Synthesis of Soluble Complexan Polymers in Organic Solvents for Using as a Polymer–Chelate Precursor to $YBa_2Cu_3O_{7-x}$ Thin Films

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A soluble complexan polymer in organic solvents, derived from 1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA), was synthesized and used as a polymer chelate precursor to $YBa_2Cu_3O_{7-x}$ thin films. Five complexan polymers (**3**) were prepared by a ring-opening polyaddition of CyDTA dianhydride (**1**) with several diamines (**2**). The polymer (**3e**) prepared with 1,2-diaminocyclohexane (**2e**) was soluble in water, dimethyl sulfoxide (DMSO), methanol, and ethanol. A clear aqueous solution (pH 8) containing **3e** and 1/2 equivalent molar amount of metal nitrates of Y, Ba, and Cu (1 : 2 : 3 in molar ratio) was poured into tetrahydrofurane (THF) to precipitate a polymer–metal chelate. The chelate formations of each metal were confirmed by C=O stretching bonds. The polymer chelate precursor was soluble in methanol, DMSO, and water, and partially soluble in ethanol. The polymer–metal chelate was dissolved in methanol, of which the metal concentration was adjusted to 3 wt%. This solution was spin-coated onto $SrTiO_3$ (100) and MgO (001) substrates for preparing $YBa_2Cu_3O_{7-x}$ thin films. According to an X-ray diffraction analysis, $YBa_2Cu_3O_{7-x}$ film with a *c*-axis orientation was formed on a $SrTiO_3$ substrate; even the precursor film was sintered at 780 °C for 1 h under air. Superconducting $YBa_2Cu_3O_{7-x}$ films with a *c*-axis orientation were also prepared on a MgO (001) substrate.

A water-soluble polymer precursor route is one of attractive synthetic methods of high-temperature superconducting oxides.[1] The basic idea of this technique is to lower the mobility of free metal ions in a polymer solution by increasing the interaction between metals and polymers. Chien et al. have developed a polymer-metal-complex (PMC) technique to prepare superconducting ceramics.[2,3] They used polymers possessing functional groups with complexation affinities for metal ions. We have recently reported a novel concept involving a polymer–metal chelate precursor technique that utilizes organic polymers possessing strong chelating ligands for metal ions.[4–7] This technique can achieve a higher homogeneity of each metal component in the polymeric precursor compared with the PMC technique, in which the complexation affinities of the individual cations to a polymer are different.

Since the discovery of the $YBa_2Cu_3O_{7-x}$ superconductor, considerable attention has been paid to film-preparation techniques, such as sputtering, activated reactive evaporation, laser ablation, and chemical-vapor deposition.[8] A wet-chemical process using a solution of metalorganic compounds has also been marked as a promising technique for preparing superconducting films, since it dose not require a high vacuum and is easily applicable to substrates of any shape and size. Sol–gel routes based upon metal alkoxides or metal chelates in a non-aqueous medium have attracted considerable interest as precursors for the synthesis of high-temperature superconducting oxides as well as ferroelectric ceramics, especially for thin-film fabrication.[9] In our preceding articles,[4–7] we used a complexan polymer prepared by a ring-opening polyaddition of ethylenediamine-tetraacetic dianhydride with ethylenediamine and poly[(*N*,*N*′-dicarboxymethyl)allylamine] as polymer chelate precursors. However, these polymer chelate precursors were soluble in water and insoluble in any organic solvents. If the polymer–metal chelate precursor can be soluble in volatile organic solvents, the polymer–metal chelate precursor technique would lead to a great advantage for fabricating thin films.

In the present work, we synthesized a soluble complexan polymer in organic solvents derived from 1,2-diaminocyclohexane-*N*,*N*,*N*′,*N*′-tetraacetic acid (CyDTA) for use as a polymer chelate precursor to the $YBa_2Cu_3O_{7-x}$ (YBCO) superconductor. The polymer–metal chelate precursor which was prepared from a 1/2 equivalent molar amount of metal nitrates having a cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 to the repeating unit of the complexan polymer was soluble in methanol. We applied the resulting polymer-chelate precursor to the preparation of $YBa_2Cu_3O_{7-x}$ thin films on $SrTiO_3$ (100) and MgO (001).

Experimental

Materials and Methods. Unless stated otherwise, all re-

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agents and chemicals were obtained from Wako Pure Chemical Co. and used without further purification. ^{1}H NMR, IR, and UV spectra were recorded on a JNM-GSX 400, a Shimadzu FT-IR-4200, and a Hitachi U-2000, respectively. Powder X-ray diffraction (XRD) was obtained with a Rigaku NO. 2013 using a Ni-filtered Cu$K\alpha$ X-ray beam excited at 30 kV and 15 mA. The inherent viscosity was measured by an Ostwald viscometer in dimethyl sulfoxide (DMSO) at 25 °C.

