Preparation of YBCO and BSCCO Superconducting Thin Films by a New Chemical Precursor Method

Takahiro Gunji,^{*} Mitsuo Unno, Koji Arimitsu, Yoshimoto Abe, Nick Long,¹ and Andrea Bubendorfer¹

Department of Pure and Applied Chemistry, Faculty of Science and Technology, Tokyo University of Science, 2641 Yamazaki, Noda, Chiba 278-8510

¹Industrial Research Ltd., PO Box 31-310, Lower Hutt, New Zealand

Received June 21, 2004; E-mail: gunji@rs.noda.tus.ac.jp

Homogeneous YBa₂Cu₃O_{7- δ} (YBCO) and Bi₂SrCa₂Cu₂O_{8+y} (BSCCO) precursors were prepared by the reaction of triethanolamine with ethyl acetoacetato complexes of Y, Ba, and Cu and those of Bi, Sr, Ca, and Cu, respectively. These precursors showed melt-spinnability and converted to ceramics on heating with the elimination and combustion of organic groups. Superconductive thin films were prepared by depositing a solution on a substrate by spin-coating, followed by calcination. Epitaxial growth of the YBCO phase, with *c* axis normal to the substrate, was observed. The critical temperature was 88.7 K and the critical current density at 77 K and 0 T was 5×10^5 A/cm². On the other hand, the epitaxial growth of the *c* axis aligned BSCCO phase was observed: the critical temperature was 77 K and the critical current density at 5 K was 6×10^4 A/cm².

Since the superconducting ceramics were reported in 1986,¹ many superconductors which have high critical temperatures have been discovered. Oxide superconductors, such as YBa₂Cu₃O_{7- δ} (YBCO) and Bi₂SrCa₂Cu₂O_{8+y} (BSCCO), are expected to be applied to large current transport or electronic devices because their critical temperatures (T_c) are higher than the boiling point of liquid nitrogen. For example, for the fabrication of Josephson junction devices, which are known as ultra high-speed circuits, the formation of superconductive thin films with high T_c and critical current density (J_c) is strongly demanded. However, the preparation of superconductive thin films or fibers by the conventional solid phase method has limitations as to the homogeneity and the shape of samples because YBCO and BSCCO superconductors are ceramics.²⁻⁴

As typical methods for the formation of superconductive ceramic thin films, the following methods and processes are mentioned:5-9 sputtering, physical vapor deposition, chemical vapor deposition, metal organic chemical vapor deposition, sol-gel process, and metal organic decomposition (MOD). Especially, the MOD method has been applied as a simple and inexpensive method for the preparation of thin films. The preparation of YBCO superconductive thin films by MOD method can be summarized as follows: McIntyre, Cima, and co-authors¹⁰ used trifluoroacetates to provide a thin film of the thickness of 200–250 nm and J_c of 2–3 × 10⁶ A/cm². T. Kumagai and co-authors¹¹ prepared thin films with J_c of 1×10^6 A/cm² using acetylacetonate precursors. Shibata and co-authors^{12,13} also made thin films with J_c of 1×10^6 A/cm² from trifluoroacetate precursors on a substrate which is covered with a buffer layer of CeO_2/YSZ .

On the other hand, superconductive fibers and bulk bodies with the critical temperature of 88.2 K for $YBa_2Cu_3O_{7-\delta}$ were prepared by the calcination of precursors obtained by the reac-

tion of (ethyl acetoacetato)metal complexes with triethanolamine (H₃tea).¹⁴ These superconductive fibers are, however, so brittle that the superconductive properties have not been fully evaluated. In this study, therefore, the preparation of superconductive films from YBCO and BSCCO precursors by the reaction of (ethyl acetoacetato)metal complexes ([M(etac)_n]: M = Y, Ba, Cu, Bi, Sr, Ca) with H₃tea according to Eq. 1 will be reported. Such films have high homogeneity, stability against condensation, solubility in organic solvents, and melt-spinnability. Furthermore, evaluation of superconductive properties and surface properties was performed for the superconductive thin films prepared by spin-coating and calcination.

