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Preparation of pure $YBa_2Cu_3O_{7-x}$ superconductors from polymer chelate precursors using poly[(*N,N*-dicarboxymethyl)allylamine]

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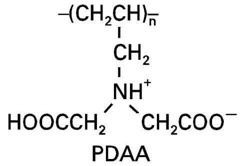
Bulk $YBa_2Cu_3O_{7-x}$ (YBCO) was prepared by a polymer chelate precursor method using poly[(*N,N*-dicarboxymethyl)allylamine] (PDAA) as a chelating polymer. An aqueous solution containing PDAA and 1/2 or 1/4 equivalent molar amount of metal nitrates (Y : Ba : Cu = 1 : 2 : 3) to the repeating unit of PDAA at pH 8 was poured into ethanol to precipitate the polymer–metal chelate precursor. The precursor containing 1/2 equivalent molar amount of metal ions was calcined at 880 °C for 10 h, sintered at 920 °C for 2 h, and annealed at 600 °C for 5 h. The product exhibited a pure superconducting orthorhombic phase. However, the precursor containing 1/4 equivalent molar amount of metal ions gave a mixture of orthorhombic and tetragonal phases under the same conditions. The influence of a purification process for PDAA on the preparation of YBCO was also examined. The electrical resistance and susceptibility of the YBCO sample prepared by optimum conditions were measured. The sintered sample showed superconductivity with T_c (onset) at 93 K and T_c (end) at 91 K. The narrow superconducting transition demonstrated here is attributed to the high purity and homogeneity of the sample prepared from optimized polymer chelate precursor technique.

1. Introduction

After the discovery of high temperature superconducting oxide many attempts have been made to synthesize precursors of higher homogeneity from solutions, which were expected to enable the formation of homogeneous superconducting products. The coprecipitation method is one such solution method, where metal oxalate, carbonate or hydroxide precipitates having the cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 are made from an aqueous solution of metal nitrates [1, 2]. A problem with this method resides in the difficulty in controlling the final metal composition in the precipitates. The requirements are that a quantitative and simultaneous precipitation of all cations should occur without phase separation in the precipitate, leaving no unprecipitated ions in the supernatant. It is difficult to find a suitable precipitating agent as the number of metal ions in superconductor system is increased. The sol–gel process is another method for making homogeneous fine powder. It is widely used for the preparation of ceramics and is known to yield very fine powders in which each metal component is well mixed on a molecular scale [2, 3]. The polymerized complex method of each metal chelate was reported to prepare superconducting precursors [4, 5]. This method contributes to the high homogeneity of each metal ion during the reaction process. However, most sol–gel processing involves many chemical steps such as heat treatment and control of the chemicals during the preparation of precursors. This is also the case with the difficulty in finding suitable reagents and reaction conditions as the number of metal ions increases.



PDAA

Previously we introduced the novel concept of a polymer–metal chelate precursor technique that utilizes organic polymers possessing strong chelating ligands for metal ions [6, 7]. Poly[(*N*, *N*-dicarboxymethyl)allylamine] (PDAA) of molecular weight 3×10^4 was synthesized and used as a chelating polymer for Y, Ba and Cu [7]. Although similar examples of using polymers possessing functional groups with complexation affinities for metal ions for preparing superconducting oxides have been reported [8–11], there was no documented example of using organic polymers possessing strong chelating ligands. Pure polymer chelate precursors can be prepared by the so-called precipitation method from precursor solutions. This process does not involve a sol–gel technique which contains solvent evaporation processes. The clear solution (pH 8) containing the polymer and