1,2-Diaminocyclohexane-*N,N,N′,N′*-tetraacetic dianhydride (1). To a solution of 1,2-diaminocyclohexane-*N,N,N′,N′*-tetraacetic acid monohydride (CyDTA) (20.0 g, 0.055 mol) in pyridine (30 ml) was added acetic anhydride (28.0 g, 0.274 mol). The mixture was stirred for 18 h at room temperature. The solution was then poured into 500 mL of diethyl ether. After the resulting precipitate was separated and dried in vacuo, a colorless solid 15.2 g (89%) was obtained. Found: C, 53.33; H, 5.96; N, 9.10%. Calcd for $C_{14}H_{18}N_2O_6$: C, 54.19; H, 5.85; N, 9.03%. ^{1}H NMR (DMSO-d_6) δ 1.05–1.25 (m, 4H, -CH$_2$-), 1.64 (t, 4H, -C*H*$_2$CHN-), 2.75 (br s, 2H, NCH), 3.7 (dd, 8H, NCH$_2$CO). IR (KBr) 1780, 1820 cm^{-1} (C=O).

Polycondensation of Diamines with 1. The polymers were prepared according to Scheme 1. The typical procedure was as follows. To a solution made from **2e** (0.57 g, 5 mmol) plus 2.5 mL of anhydrous DMSO was added **1** (1.55 g, 5 mmol) under nitrogen with stirring for 18 h at room temperature. The solution was poured into 100 mL of tetrahydrofurane (THF) to precipitate the product, which was further purified by repeated reprecipitation from methanol to diethyl ether. After the resulting precipitate was separated and dried in vacuo, a colorless solid polymer was obtained. The polymer yield was 84%. Found: C, 55.79; H, 7.72; N, 12.28%. Calcd for $(C_{20}H_{32}N_4O_6\cdot 0.5H_2O)_n$: C, 55.41; H, 7.67; N, 12.91%. ^{1}H NMR (DMSO-d_6) δ 1.05–1.25 (m, 4H, -CH$_2$-), 1.64 (t, 4H, -C*H*$_2$CHN-), 2.75 (br s, 2H, NCH), 3.7 (dd, 8H, NCH$_2$CO). IR (KBr) 3400 (NH), 1670–1660 (C=O), 1550–1540 cm^{-1}.

Other polyamides were synthesized by a similar procedure using 1-methyl-2-pyrrolidinone (NMP) as a solvent.

Preparation of YBCO Precursor. To a solution made from **3e** (2.54 g, 6 mmol by repeating unit) plus 60 mL of deionized water was added 40 mL of a 0.1 M (1 M = 1 mol dm^{-3}) metal nitrates aqueous solution having a cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 with adding a 25% NH$_3$ solution to maintain the solution's pH at 8 to give a metal chelate. The solution was then concentrated to 50 mL, and poured into 500 mL of THF to precipitate the polymer–metal chelate. The resulting solid was collected, washed with 20 mL of THF, and dried at 110 °C for 12 h in air.

Preparation of Bulk YBCO Powder. 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}.

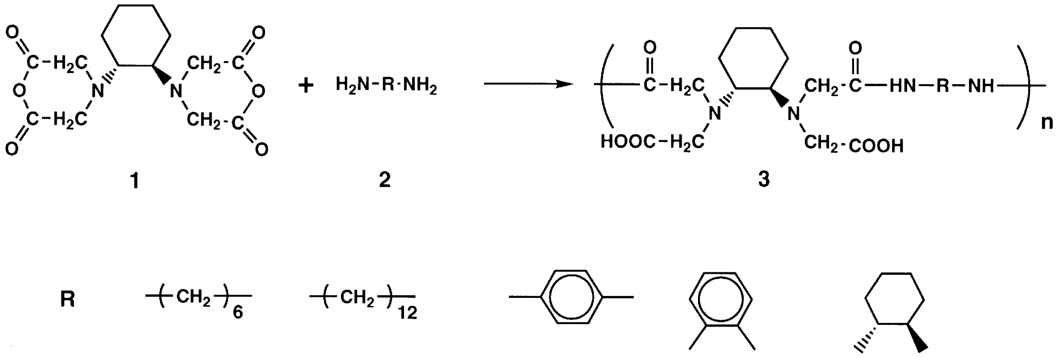
Preparation of $YBa_2Cu_3O_{7-x}$ Films. A polymer–metal chelate precursor which was prepared from the 1/2 equivalent molar amount of metal nitrates to the repeating unit of **3e** was dissolved in methanol, of which the metal concentration was adjusted to 3 wt%. This coating solution was spin-coated (7500 rpm) onto SrTiO$_3$ (100) or MgO (001) substrates and heated in air at 500 °C for 15 min. This procedure was repeated 10 times to form prefired precursor films on the substrates. The resulting precursor films were subjected to several heat treatments in air at a heating rate of 3 °C min^{-1}. The sintered samples were cooled to 600 °C at a rate of 3 °C min^{-1} and annealed at 600 °C for 3 h under flowing oxygen.