$$\begin{array}{c} \mathsf{M}(\mathsf{etac})_n + m \ \mathsf{N}(\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH})_3 & \longrightarrow \\ (\mathsf{etac})_{n-m}\mathsf{M} & \overbrace{\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH}}^{\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH}} & (1) \\ & \overset{(1)}{\mathsf{CH}_2\mathsf{CH}_2\mathsf{OH}} & \underset{m}{\overset{(1)}{\mathsf{H}}} + m \ \mathsf{Hetac} \end{array}$$

Results and Discussion

Preparation of YBCO and BSCCO Precursors. The reaction of H_3 tea with ethyl acetoacetato complexes was followed by the determination of the amount of Hetac formed, using gas chromatography on the reaction of H_3 tea with metal chelate in the molar ratio of 1:1. The results are summarized in Table 1. On the reaction of [Bi(etac)_3] with H_3 tea, 3 equivalent amounts of Hetac was recovered. Similarly, [Y(etac)_3] produced 2 equivalent amounts of Hetac. [Cu(etac)_2], [Sr(etac)_2], and [Ca(etac)_2] produced 1 equivalent amount of Hetac. On the other hand, Hetac was not formed when the reaction was with [Ba(etac)_2]. These results suggest the formation of YBCO and BSCCO precursors by the reaction of H_3 tea with ethyl

Table 1. Results of the Reaction of Chelate with H₃tea^{a)}

Molar ratio of Hetac formed ^{b)}			
Hetac/chelate			
2.0			
0.0			
1.0			
3.0			
1.0			
1.0			

a) Reaction condition: reflux 1 h in ethanol. Molar ratio of H_3 tea/chelate: 1.0. b) Calculated from the amount of Hetac in the reaction mixture by gas chromatography.

acetoacetato complexes based on a ligand exchange reaction between H_3 tea and Hetac.

The results on the preparation of YBCO and BSCCO precursors are shown in Table 2. When the molar ratio of H_3 tea to [Cu(etac)₂] was lower than 1.3 (for YBCO) or 4.5 (for BSCCO), a copper compound precipitated during the concentration process and a heterogeneous precursor was formed. The YBCO precursors showed spinnability on melting at 70–80 °C. The YBCO and BSCCO precursors decomposed on heating above the temperatures of 90 °C and 60 °C, respectively. The DTA-TG analyses of these precursors are shown in Figs. 1 and 2. These traces showed exothermic peaks with weight losses at 450 °C (YBCO) and 400 °C (BSCCO). The ceramic yields were calculated based on the residual weight after the DTA-TG analysis at 800 °C, which decreased gradually with increasing molar amount of H₃tea. The YBCO and BSCCO precursors were soluble in acetone, tetrahydrofuran, methanol, and ethanol, while they were less soluble in chloroform, carbon tetrachloride, and benzene.

As $[Y(etac)_3]$, $[Ba(etac)_2]$, and $[Cu(etac)_2]$ behave as difunctional, inert, and monofunctional, against H₃tea, respectively, a plausible structure of YBCO precursor is shown in Scheme 1. Yttrium and copper are connected by means of a ligand exchange reaction between H₃tea and etac. The coordination of the oxygen and nitrogen atoms in H₃tea to Ba atom in $[Ba(etac)_2]$ can be postulated, because no precipitation was observed on mixing $[Ba(etac)_2]$ and H₃tea. Moreover, the BSCCO precursors are considered to be formed by the same systems.

Superconductive Properties of YBCO Superconductive Thin Films. In this study, SrTiO₃ (a = 3.905 Å), MgO (a = 4.203 Å), and LaAlO₃ (a = 3.792 Å) were used as substrates for the epitaxial growth of a superconductive phase because the lattice constants are close to YBa₂Cu₃O_{7-δ} (a = 3.82 and b = 3.89 Å). The X-ray diffraction pattern of YBCO superconductive thin film, which was formed on the

