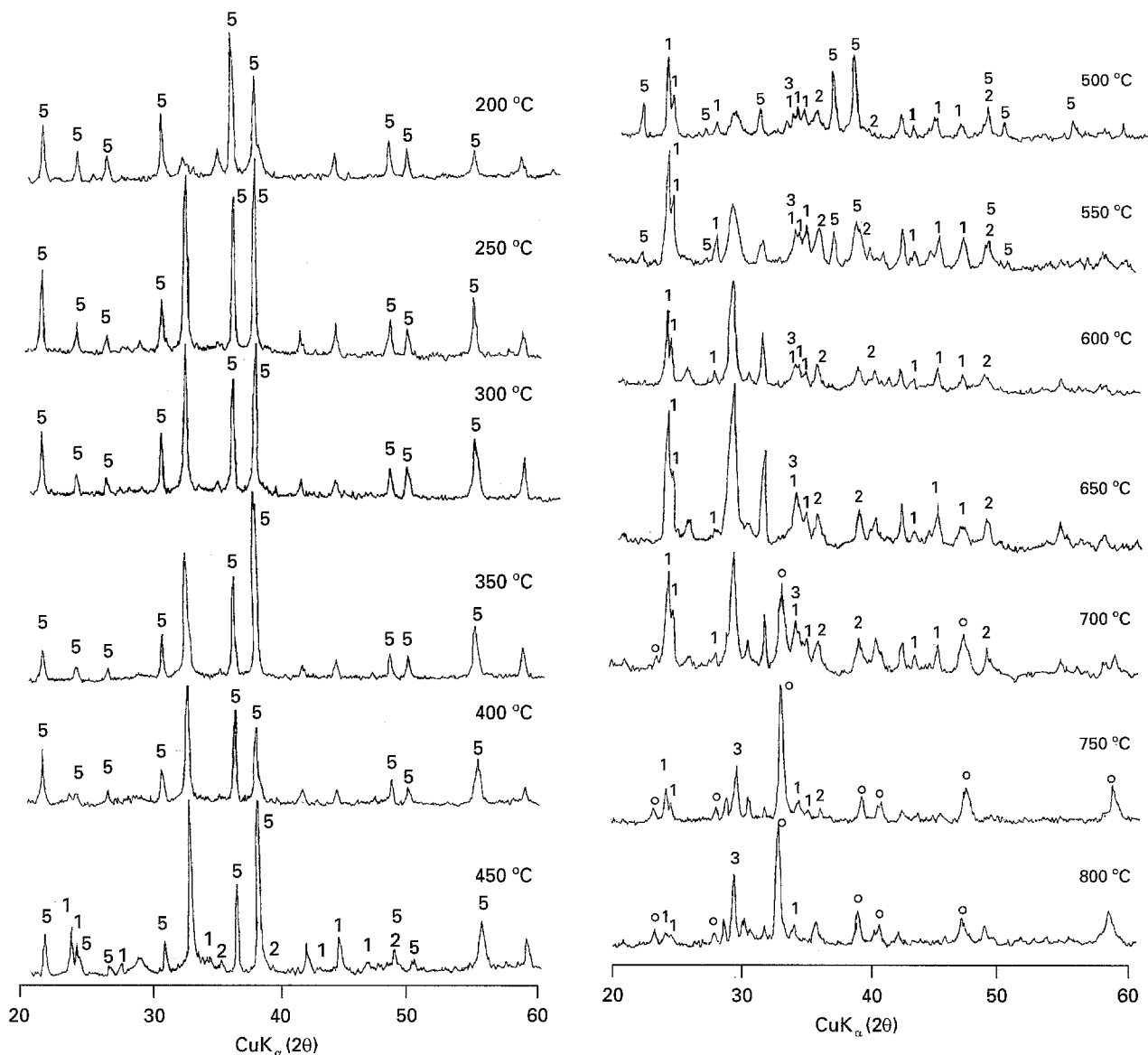


Figure 3 The X-ray diffraction patterns for the sample prepared from metal nitrates solution without PDAA as a function of calcined temperature from 200 °C to 800 °C. ○:  $\text{YBa}_2\text{Cu}_3\text{O}_x$ , 1:  $\text{BaCO}_3$ , 2:  $\text{CuO}$ , 3:  $\text{Y}_2\text{O}_3$ , 4:  $\text{BaO}$ , 5: metal nitrates.

observed. Large amounts of impurity phases were still observed even when the nitrate precursor was calcinated at 800 °C for 10 h.