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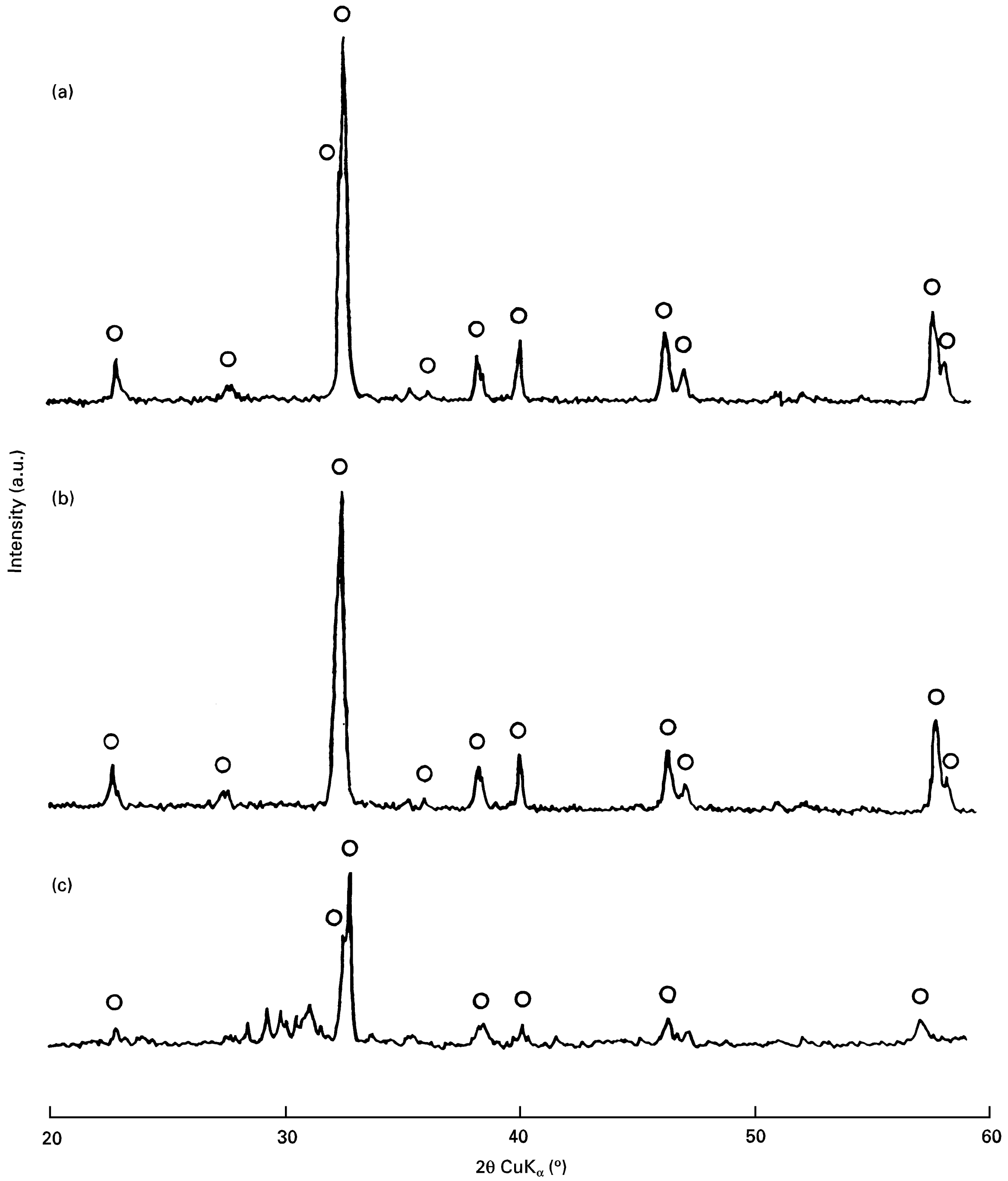

Figure 1 X-ray diffraction patterns for the calcined samples prepared from polymer–metal chelate: (a) [repeating unit of PDAA] : [metal] = 2 : 1, (b) = 4 : 1 and (c) sample prepared from metal nitrates.

the metal nitrates of Y, Ba and Cu (1 : 2 : 3 in molar ratio) was poured into ethanol to precipitate the polymer–metal chelate. This procedure can exclude contaminations from inorganic salts and therefore can improve the purity of a superconducting phase after firing the polymer chelate precursor.

The purpose of this paper is to examine the conditions suitable for preparing polymer chelate precursor from PDAA to produce homogeneous fine YBCO superconductor. Polymer chelate precursors containing different molar ratios of polymer and metal ions were prepared and their homogeneity after heat treatment was studied. We also considered the influence of impurities contained in PDAA on the preparation of YBCO. The materials obtained from these polymer chelate precursors were characterized by X-ray diffraction (XRD).

2. Experimental procedure

Unless otherwise stated, all reagents and chemicals were obtained from Wako Pure Chemical Co. and used without further purification. Poly(allylamine) (PAA) of average molecular weight 1×10^4 (PAA-L) was obtained from Nittobo Co.. Poly[(*N*, *N*-dicarboxymethyl)allylamine] (PDAA) was prepared from PAA-L according to the method given in [12]. Powder X-ray diffraction was performed on a Rigaku NO. 2013 using a Ni-filtered CuK$_\alpha$ X-ray beam excited at 30 kV and 15 mA.