Table 2. Preparation Condition and Properties of Precursors

No.	Composition	Molar ratio H ₃ tea/[Cu(etac) ₂]	Softening point/°C	Spinnability at 90 °C/cm	Decomposition point/°C	Ceramic yield ^{a)} /%
1	YBCO ^{b)}	1.3	70-80	2–3	>90	36
2		1.5		20-30		34
3		1.7		120-150		32
4		2.0		150-200		31
5	BSCCO ^{c)}	4.5	58-68	0	>60	33
6		4.7		5		27
7		5.0		15		20
8		5.5		30		18
9		6.0		60		15

a) Calculated based on the remaining weight at 800 °C by thermogravimetry. b) Scale in operation (g (mmol)): [Y(etac)₃], 1.9918 (4.182); [Ba(etac)₂], 3.3080 (8.363); [Cu(etac)₂], 4.0366 (12.55). Solvent: EtOH, 180 mL. Time and temp.: 1 h under reflux. c) Scale in operation (g (mmol)): [Bi(etac)₃], 5.23 (8.78); [Sr(etac)₂], 2.7095 (7.8979); [Ca(etac)₂], 1.3079 (4.3877); [Cu(etac)₂], 3.1038 (9.653). Solvent: EtOH, 200 mL. Time and temp.: 2 h at 50 °C.



Fig. 1. DTA-TG traces of YBCO precursor (Y:Ba:Cu = 1:2:3; H₃tea/[Cu(etac)₂] = 2.0).



Fig. 2. DTA-TG traces of BSCCO precursor (Bi:Sr:Ca: Cu = 2:1.8:1.0:2.2; H_3 tea/[Cu(etac)₂] = 4.5).



Scheme 1. A possible structure of YBCO precursor.



Fig. 3. X-ray diffractogram of YBCO superconducting thin film.

SrTiO₃ substrate by calcination at 850 °C, is shown in Fig. 3. The epitaxial growth toward the *c* axis of YBa₂Cu₃O_{7- δ} phase was observed because all peaks observed were ascribed to (00*l*) peaks, while a slight contamination of YBa₂Cu₄O₈ phase was observed. A relatively narrow peak width suggests an excellent orientation and good crystallinity of this thin film. The peaks at $2\theta = 44$, 49, and 52° are ascribed to the diffraction pattern of the substrate. The main diffraction peaks of the substrate have overlapped with the peaks of the YBa₂Cu₃O_{7- δ} phase due to (003) and (006) diffractions. A similar *c* axis orientation was observed when MgO and LaAlO₃ were used as substrates.

The SEM image of the surface of a YBCO superconductive thin film, which was prepared by calcination at 850 °C on SrTiO₃ substrate with the film thickness of 10 μ m, is shown in Fig. 4. A flat and smooth surface consisting of crystal grains of 1–2 μ m size was observed. The white portion would reflect the high electric conductivity, which, in turn, is ascribed to the crystal grain of CuO due to the incomplete calcination to form YBa₂Cu₃O_{7– δ} phase.

The temperature dependency of the electric resistance of YBCO superconductive thin film, which was prepared on SrTiO₃ substrate by calcination at 850 °C and $pO_2 = 2.7 \times 10^2$ Pa, is shown in Fig. 5. The resistivity decreased rapidly at 90.0 K ($T_{c(onset)}$) and decreased to zero at 88.7 K ($T_{c(zero)}$). The difference between $T_{c(onset)}$ and $T_{c(zero)}$ was very small, 1.3 K. The J_c of YBCO superconductive thin film was 5×10^5 A/cm² at 77 K and 0 T.



Fig. 4. SEM image of YBCO film prepared from the precursor.



Fig. 5. Temperature dependence of the resistivity of YBCO film.



Fig. 6. X-ray diffractogram of the BSCCO superconducting film.

Superconductive Properties of BSCCO Superconductive Thin Films. During the preparation of BSCCO superconductive thin films, MgO was used as a substrate for the epitaxial growth of a superconductive phase. The X-ray diffraction pattern of BSCCO superconductive thin film is shown in Fig. 6. The epitaxial growth toward the *c* axis of Bi₂SrCa₂Cu₂O_{8+y} phase was observed because all peaks observed were due to (00*l*) peaks. The peak due to the substrate was observed at $2\theta = 43^{\circ}$. Moreover, the diffraction peaks at $2\theta = 17$ and 22° are considered to be from the Bi₂SrCa₂Cu₂O_{8+y} phase.

The observation of the surface of a film by the laser beam microscope is shown in Fig. 7. The white portions have swollen up and the black portions serve as holes. Moreover, the measurement of the surface profile of the section from points A to B showed that the largest hole within the measured area was 1.1 μ m with a radius of 0.9 μ m. Since the difference of peaks and troughs on the film surface was about 1 μ m and film



Fig. 7. Surface depth profile of BSCCO thin film.