Results and Discussion

Synthesis of Complexan Polymers Derived from CyDTA. CyDTA dianhydride (**1**) was obtained by the reaction of CyDTA with excess acetic anhydride. When the reaction mixture was heated at 65 °C for 18 h using the same procedures as in the preparation of EDTA dianhydride,[10] the compound decomposed to unknown products. When CyDTA reacted with acetic anhydride at room temperature, we found that CyDTA was fully converted to the corresponding dianhydride after 18 h of stirring. The IR spectra of the resulting dianhydride showed the characteristic anhydride absorption at 1780 and 1820 cm^{-1}.

Complexan polymers were prepared by the ring-opening polyaddition of **1** with several diamines in NMP according to Scheme 1. All polycondensations, except for **3e**, proceeded in homogeneous solutions. The IR spectra of all the polymers showed the characteristic amide absorption near 1670 and 1550 cm^{-1}. All polyamides were obtained in almost quantitative yield. **3a** was soluble in water, but insoluble in organic solvents, whereas more hydrophobic **3b** was soluble in DMSO, but insoluble in water. Polymers (**3c** and **3d**) of aromatic diamines were also soluble in DMSO, but insoluble in water. Only **3e** was soluble in both DMSO and water. It should be emphasized that **3e** was also soluble in volatile organic solvents, such as methanol and ethanol. We therefore used **3e** as a candidate for the following polymer–metal chelate precursor system.

As mentioned above, **3e** was precipitated in NMP during



Scheme 1.

polycondensation at room temperature. Therefore, we tried to carry out the polycondensation of **1** with **2e** in DMSO to proceed in a homogeneous solution. The inherent viscosity of **3e** prepared in NMP was 0.26 dL g^{-1}, whereas that of prepared in DMSO was 0.39 dL g^{-1}, which indicated that the molecular weight of **3e** prepared in DMSO was higher than that of **3e** prepared in NMP. The polyamide structure of **3e** prepared in DMSO was identified by the IR and NMR spectrum as well as by elemental analysis. We used **3e** prepared in DMSO for the following polymer chelate precursor system.

Chelating Properties of 3e. To evaluate the chelating abilities of the obtained polymer (**3e**), a potentiometric titration method has been employed. Figure 1 shows the titration curves of **3e** in a 2.0 M KCl solution with a 0.1 M NaOH aqueous solution in both the absence and presence of each metal ion. From the curve (no metal), one equivalent point corresponding to the neutralization of COOH was obtained as pH 7.0. A second equivalent point corresponding to the neutralization of NH^+ was not clearly observed. In the presence of Cu and Y, the titration curves shifted downward, suggesting the chelate formation of a metal ion. Although the titration curve did not shifted like that in the case of the Ba system, curve Ba also shows the chelate formation at pH > 3. The titration curve of EDTA–ED polyamide also shows a similar property to those of **3e**.[4]

Polymer–Metal Chelate Precursor Synthesis. **3e** was dissolved in deionized water and a 1/2 equivalent molar amount of metal nitrates having a cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 were added to form a homogeneous dark blue solution with adding a 25% NH_3 solution to maintain the solution's pH at 8. The solution was then concentrated, and poured into THF to precipitate the polymer–metal chelate (Scheme 2). Removal of the solvent from the filtrate caused a white residue in which the polymer and the metal ions were hardly found by a ^1H NMR or TG analysis, respectively. These results indicated that the polymer chelate having a cation mole ratio of Y : Ba : Cu = 1 : 2 : 3 was obtained without any deviation of the metal compositions. The polymer chelate precursor was soluble in methanol, DMSO, and water, and partially soluble in ethanol.

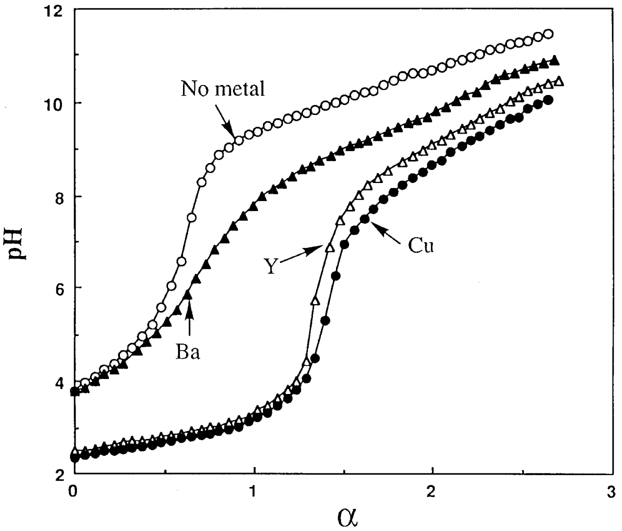
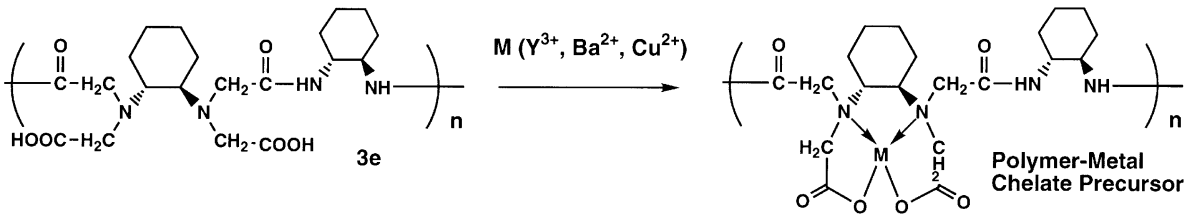