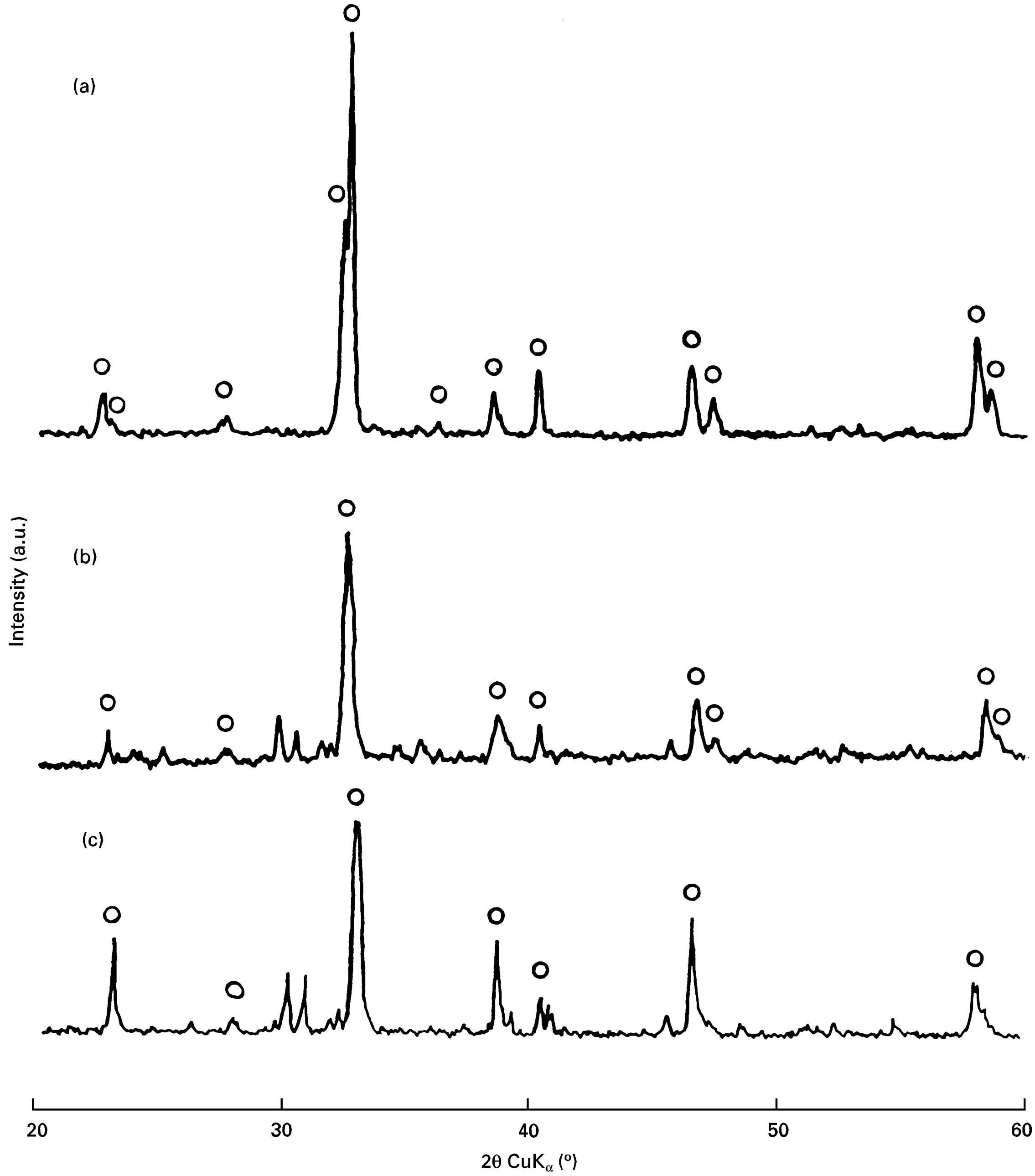

Figure 2 X-ray diffraction patterns for the sintered samples at 920 °C for 10 h prepared (a) from metal nitrates, and (b) from polymer–metal chelate. [repeating unit of PDAA] : [metal] = 2 : 1, (c) = 4 : 1.

