

Review

Application of Sol-Gel Processing to Preparation of High Temperature Superconducting Materials

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Received May 10, 1988

Preparation of high temperature superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ through sol-gel method has been described. Two kinds of precursors for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ have been presented; an aqueous solution of metal acetates and a triethanolamine solution of metal alkoxides. Analysis of phases formed on heat-treatment of the acetate-derived gel has shown that $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase is formed at lower temperatures than in the conventional powder-route method and superconductors with critical temperature of zero resistivity higher than 90 K can be obtained in a short time without repeated grinding and calcination. Gel fibers can be drawn from the acetate-derived viscous sol, and heat treatment of the gel fibers results in formation of superconducting ceramic fibers with a hollow structure. The metal alkoxide solution is shown to be used as a precursor for superconducting coating films. Repeated application of the solution on a zirconia substrate and annealing the film under flowing O_2 gives superconducting film of 7 μm in thickness.

KEY WORDS: Superconductor/ Sol-Gel Method/ Fibers/ Coating Films/

1. INTRODUCTION

Chemistry of precursors for processing of the new high temperature superconducting ceramics is attracting a great attention, because homogeneity and microstructure of ceramics, which seriously affect superconducting nature, are much influenced by the nature of the precursor. The most common precursor for the superconducting oxide $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is the mixture of Y_2O_3 , BaCO_3 and CuO powders, which transforms into $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics through solid-state reaction.¹⁾ Because of the inhomogeneous nature of the starting materials, preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ ceramics having critical temperature T_c higher than 90 K through the solid-state powder route requires repeated grinding and calcination over extensive periods in order to improve homogeneity and obtain higher yield of the superconducting phase.²⁾

Many attempts have been made to synthesize precursors of higher homogeneity from solutions, which are expected to enable the formation of homogeneous super-

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conducting ceramic products at lower temperatures in shorter times. Coprecipitation method is one of the solution methods, 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.³⁻¹¹⁾ In this method, the resultant precursors are obtained in the form of fine powder. A problem in this method resides in difficulty in controlling the final composition of the precipitates. Codecomposition of the mixture of metal nitrates is a quite simple technique, where a concentrated aqueous solution of metal nitrates is directly thermally decomposed.^{3,12)} Sol-gel emulsion technique is another method for making homogeneous fine powder. In this method, micrometer-sized droplets of metal salt solution dispersed in heptane are transformed into hydroxide particles by raising the pH of the droplets by adding high molecular-weight primary amine.¹³⁾

Compared with the powder-form precursors obtained through the chemical routes mentioned above, precursors obtained in the form of homogeneous sol or gel are more favorable in some cases, because generally sol can be used as the precursors for coating films, gel fibers, and monolithic gels, which can be directly transformed into shaped ceramic bodies.^{14,15)} The amorphous citrate process provides a homogeneous sol and gel in the Y-Ba-Cu-O system, where citric acid added to aqueous solutions of Y, Ba and Cu nitrates can bridge metal cations in the solution to form a gel matrix.^{16,17)} Polyacrylic acid can also be used as Y-Ba-Cu-O gel matrix.¹⁸⁾ Polymerization reaction between Y, Ba and Cu methacryloxides was shown to be used to make viscous polymers.¹⁹⁾

Metal alkoxides are of great importance as the raw materials in the solution methods, since hydrolyzed species of alkoxides are expected to be condensed to form metal-oxygen-metal bond in the solutions, and alcohols produced as a result of hydrolysis reaction are so chemically stable that remarkable undesired chemical reactions in the subsequent process can be avoided. Solvents which dissolve copper alkoxides have to be sought, however, in order to apply this method to the Y-Ba-Cu-O system. Copper alkoxides are known to be insoluble in alcohols, which have been widely used as solvents in the alkoxide method. So far, some attempts have been made to prepare homogeneous alkoxide solutions.²⁰⁻²²⁾

Preparation of superconducting coating films from metal carboxylates,²³⁻²⁷⁾ inorganic salts,^{24,29)} citrates,³⁰⁾ and alkoxides,^{31,32)} and fiber drawing from viscous sols or solutions of metal alkoxides,^{21,22)} metal-methacryloxides¹⁹⁾ and metal nitrates³³⁾ have been reported.