Fig. 1. Titration of 4.4 mM (repeating unit) **3e** and **3e** in the presence of 2.2 mM Cu^{2+}, Y^{3+}, and Ba^{2+} in 2.0 M KCl solution with 0.1 M NaOH solution.

To discuss the chelate formation between the ligand and each metal ion in the solid phase, the infrared technique is useful to determine whether the bonding is covalent or ionic. The IR spectrum of metal-free **3e**, which was isolated from an acidic solution, showed the presence of two varieties of carboxyl group: the 1730 cm^{-1} band is due to C=O stretching in $>HN^+–CH_2COOH$ group and the 1650 cm^{-1} band due to C=O stretching in $>HN^+–CH_2COO^-$ group. A similar result is known for the acid EDTA. The spectrum of the deprotonated polymer isolated from a pH 8.0 solution showed that only the 1650 cm^{-1} band was observed. These results correspond to the potentiometric titration curve. The spectrum of fully deprotonated EDTA also shows the 1590–1600 cm^{-1} band due to C=O stretching in the $>N–CH_2COO^-$ group.[11,12] For EDTA, an interpretation has been given that as the bonding becomes more ionic the frequency decreases; chelates with frequencies of 1610 cm^{-1} or less are considered to be ionically bonded. An increase in the absorption frequency for the COO^- group corresponds to an increase in the covalent character of the metal–carboxylate bond.[13] The IR spectra of the polymer chelate precursors isolated from a pH 8.0 solution in the presence of Cu, Ba, or Y showed that the absorption band for the C=O in $>HN^+–CH_2COO^-$ group shifted to lower frequencies, i.e., 1620–1630 cm^{-1}, compared with that of metal-free polymer isolated from the pH 8.0 solution. Our infrared data indicated that each metal formed a chelate with a $>N–CH_2COO^-$ group in the polymer. It should be noted in the case of the Ba system that the spectrum showed the presence of two varieties of the carboxyl group: the 1620–1630 cm^{-1} band and the 1580 cm^{-1} band. The former was due to chelate formation and the latter which was due to C=O stretching in the $>H–CH_2COO^-$ group, indicating the Ba ion was bonded ionically in a basic media.

The X-ray diffraction (XRD) pattern of the polymer metal precursor has no crystal structure peak, which means that no metal nitrates remained unreacted in the polymer metal precursor. However, the patterns of the samples isolated from each metal nitrate solution by removal of the solvent has each metal nitrate peak.

The TG data for the polymer chelate precursor, which was prepared from the 1/2 equivalent molar amount of metal nitrates to the repeating unit of **3e**, is shown in Fig. 2. The thermolysis results of the polymer–metal chelate took place between 200 and 500 °C. The TG curve of the metal–polymer chelate showed a rapid decomposition at 456 °C, which is considered to be due to degradation of the EDTA–metal chelate.[4,14] The plateau observed above 500 °C in which the final weight remained was 12.5% corresponding to the metal oxides. This value agrees fairly well with the theoretical value (11.8%) when the polymer chelate precursor is converted to $YBa_2Cu_3O_{7-x}$.



Scheme 2.

Conversion of Polymer–Metal Chelate Precursor to $YBa_2Cu_3O_{7-x}$ Powder. **3e** was dissolved in deionized water, and a 2/3 or 1/2 equivalent molar amount of metal nitrates to the 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. The solutions were then poured into THF to precipitate the polymer–metal chelate precursors. Both precursors containing 2/3 and 1/2 equivalent molar amounts of the metal ions were calcined at 880 °C for 10 h. Both tetragonal $YBa_2Cu_3O_{7-x}$ (Y123) phases of the calcined samples were almost pure, according to XRD (Fig. 3a, b). Figure 3c shows the XRD of the sample prepared from metal nitrates solution without a chelating polymer. It is clear that the sample without **3e** was not fully transferred to the pure Y123 phase after being calcined at 880 °C for 10 h. These results suggested that the each metal ions in the polymer chelate precursor was well-dispersed to develop the pure superconducting phase. A precursor containing a 2/3 equivalent molar amount of metal ions was calcined; although the X-ray diffraction pattern showed a nearly pure superconducting tetragonal phase, an impurity peak was observed at 35.4° corresponding to CuO. Whereas the precursor containing a 1/2 equivalent molar amount of metal ions was used, the impurity peak was hardly recognized after calcinating under the same conditions.