Fig. 8. Temperature dependence of the resistivity of the BSCCO film.

thickness was 10 μ m, the Bi₂SrCa₂Cu₂O_{8+y} superconductive thin film had a relatively flat and smooth surface.

The temperature dependence of the resistance of the BSCCO superconductive thin film is shown in Fig. 8. The $T_{c(onset)}$ was 92 K and the $T_{c(zero)}$ was 77 K. The relatively big difference between $T_{c(onset)}$ and $T_{c(zero)}$ is considered to be due to the low degree of orientation toward the *c* axis and the degradation of the superconductive property due to contamination by impurity phases, which are understood from the relatively broad peaks in X-ray diffraction pattern. The J_c at 5 K was 6×10^4 A/cm².

Experimental

Reagents. Reagent grade yttrium(III) trichloride hexahydrate, barium, copper(II) acetate anhydride, bismuth(III) chloride, calcium, and sodium (Wako Pure Chemical) were used as purchased. Reagent grade strontium (Soekawa Chemical) was used as purchased. Other reagents (Wako Pure Chemical) were purified by conventional methods.

Synthesis of Tris(ethyl acetoacetato)yttrium(III) ([Y-(etac)₃]). Yttrium(III) trichloride hexahydrate 9.1 g (0.030 mol) was mixed with 50 mL of benzene and 50 mL of isopropyl alcohol. The mixture was heated to evaporate water by azeotropic distillation. When almost all of the liquid was distilled, another 50

mL of benzene and isopropyl alcohol were added. This procedure was repeated 4 times. Tetrahydrofuran 250 mL, ethyl acetoacetate 13.0 g (0.11 mol), and triethylamine 11.0 g (0.11 mol) were added at the temperature of 5–10 °C; then stirring was continued for 5 h at room temperature. After filtration of triethylamine hydrochloride followed by concentration, the residual solid was subjected to recrystallization using carbon tetrachloride. White pellet-like crystals were obtained by drying under reduced pressure. The yield was 54%.

Synthesis of Bis(ethyl acetoacetato)barium(II) ([Ba(etac)_2]). Barium, 10.80 g (0.079 mol), was put into the mixture of 200 mL of cyclohexane, and ethyl acetoacetate, 61.40 g (0.472 mol); then the mixture was stirred in an ice bath until the barium disappeared. The white precipitate was washed with hexane and dried under reduced pressure. The solid was dissolved in 250 mL of tetrahydro-furan and then subjected to hot filtration and condensation. White pellet-like crystals were obtained by recrystallization with ethanol. The yield was 57%.

Synthesis of Bis(ethyl acetoacetato)copper(II) ([Cu(etac)₂]). Ethyl acetoacetate, 32 g (0.26 mol), was added to anhydrous copper(II) acetate, 10.0 g (0.55 mol), dissolved into ethanol (450 mL), and then the mixture was subjected to reflux and cooling to obtain crystals of crude product. Green needle-like crystals were isolated by recrystallization using ethanol; decantation and drying under reduced pressure followed. The yield was 91%.

Synthesis of Tris(ethyl acetoacetato)bismuth(III) ([Bi-(etac)₃]). Into a refluxing solution of bismuth trichloride, 14.85 g (0.047 mol) in 45 mL of ethanol, a solution of sodium ethoxide 9.61 g (0.14 mol) in 120 mL of ethanol was added, followed by addition of 28 mL of benzene. The solution was refluxed for 5 h under dark condition. The white solid thus formed was separated by hot filtration. Bismuth(III) triethoxide was isolated by recrystallization of the filtrate as colorless pillar-like crystals in the yield of 5.55 g (0.016 mol).

Into bismuth(III) triethoxide 5.55 g (0.016 mol) suspended in 60 mL of benzene, 6.28 g (0.0483 mol) of ethyl acetoacetate was added. After stirring for 2 h at room temperature, insoluble material was filtered and then concentrated. Colorless pillar-like crystals were obtained by recrystallization from the mixed solvents of hexane and benzene in 4/1 volume ratio. The yield was 85%.