2.1. Preparation of polymer chelate precursor

The typical procedure is as follows. The mixture consisted of 25 ml of $Y(NO_3)_3 \cdot 6H_2O$ (0.1 M), 50 ml $Ba(NO_3)_2$ (0.1 M), and 75 ml $Cu(NO_3)_3 \cdot 3H_2O$ (0.1 M) was added to 300 ml of the polymer solution (0.03 mol by repeating unit) with 25% NH_3 solution added to maintain the solution pH at 8 in order to give metal chelates of 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. Metal nitrate precursors were prepared by removal of water from each of the metal nitrate containing solutions (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 880 °C at a heating rate of 3 °C min^{-1}, calcined for 10 h, and cooled to room temperature at a rate of 3 °C min^{-1}. The calcined powder was milled and pressed into pellet form (10 mm diameter and 1 mm thick) at 500 kg cm^{-2}. The pellet was sintered at 920 °C for 2 h in air and then annealed at 600 °C for 5 h under flowing oxygen (0.3 l min^{-1}).

3. Results and discussion

3.1. Optimized molar amount of metal ions to PDAA

PDAA was dissolved in deionized water and the 0.5 equivalent molar amount of metal nitrates to the

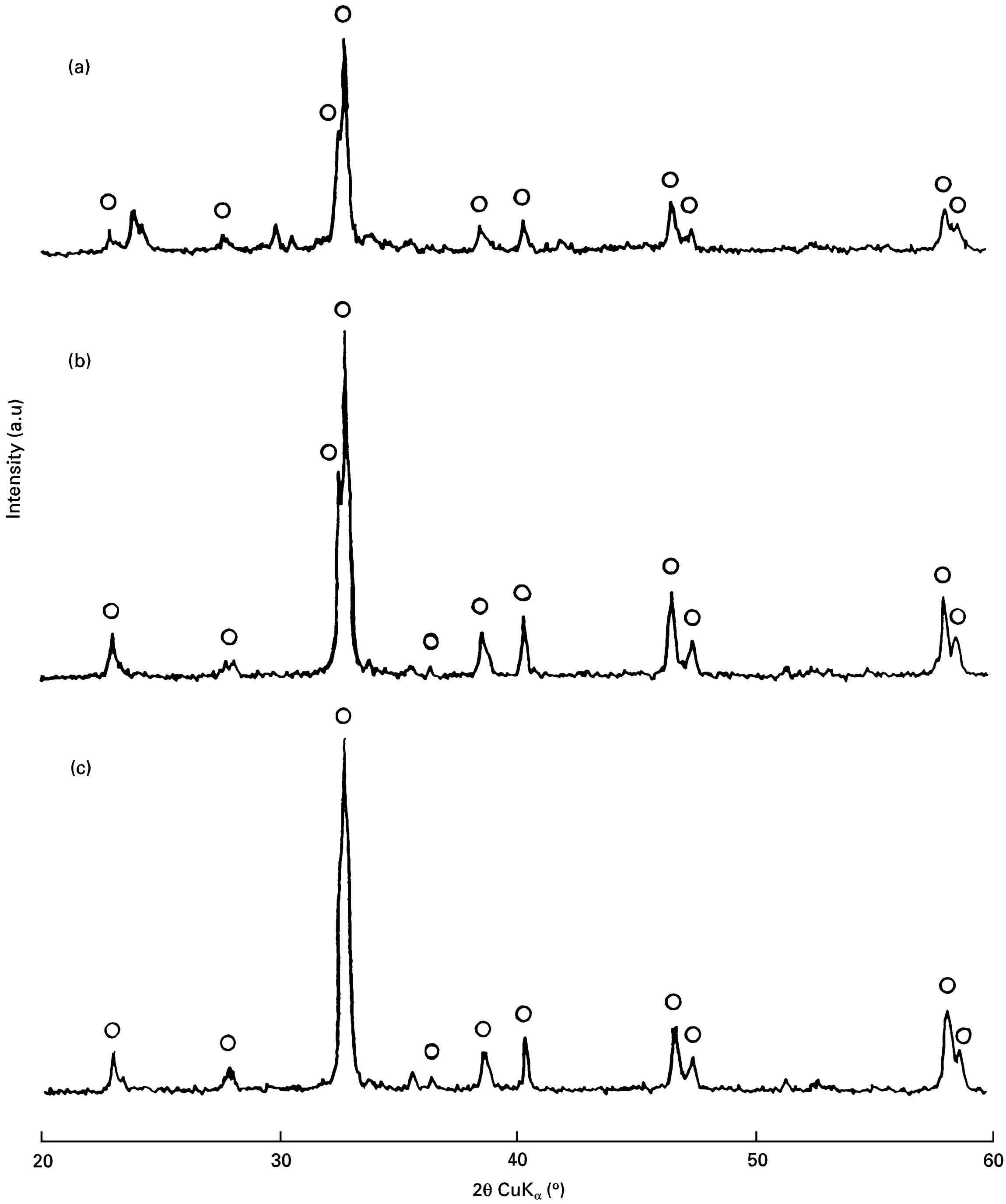

Figure 3 X-ray diffraction patterns for the sintered samples at 920 °C for 2 h prepared (a) from metal nitrates, and (b) from polymer–metal chelate. (a) [repeating unit of PDAA] : [metal] = 2 : 1, (c) = 4 : 1.