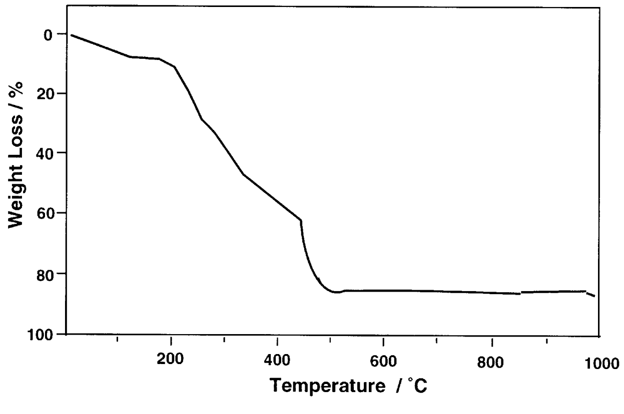


Fig. 2. TG curve for the polymer chelate precursor which was prepared from the 1/2 equivalent molar amount of metal nitrates to the repeating unit of **3e**. The precursor was heated from room temperature to 1000 °C at a heating rate of 10 °C min^{-1} under air.

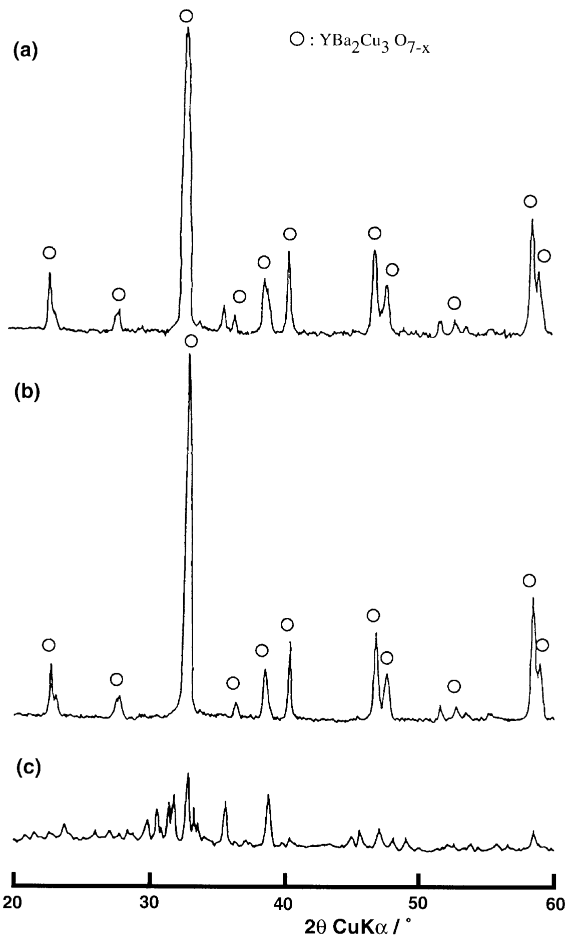


Fig. 3. X-ray diffraction patterns for the calcined samples prepared from polymer–metal chelate. [repeating unit of **3e**]:[metal] = 3:2 (a), = 2:1 (b), and sample prepared from metal nitrates (c).

Preparation of $YBa_2Cu_3O_{7-x}$ Films on $SrTiO_3$ (100) Substrate. A polymer–metal chelate precursor which was prepared from a 1/2 equivalent molar amount of metal nitrates to the repeating unit of **3e** was dissolved in methanol, of which the metal concentration was adjusted to 3 wt%. This solution was spin-coated (7500 rpm) onto $SrTiO_3$ (100) substrates and heated in air at 500 °C for 15 min. This procedure was repeated 10 times to form prefired precursor films on the substrates. Figure 4 shows XRD patterns of the thin films deposited on a $SrTiO_3$ substrate, which were sintered at 780, 815, 825, and 835 °C for 1 h, then annealed at 600 °C for 3 h. Although the XRD patterns of the films sintered at low temperature, i.e., 780 and 815 °C, gave unknown peaks at around 20 °, all of the films exhibited peaks corresponding to the $YBa_2Cu_3O_{7-x}$ (Y123)