Fig. 4 shows the phase evolution of the precursor from PDAA-H during an isothermal experiment at 800 °C. The precursor was heated from room temperature to 800 °C at a heating rate of  $3\text{ °C min}^{-1}$ , kept at 800 °C for the desired time and cooled to room temperature at a rate of  $3\text{ °C min}^{-1}$ . A tetragonal Y123 phase produced was pure according to the X-ray diffraction pattern even after the polymer chelate precursor was heated at 800 °C for 2 h, although a very small amount of  $\text{BaCO}_3$  was recognized.  $\text{BaCO}_3$  phase was hardly recognized after 4 h calcination. The precursor prepared from PDAA-L was also heated from room temperature to 800 °C at a heating rate of  $3\text{ °C min}^{-1}$  and kept at 800 °C for the desired time. Fig. 5 shows the phase evolution of the precursor from PDAA-L during an isothermal experiment at 800 °C. A tetragonal Y123 phase produced was almost pure according to the X-ray diffraction pattern even after the polymer chelate precursor was heated at 800 °C for

1 h, and the precursor was fully converted to a pure tetragonal Y123 after 3 h calcining at 800 °C.

Most general methods require long processing times and high temperatures. The XRD analysis of the sample prepared from metal nitrate solution without PDAA shows that the sample was not fully transferred to pure 123 phase even after calcining at 800 °C for 10 h, whereas almost pure tetragonal Y123 phase was produced after both polymer chelate precursors were calcined at 800 °C for 2 h. These results indicated that the greater homogeneity in the polymer chelate precursor leads to reduced firing times and temperature compared with the metal nitrates precursor.

### 3.4. Conversion to orthophobic Y123 phase

In a previous report [7], the polymer-metal chelate precursor which was prepared from PDAA-L was calcined at 880 °C for 10 h and sintered at 920 °C for 10 h to develop a pure superconducting Y123 phase. The calcined sample (880 °C, 10 h) showed almost pure orthophobic Y123 phase according to an XRD