repeating unit having the cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 were added to form a homogeneous dark blue solution at pH 8 [7]. When metal nitrates were added beyond 1/2 equivalent to the polymer solution, precipitation occurred even when the solution's pH was adjusted to 8. A heterogeneous dispersion of the precursor containing one equivalent molar amount of metal ions was poured into ethanol and the resulting precipitate was dried, calcined and sintered. The XRD chart of this sample shows many impurity peaks. This can be explained by the deviation of the metal compositions during the precursor synthesis. Therefore, addition of the molar amount of metal nitrates should not exceed 1/2 equivalent to the polymer solution.

The polymer chelate precursors with 1/2 and 1/4 molar amount of metal ions were prepared and the effect of the metal content on their firing processes was estimated. Metal nitrates (Y : Ba : Cu = 1 : 2 : 3) were added in a molar equivalent amount of 1/2 or 1/4 of the repeat unit of PDAA in aqueous solution of pH 8, to form homogeneous dark blue solutions. Then the solutions were poured into ethanol to precipitate the polymer–metal chelate precursors. Both precursors containing 1/2 and 1/4 equivalent molar amount of metal ions were calcined at 880 °C for 10 h. The tetragonal $YBa_2Cu_3O_{7-x}$ (Y123) phase of each of the calcined samples was almost pure according to XRD (Fig. 1a and b). Fig. 1c shows the XRD of the sample prepared from metal nitrate solutions without