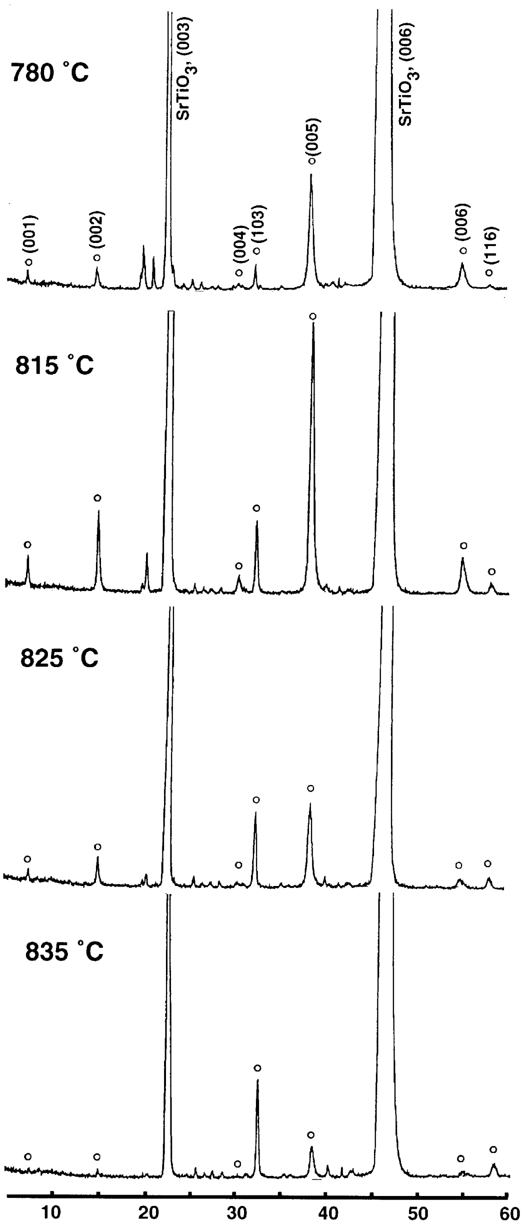


Fig. 4. X-ray diffraction patterns of the thin films deposited on a $SrTiO_3$ substrate. Sintering at 780, 815, 825, and 835 °C for 1 h in air, then annealing at 600 °C for 3 h.

phases. The XRD pattern of films sintered at 780 and 815 °C shows strong (00*l*) peaks, which correspond to a *c*-axis orientation perpendicular to the substrate surface. A much lower intensity of the (103)/(110) reflection suggests that the fraction of randomly oriented grains is considerably small. The ratios of the *c*-axis orientation were estimated using the following equation:

$$I_{\mathrm{R}(c\text{-axis})} = (005)/\{(005) + (103)\}$$

Expressions (005) and (103) mean the intensity of the (005) and (103) peaks, which correspond to the *c*-axis orientation and the randomly oriented grains, respectively. The ratios of the *c*-axis orientation, $I_{\mathrm{R}(c\text{-axis})}$, sintered at 780 and 815 °C, were 0.735 and 0.789, respectively. The XRD pattern sintered at 825 and 835 °C gave weak (00*l*) peaks. The ratios of the *c*-axis orientation, $I_{\mathrm{R}(c\text{-axis})}$, sintered at 825 and 835 °C, were 0.527 and 0.270, respectively. These results suggested that a higher sintering temperature reduced the *c*-axis orientation.

Superconducting $YBa_2Cu_3O_{7-x}$ films with the *c*-axis orientation were already prepared on $SrTiO_3$ (100) substrates at 750–800 °C for several hours by decomposition of metal-organic precursor films.[15] However, the precursor films were heat-treated under a low-oxygen partial pressure to avoid the formation of $BaCO_3$. The present results demonstrated that $YBa_2Cu_3O_{7-x}$ films with the *c*-axis orientation were achieved at 780 °C for 1 h under air. These results indicated that a greater homogeneity in the polymer chelate precursors leads to reduced firing times and temperature compared with previous wet-chemical methods.

Preparation of $YBa_2Cu_3O_{7-x}$ Films on MgO (001) Substrate. Since MgO is relatively inexpensive and has favorable dielectric properties which are suitable for microwave applications, the fabrication of epitaxial $YBa_2Cu_3O_{7-x}$ films on MgO is required. Due to a large lattice mismatch (9%) between $YBa_2Cu_3O_{7-x}$ and MgO, there have been very few reports on the successful growth of epitaxial $YBa_2Cu_3O_{7-x}$ films on a MgO substrate by wet-chemical methods.[16] Here, we applied a polymer–metal chelate precursor technique to the preparation of $YBa_2Cu_3O_{7-x}$ thin films on a MgO (001) substrate.

The methanol solution of the polymer–metal chelate precursor was spin-coated onto MgO (001) substrates using the same procedure as that described above. The precursor films were sintered at 880–1000 °C for 10 min, then annealed at 600 °C for 3 h. Figure 5 shows XRD patterns of thin films deposited on a MgO substrate which were sintered at 880, 920, 950, 970, and 1000 °C for 10 min under air. The XRD pattern sintered at 880 °C for 10 min exhibited peaks corresponding to pure $YBa_2Cu_3O_{7-x}$ (Y123) phases. However, the peaks corresponding to the *c*-axis orientation were very weak, i.e., $I_{\mathrm{R}(c\text{-axis})} = 0.132$. Figure 5 clearly indicates that a higher sintering temperature gave a higher *c*-axis orientation. The ratios of the *c*-axis orientation, $I_{\mathrm{R}(c\text{-axis})}$, sintered at 920, 950, 970, and 1000 °C were 0.326, 0.502, 0.647, and 0.934, respectively. Although the XRD pattern sintered at 1000 °C for 10 min gave the highest *c*-axis orientation, the film surface showed a granular structure with a coarse surface by a scanning electron-micrographic analysis.