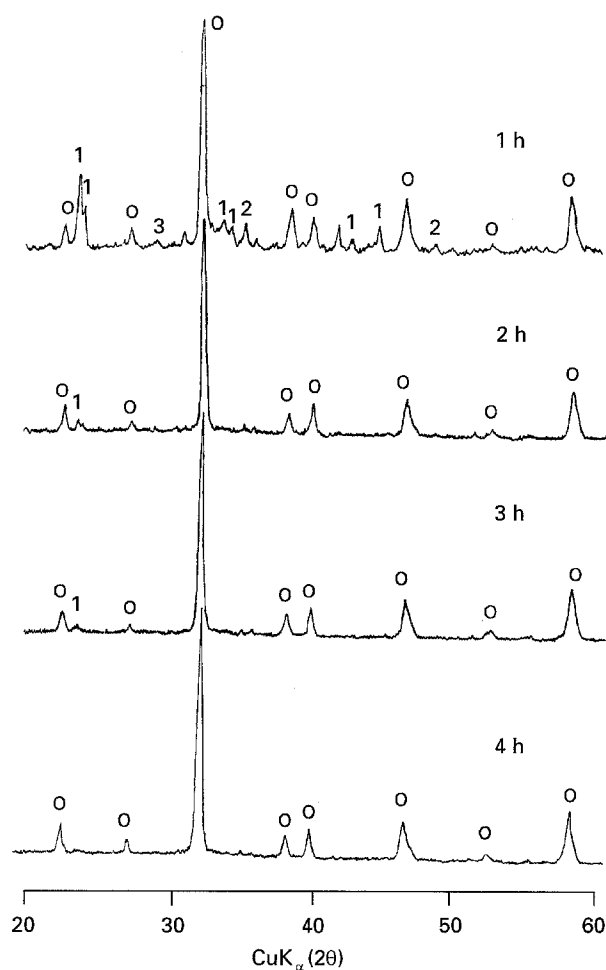


Figure 4 The X-ray diffraction patterns of an isothermal experiment for the precursor from PDAA-H at 800 °C. ○:  $\text{YBa}_2\text{Cu}_3\text{O}$ , 1:  $\text{BaCO}_3$ , 2:  $\text{CuO}$ , 3:  $\text{Y}_2\text{O}_3$ .

chart, whereas the XRD pattern after the polymer chelate precursor prepared from PDAA-H was heated at 800 °C for 4 h shows a tetragonal Y123 phase in the present study (Fig. 3). Several researchers reported that “low-temperature” tetragonal phase or a tetragonal X phase was found in low-temperature processing route [1, 8, 9]. The X phase has a similar tetragonal structure to that of the superconductor phase but it has a high oxygen stoichiometry. The X phase does not transform to the superconducting orthorhombic phase at lower temperatures, even after extended annealing with oxygen. The simplest way to convert it to the orthorhombic phase is to heat it overnight in air above 850 °C followed by slow cooling. After a calcined sample from PDAA-H was sintered at 920 °C for 10 h, as in the usual process, a large amount of  $\text{Y}_2\text{BaCuO}_5$  (Y211) phase was observed by XRD (Fig. 6). Based on the fact that Y211 phase is usually developed from Y123 phase by excess heat treatment, the sintering time of the calcined sample was too long. Therefore we reduced its sintering time and found that a pure orthorhombic Y123 phase was developed after calcined sample was sintered for 1 h, according to the XRD analysis.

#### 4. Conclusions

Polymer chelate precursors prepared from PDAA-H and PDAA-L reduced the firing temperature and time