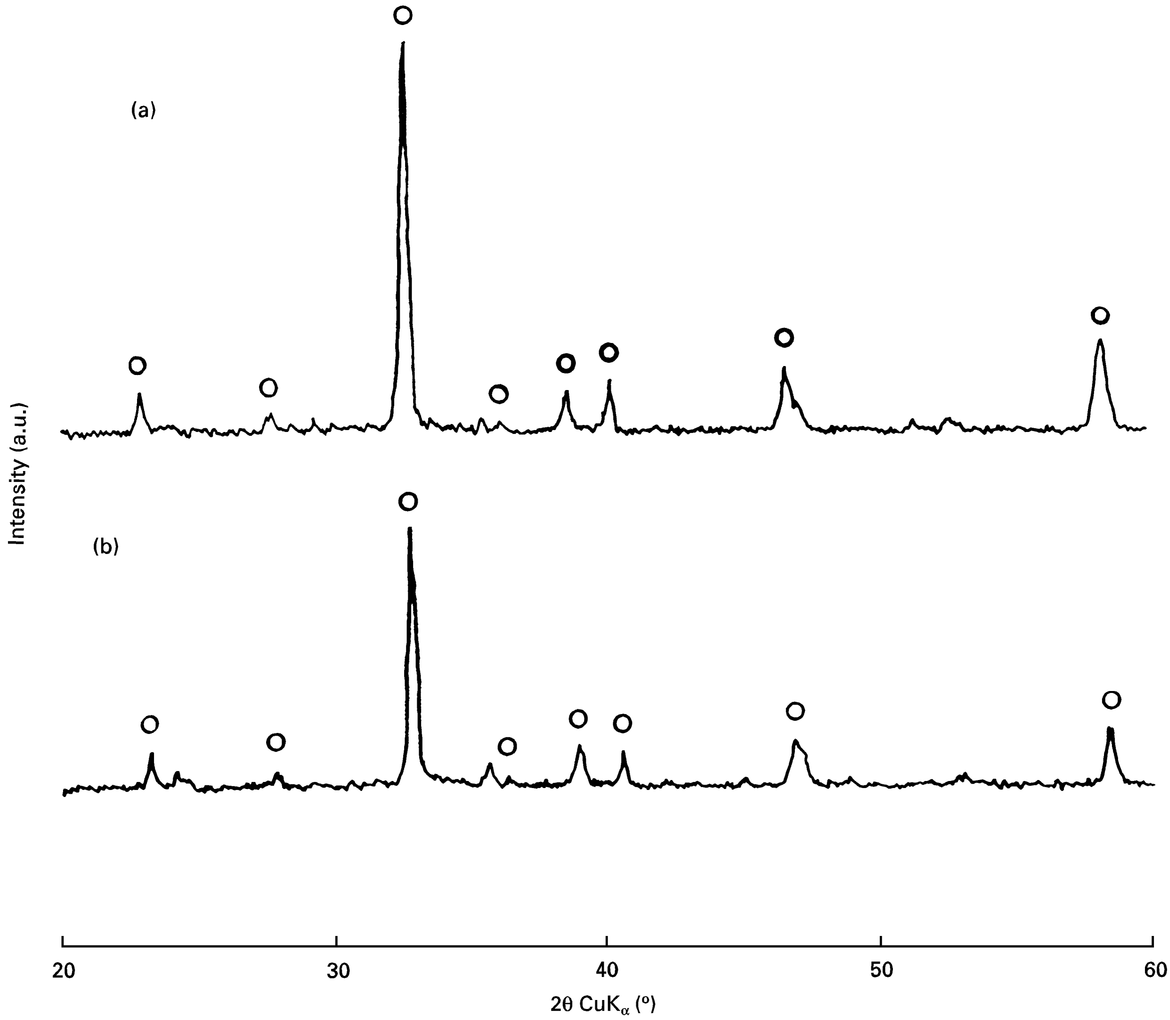

Figure 4 The X-ray diffraction patterns for the calcined samples at 800 °C for 10 h prepared from PDAA purified (a) with NH_4OH and (b) with NaOH.

chelating polymer. It is clear that the sample did not fully transform to pure Y123 phase after being calcined at 880 °C for 10 h. These results suggested that the metal ions in each polymer chelate precursor was well dispersed such that pure superconducting phase could develop. Both calcined samples from polymer chelate precursors were sintered at 920 °C for 10 h and large amounts of Y_2BaCuO_5 (Y211) phase were observed (Fig. 2b and c). 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 reduced to 2 h. The X-ray diffraction pattern of the sintered sample containing 1/2 molar amount of metal ions showed a pure orthorhombic phase (Fig. 3b). The sample from the precursor containing 1/4 molar amount of metal ions showed almost pure orthorhombic phase but contained some tetragonal phase according to the X-ray diffraction pattern (Fig. 3c). Peaks at 32.6° and 47° were not clear (due to overlapping) compared to those of the sample from the precursor containing 1/2 molar amount of metal ions. After the calcined sample prepared from metal nitrates solution without chelating polymer was sintered at 920 °C for 10 h, the pure orthophobic phase developed (Fig. 2a). However, the calcined sample did not fully transform to pure Y123 phase after sintering at 920 °C for 2 h (Fig. 3a). These results indicate that the polymer chelate precursor reduced the sintering times compared to those for metal nitrate mixtures, which means that the greater homogeneity in the polymer–metal precursor leads to reduced firing times. We also concluded that the precursor containing 1/2 equivalent molar amount of metal ions transform to pure orthorhombic 123 phase, whereas the sample from1/4 equivalent metal ions contained some tetragonal phase for the same conditions.

3.2. Purity of PDAA

PDAA was prepared from PAA with chloroacetic acid according to the method given previously [6, 12]. The reaction was carried out with the addition of 30% NaOH solution to maintain the pH at 10. After the reaction mixture was kept at room temperature for overnight and the pH was adjusted to 1 by addition of concentrated HCl. The resulting precipitate was dissolved in aqueous NaOH and the pH adjusted to 1 by the addition of concentrated HCl. This reprecipitation process was repeated twice. During these processes the polymer could be contaminated with Na ions. Although the Na impurity level in the isolated polymer was negligible, as established by elementary analysis, existence of a trace amount of impurity may