Figure 6 shows the XRD patterns of thin films deposited on a MgO substrate which were sintered at 950 and 970 °C for 20 min. The XRD pattern sintered at 950 °C for 20 min gave a strong *c*-axis orientation, i.e., $I_{\mathrm{R}(c\text{-axis})} = 0.977$. Although the XRD pattern sintered at 970 °C for 20 min gave a high *c*-axis orientation, i.e., $I_{\mathrm{R}(c\text{-axis})} = 0.886$, an impurity phase was observed. The ratios of the *c*-axis orientation, $I_{\mathrm{R}(c\text{-axis})}$, of thin films deposited on a MgO substrate sintered at 920 °C for 3 and 5 h were 0.720 and 0.838, respectively.

Superconducting Properties. The resistivities of an-

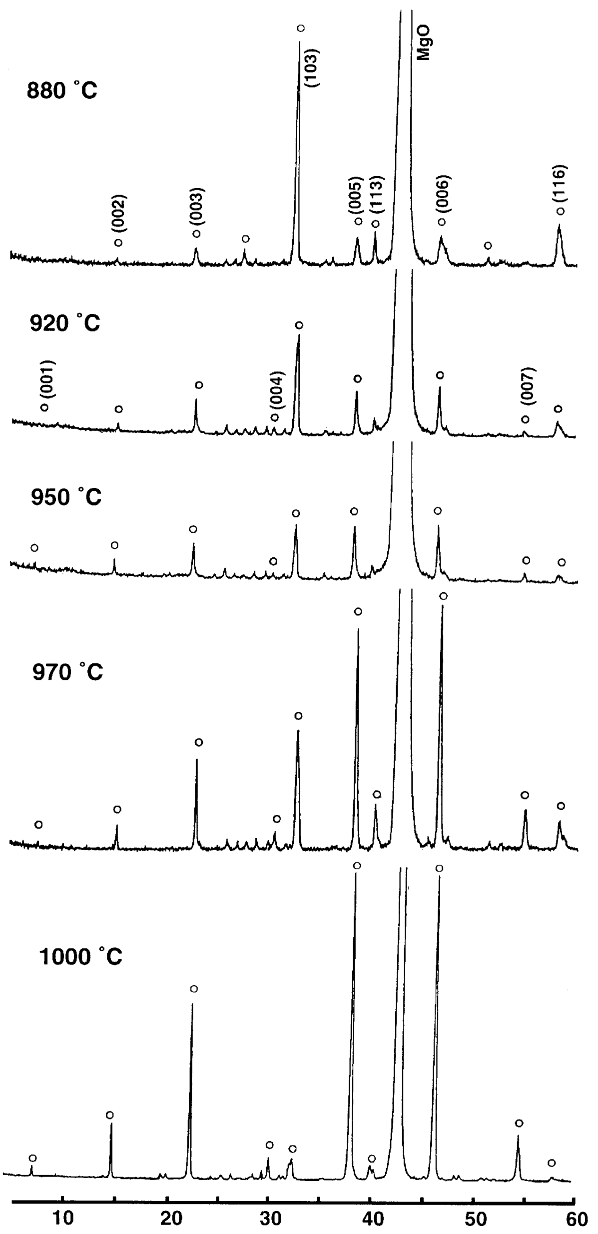


Fig. 5. X-ray diffraction patterns of the thin films deposited on a MgO substrate. Sintering at 880, 920, 950, 970, and 1000 °C for 10 min in air, then annealing at 600 °C for 3 h.