Synthesis of Bis(ethyl acetoacetato)strontium(II) ([Sr-(etac)₂]). A mixture of 40 mL of hexane, 74.10 g (0.57 mol) of ethyl acetoacetate, and 25.00 g (0.29 mol) of strontium was stirred at room temperature for 20 h. After concentration and dissolving in ethanol, insoluble matter was separated by hot filtration. The filtrate was subjected to concentration and recrystallization from ethanol. White pellet-like crystals were obtained by washing the precipitate with hexane and drying. The yield was 24%.

Synthesis of Bis(ethyl acetoacetato)calcium(II) ([Ca(etac)_2]). A mixture of 5 mL of tetrahydrofuran, 167.50 g (1.3 mol) of ethyl acetoacetate, and 5.48 g (0.14 mol) of calcium was stirred at room temperature until the calcium totally disappeared. After concentration and dissolving in ethanol, insoluble matter was separated by hot filtration. The filtrate was subjected to concentration and recrystallization from ethanol. White pellet-like crystals were obtained by washing the precipitate with hexane and drying. The yield was 55%.

Preparation of YBCO and BSCCO Precursors. All reactions were performed under a dry nitrogen atmosphere.

(Ethyl acetoacetato)metal complexes were mixed in the stoichiometric molar ratio Y:Ba:Cu = 1:2:3 for YBCO and Bi:Sr: Ca:Cu = 2.0:1.8:1.0:2.2 for BSCCO. The stated amount of H₃tea was added and the mixture was refluxed for a certain period. Highly viscous liquid was obtained by condensation under reduced pressure, and then foamed and solidified by further heating. The precursor was obtained by grinding this solid. The spinnability was evaluated by measuring the length of a fiber drawn by pulling a glass rod up from the solution.

Preparation of YBCO Superconductive Thin Films. The YBCO precursor, which was prepared by adding 2.0 equivalent moles of H₃tea compared to copper, was dissolved in ethanol to provide a 16 wt % solution. This solution was dropped on the substrate of SrTiO₃, MgO, or LaAlO₃ (10 mm × 10 mm) and spun at 3000 rpm for 30 s and then heated at 150 °C for 10 min. This procedure was repeated 10 times. The YBCO superconductive thin film was obtained by the calcination of the coating film under the following conditions: the film was placed under low oxygen pressure (2.7×10^2 Pa) and the temperature was raised quickly to 850 °C and then held there for 2 h. The atmosphere was changed to pure oxygen and the film was heated at 450 °C for 48 h then cooled to room temperature.

Preparation of BSCCO Superconductive Thin Films. The BSCCO precursor, which was prepared by adding 4.0 equivalent moles of H₃tea compared to copper, was dissolved in ethanol to provide a 20 wt % solution. Spin-coating on the substrate of MgO (10 mm \times 10 mm) was carried out by the following process: dropping the solution and spinning at 1000 rpm for 5 s, dropping the solution and spinning at 4000 rpm for 5 s, and then heating for 15 min at 500 °C. This procedure was repeated 10 times. The BSCCO superconductive thin film was obtained by the calcination of the coating film at 810 °C for 10 min under air atmosphere.

Measurements. Softening point and decomposition point were measured by a YANACO Micro Meltingpoint Apparatus MP-S3. Each sample was sealed in a glass tube and heated at the heating rate of $1 \, ^{\circ}C/min$.

Differential thermal analysis-thermogravimetry (DTA-TG) results were recorded by a MAC Science TG-DTA2020S under air atmosphere at the heating rate of 2 $^{\circ}$ C/min.

X-ray diffraction results were recorded by a Rigaku RAD-X system using $Cu K \alpha$ radiation.

Scanning electron microscopy (SEM) was performed on a JEOL JSM-T330A.

The resistivity of the thin film was measured using a laboratory-made system by direct current four-pin method. The interval of temperature measurement was 2 K when away from T_c , and 0.5– 0.2 K near the T_c . The current used in the measurement was 0.05 mA. The temperature at which resistivity begins to decrease rapidly was taken as $T_{c(onset)}$, and the temperature at which the resistivity becomes unmeasureable was taken as $T_{c(zero)}$.

The J_c was measured by a laboratory-made system by direct current four-pin method. Pulsed current was applied for 1 s in every 4 s. The critical current (I_c) was obtained using a voltage criterion of 1 μ V/cm. The film thickness was measured by SEM for the cross-section of the films. J_c was calculated based on the distance between two patterned bridges and the film thickness.