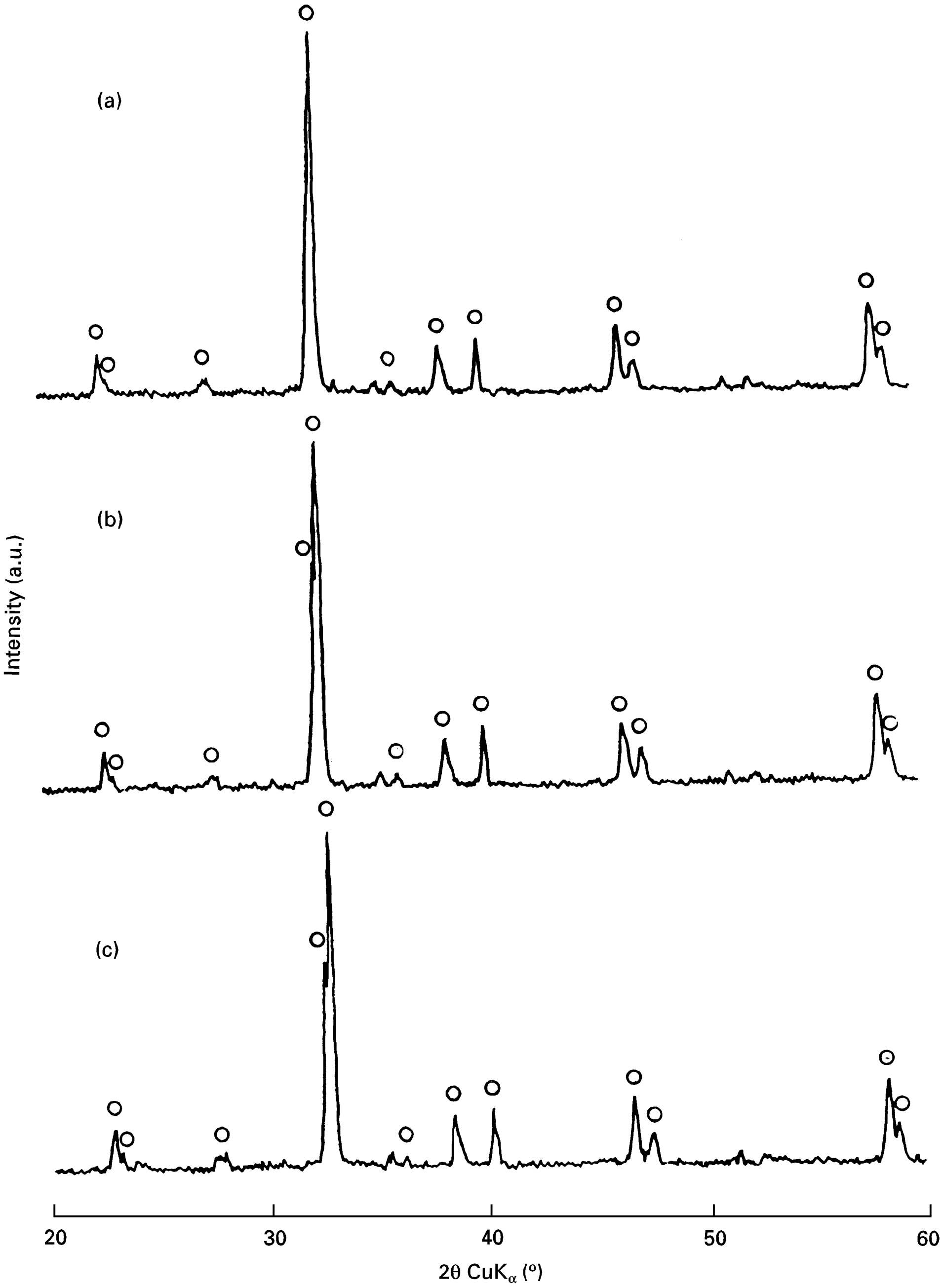

Figure 5 The X-ray diffraction patterns for the samples (a) calcinated at 880 °C for 10 h, (b) sintered at 920 °C for 2 h and (c) annealed at 600 °C for 10 h. Samples were prepared from PDAA purified with NH_4OH. [repeating unit of PDAA] : [metal] = 2 : 1.

not be inconsequential. Although bulk superconducting YBCO was produced using this NaOH-purified PDAA as described earlier and in a previous paper [7], a trace amount of Na impurity could interfere with the superconducting properties. Therefore PDAA was purified with NH_4OH instead of aqueous NaOH in order to remove trace amounts of Na. PDAA was dissolved in water with NH_4OH and the solution's pH was adjusted to 1 with concentrated HCl to precipitate the polymer. This reprecipitation process was repeated twice to remove trace amounts of Na. A 1/2 equivalent molar amount of metal nitrates (Y : Ba : Cu = 1 : 2 : 3) was added to an aqueous solution containing NH_4OH-purified PDAA at pH 8 to form homogeneous dark blue solutions. Then the solutions were poured into ethanol to precipitate the polymer–metal chelate precursor. When PDAA purified with NaOH was used, the X-ray diffraction patterns of the sample calcined at 800 °C for 10 h showed nearly pure superconducting tetragonal phase but impurity peaks were observed at 23.5° and 35.4° which correspond to $BaCO_3$ and CuO, respectively (Fig. 4b). Whereas when PDAA purified with NH_4OH was used, the impurity peak was negligible after calcination under the same conditions (Fig. 4a). These results indicated that the purified polymer served as a suitable precursor to produce highly pure Y123 phase.