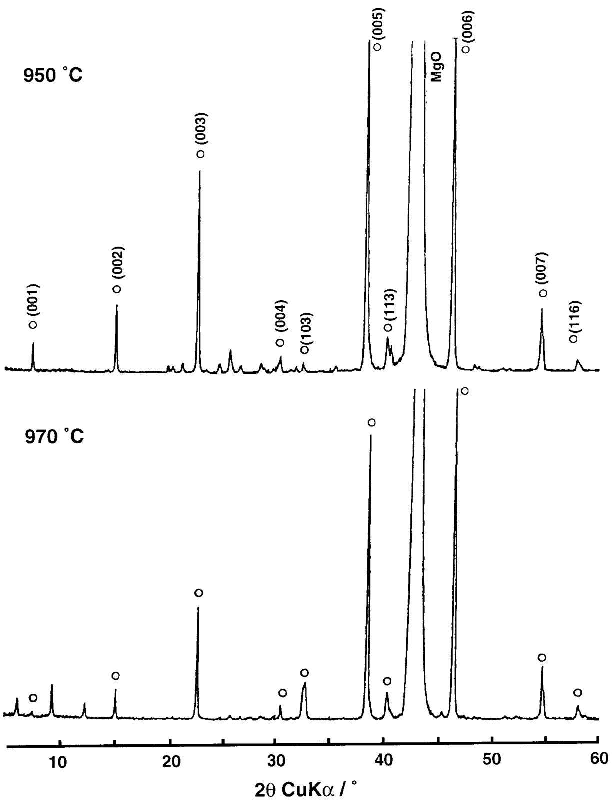


Fig. 6. X-ray diffraction patterns of the thin films deposited on a MgO substrate. Sintering at 950 and 970 °C for 20 min in air, then annealing at 600 °C for 3 h.

nealed films were measured by a four-probe method. Figure 7 shows the temperature dependence of the electrical resistance of $YBa_2Cu_3O_{7-x}$ thin films prepared on a MgO substrate, which gave a strong *c*-axis orientation. For a thin film heat-treated at 950 °C for 20 min, the superconducting transition started at about 60 K, and the resistance reached zero at 47 K. For a thin film heat-treated at 970 °C for 10 min, the superconducting transition started at about 65 K, and the resistance reached zero at 50 K. Although a thin film heat-treated at 970 °C for 20 min gave a strong *c*-axis orientation, the film showed no superconducting properties. This was due to the fact that an impurity phase was formed, as described above. As the temperature was lowered from room temperature, the resistivity of the film increased like a semiconductor. However, neither the transition temperature nor the transition width has yet been fully optimized. This is attributed to an insufficient lattice oxygen stoichiometry resulting from the presence of a small amount of residual carbon.

Conclusion. In this study, we described the first example of a soluble complexan polymer (**3e**) in organic solvents, which was derived from 1,2-diaminocyclohexane-*N*,N,N′,N′-tetraacetic acid (CyDTA) with 1,2-diaminocyclohexane (**2e**) in DMSO at room temperature. A clear aqueous solution (pH8) containing **3e** and the metal nitrates of Y, Ba, and Cu (1 : 2 : 3 in molar ratio) was poured into THF to precipitate the polymer–metal chelate. The polymer chelate precursor was soluble in methanol. This soluble polymeric precursor should lead to a great advantage for the fabrication of a thin film. According to an X-ray diffraction analysis, $YBa_2Cu_3O_{7-x}$ films with a *c*-axis orientation were formed on $SrTiO_3$ (100) and MgO (001) substrates after a methanol solution of the polymer–metal chelate precursor was spin-coated onto the substrates. Our present results demonstrate that a greater homogeneity in the polymer chelate precursors leads to reduced firing times and temperature compared to previous wet-chemical methods.

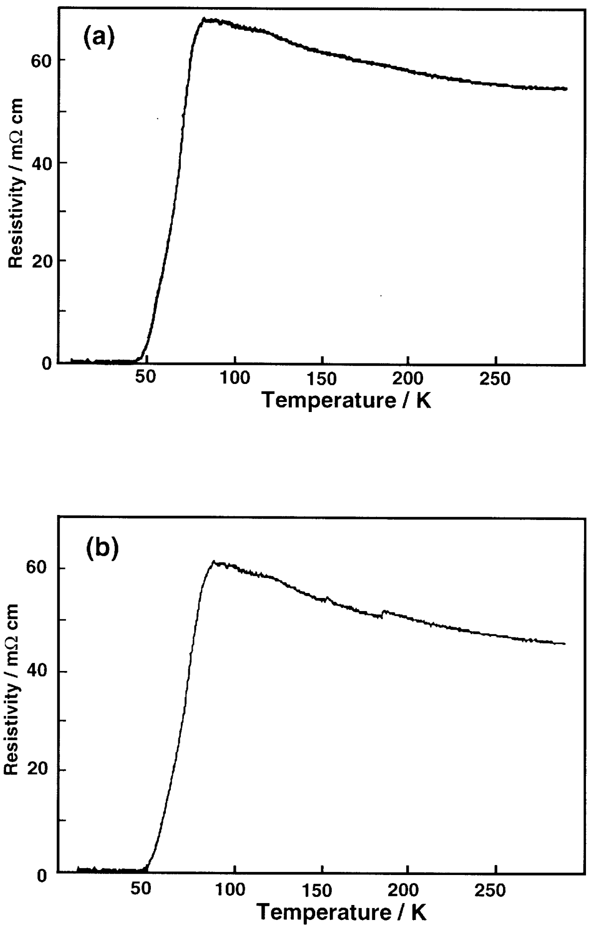


Fig. 7. Resistance versus temperature for thin films deposited on a MgO substrate. Sintering at 950 °C for 20 min (a) and 970 °C for 10 min (b).

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