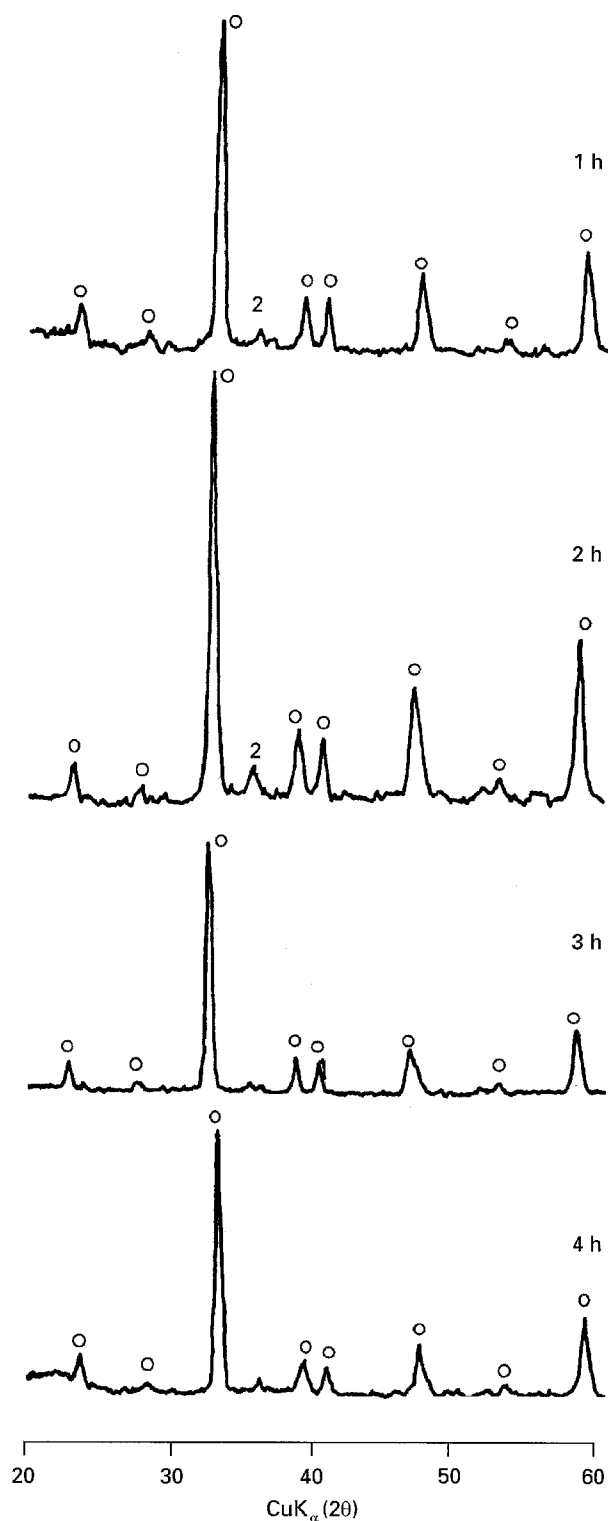


Figure 5 The X-ray diffraction patterns of an isothermal experiment for the precursor from PDAA-L at 800 °C. ○:  $\text{YBa}_2\text{Cu}_3\text{O}$ , 1:  $\text{BaCO}_3$ , 2:  $\text{CuO}$ , 3:  $\text{Y}_2\text{O}_3$ .

to produce highly pure tetragonal Y123 phase, compared with a sample prepared from metal nitrate solution without PDAA. According to the X-ray diffraction pattern, the precursors from PDAA-H and PDAA-L were converted to almost pure tetragonal phases, even after polymer chelate precursors were heated at 800 °C for 2 and 1 h, respectively. The XRD analysis of the sample prepared from metal nitrate solution without PDAA shows that the sample was not fully transferred to pure 123 phase even after

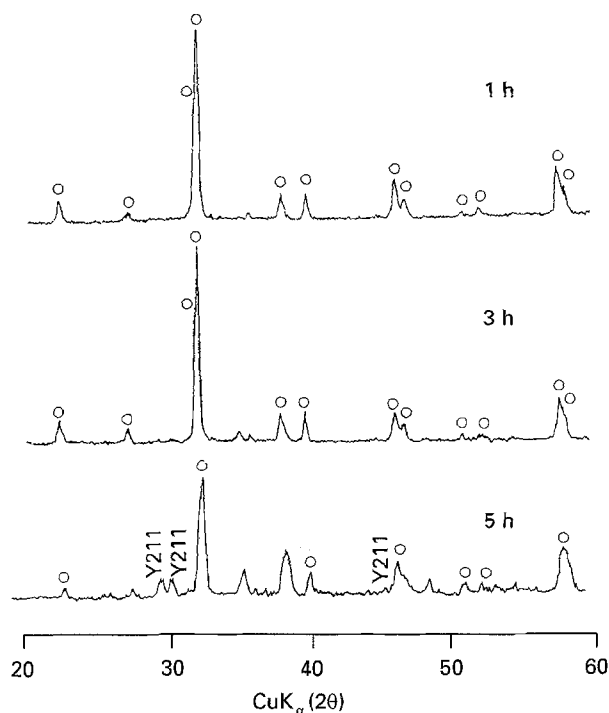


Figure 6 The X-ray diffraction patterns for the sintered samples at 920°C as a function of sintered time. Calcined sample was prepared from the precursor from PDAA-H at 800°C for 5 h.

calcining at 800°C for 10 h. These results indicated that the greater homogeneity in the polymer chelate precursors leads to reduced firing times and temperature compared with the metal nitrate precursor.

Low-temperature processing of Y123 in air usually produces tetragonal X phase, which has a similar tetragonal structure to that of the superconductor phase, but has a high oxygen stoichiometry. To eliminate the production of X phase, a low oxygen atmosphere is required [8, 11]. Even though tetragonal X phase was produced in the present study, the polymer chelate precursor technique is advantageous over the other solution processing because of the high homogeneity of each metal in the polymer precursor and simple precursor preparation. This method

provides a good alternative for producing superconducting ceramics. Applications of the polymer chelate precursor technique are now in progress.

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