3.3. Superconducting properties

The polymer chelate precursor prepared from purified PDAA with NH_4OH containing 1/2 equivalent molar amount of metal ions (Y : Ba : Cu = 1 : 2 : 3) was calcined at 880 °C for 10 h, sintered at 920 °C for 2 h,

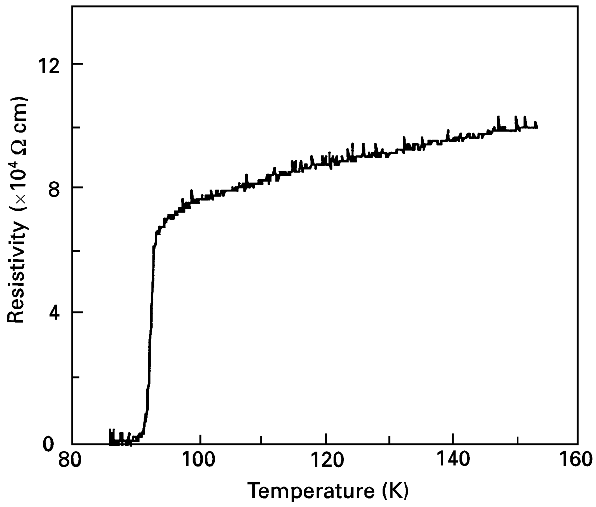

Figure 6 Resistance versus temperature for the samples prepared from optimized polymer metal chelate precursor.

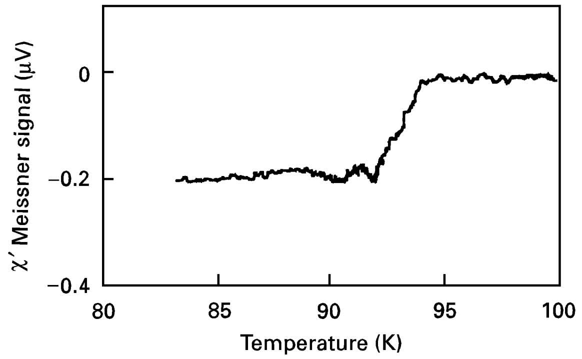

Figure 7 The susceptibility of the sample prepared from optimized polymer chelate precursor.

and annealed at 600 °C for 5 h. The X-ray diffraction patterns after each processing step are shown in Fig. 5. These three XRD patterns show that orthorhombic Y123 phase was produced at the calcination step and the peak resolution of the two strong lines at 32.6° are improved with increased processing steps. Resistivities of the annealed sample was measured by the four-probe method. Fig. 6 shows the temperature dependence of the electrical resistance of the annealed sample, which shows superconductivity of T_c (onset) at 93 K and T_c (end) at 91 K. The narrow superconducting transition (2 K) demonstrated here is attributed to the high purity and homogeneity of the sample prepared using the optimized polymer chelate precursor technique. Whereas our previous report concerned with the sample prepared by PDAA purified with NaOH shows superconductivity of T_c (onset) at 92 K and T_c (end) at 88 K [7]. These results suggested that the purification process was important when using the polymer chelate precursor method for preparing pure superconducting ceramics.

A susceptibility versus temperature curve for the sample is given in Fig. 7. The Meissner effect curve is in good agreement with the resistance curve shown in Fig. 6 and indicates a similar transition temperature of 94 K with a sharp transition width of 2.0 K.

4. Conclusions

The polymer–metal chelate precursors were prepared from an aqueous solution containing PDAA with 1/2 or 1/4 equivalent molar amount of metal nitrates (Y : Ba : Cu = 1 : 2 : 3) at pH 8. Th precursor containing 1/2 equivalent molar amount of metal ions was transformed to pure orthorhombic Y123 phase after being calcined at 880 °C for 10 h and sintered at 920 °C for 2 h, whereas the 1/4 sample contained some tetragonal phase for the same conditions. Metal nitrates precursor prepared from metal nitrates without PDAA did not fully transform to pure Y123 phase under the same conditions. These results indicated that the polymer chelate precursor reduced sintering times compared to those for the metal nitrates mixture, which means that the greater homogeneity in the polymer–metal precursor leads to reduced firing times. The precursor prepared from purified PDAA with NH_4OH shows good Y123 patterns compared with that from PDAA purified with NaOH, which indicated that the purification process can improve the purity of superconducting ceramics. The narrow superconducting transition was demonstrated for the sample prepared by the optimized polymer chelate precursor technique compared with our previous result [4].

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