Conclusion

Homogeneous YBCO and BSCCO precursors were prepared by the reaction of triethanolamine with ethyl acetoacetato complexes of Y, Ba, and Cu and those of Bi, Sr, Ca, and Cu, respectively. These precursors were considered to be polymers in which the metals are connected by bridges of triethanolamine with the elimination of ethyl acetoacetate. These precursors were highly stable against self-condensation and showed high solubility in organic solvents.

Superconductive thin films were prepared simply by dissolving the precursor in an organic solvent, spin-coating the precursor solution on a substrate, and then calcining the spun film. The epitaxial growth, with the *c* axis normal to the substrate surface, of YBa₂Cu₃O_{7- δ} and Bi₂SrCa₂Cu₂O_{8+y} phases was observed. The critical temperature of YBCO superconductive thin film was 90.0 K ($T_{c(onset)}$) and 88.7 K ($T_{c(zero)}$) and the critical current density at 77 K and 0 T was 5 × 10⁵ A/cm². The $T_{c(onset)}$ and $T_{c(zero)}$ of BSCCO superconductive thin film were 92 K and 77 K, respectively. The J_c at 5 K was 6 × 10⁴ A/cm².

The authors thank Mr. Yohei Tsunochi for his helpful guidance and cooperation on the preparation and characterization of superconductive thin films.

References

1 J. G. Bednorz and K. A. Muller, Z. Phys. B: Condens. Matter, 64, 189 (1986).

2 S. Sakka, "The Science of Sol–Gel Process," Agne Shofu, Tokyo (1999), pp. 142–145.

3 Materials Science Society of Japan, "The Foundation and Materials of Electric Conduction," Sho Kabo, Tokyo (1991), pp. 218–227.

4 Materials Science Society of Japan, "The Ferroelectricity, High-temperature Superconductivity," Sho Kabo, Tokyo (1993), pp. 178–203.

5 D. P. Norton, A. Goyal, J. D. Budai, D. K. Christen, D. M. Kroeger, E. D. Specht, Q. He, B. Saffian, M. Paranthaman, C. E. Klabunde, D. F. Lee, B. C. Sales, and F. A. List, *Science*, **274**, 755 (1996).

6 H. Zama, N. Tanaka, and T. Morishita, J. Cryst. Growth, **221**, 440 (2000).

7 X. D. Wu, S. R. Foltyn, P. N. Arendt, W. R. Bluenthal, I. H. Campbell, J. Y. Coulter, W. L. Hults, M. P. Maley, H. F. Safar, and J. L. Smith, *Appl. Phys. Lett.*, **67**, 2397 (1995).

8 Y. Iijima, N. Tanabe, O. Kohno, and Y. Ikeno, *Appl. Phys. Lett.*, **60**, 769 (1992).

9 M. Paranthaman, C. Park, X. Cui, A. Goyal, D. F. Lee, P. M. Martin, T. G. Chirayil, D. T. Verebelyi, D. P. Norton, D. K. Christen, and D. M. Kroeger, *J. Mater. Res.*, **15**, 2647 (1992).

10 P. C. McIntyre, M. J. Cima, J. A. Smith, Jr., R. B. Hallock, M. P. Siegal, and J. M. Phillips, *J. Appl. Phys.*, **71**, 1868 (1992).

11 T. Kumagai, T. Manabe, W. Kondo, H. Minamiue, and S. Mizuta, *Jpn. J. Appl. Phys.*, **29**, L940 (1990).

12 T. Araki, Y. Takahashi, K. Yamagiwa, Y. Iijima, K. Takeda, Y. Yamada, J. Shibata, T. Hirayama, and I. Hirabayashi, *Physica C*, **357–360**, 991 (2001).

13 H. Fuji, T. Honjo, Y. Nakamura, T. Izumi, T. Araki, I. Hirabayashi, Y. Shiohara, Y. Iijima, and K. Takeda, *Physica C*, **357–360**, 1011 (2001).

14 Y. Abe, K. Hara, K. Hirai, T. Gunji, Y. Nagao, and T. Misono, *J. Ceram. Soc. Jpn.*, **102**, 765 (1994).