The present authors have presented two kinds of sol-gel routes for preparing YBa₂Cu₃O_{7-x} superconductor.³⁴⁻³⁷⁾ One is the gel formation from an aqueous solution of metal acetates. Transparent spinnable sols and gel pieces have been formed by adjusting the pH of the solution and concentrating the pH-controlled solution.³⁴⁻³⁶⁾ The other one is the homogeneous sol formation from metal alkoxides, where triethanolamine is used to dissolve copper alkoxide.³⁷⁾ In the present review, synthesis of solutions, sols and gels as precursors for YBa₂Cu₃O_{7-x} ceramics, conversion of the acetate-derived gel to superconducting oxide by heat treatment, fabrication of super-

conducting fibers from the acetate sol, and preparation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ coating films from the alkoxide solution will be described.

2. PREPARATION OF SOLUTION, SOL AND GEL

2.1 Metal Acetate Route

Transparent homogeneous viscous sol and glassy gel are obtained by concentrating the pH-controlled aqueous solution of metal acetates. 2.12 g $\text{Y}(\text{CH}_3\text{COO})_3 \cdot 4\text{H}_2\text{O}$, 3.20 g $\text{Ba}(\text{CH}_3\text{COO})_2$ and 3.41 g $\text{Cu}(\text{CH}_3\text{COO})_2$ are dissolved in 100 ml water. After raising the pH of the solution from 5.6 to 6 by ammonia water, the solution is kept in a 100 ml beaker without cover at 60°C , in order to evaporate and concentrate the solution. Dark blue transparent gel is obtained in 3 days accompanied with 90% loss of the solvent in volume. Figure 1 shows dried gel pieces vacuum-treated at 90°C . The amorphous nature of the gel is confirmed in the X-ray diffraction pattern of the gel.³⁴⁾ No distinct microstructure is seen in the scanning electron micrograph of the gel, which reflects its chemically homogeneous nature (see Fig. 2).

It should be pointed out that gel formation is possible only in a limited pH range of the solution at around 6, meaning that a definite amount of ammonium ions in the solution is necessary for gel formation. pH-controlled aqueous solutions consisting of metal nitrates instead of metal acetates were investigated, but no gel formation could be found, indicating that acetate ions present in the solution should play an important role in gel formation. Formation of metal-oxygen-metal bond during the sol-gel reaction as usually found in the hydrolyzed silicon alkoxide solutions¹⁴⁾ does not appear to be present in the acetate solution, which could be seen from the absence of the infrared absorption band of the gel in the frequency range below 600 cm^{-1} , attributed to the vibration of metal-oxygen-metal bonds.³⁴⁾ Thus the acetate-derived gel is thought to consist of weakly bonded metal cation complexes. On the basis of the fact that copper acetate crystals precipitated from the concentrated solution containing no ammonia water, ammonia molecules are thought to transform the coordinated structure of copper acetates, acting as ligands of copper ions. The

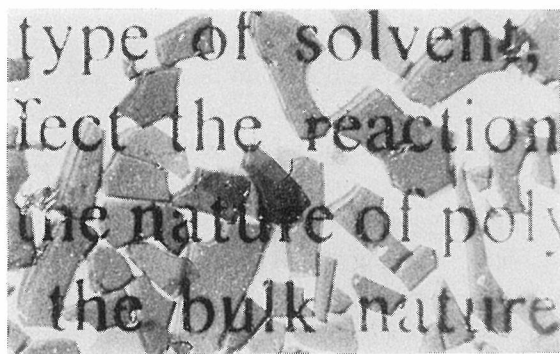


Fig. 1. Appearance of the acetate-derived gel pieces.

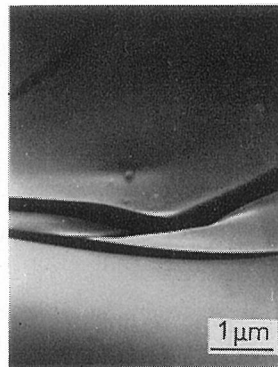


Fig. 2. Scanning electron micrograph of the acetate-derived gel.

role of the acetate ions in the gel formation may consist in bridging between metal cations through the two electrically negative oxygens of the $-\text{COO}$ group.³⁸⁾ Linear linking of the metal cations may cause spinnability of the viscous sol.³⁹⁾

2.2 Metal Alkoxide Route

As mentioned above, copper alkoxides are insoluble in alcohols,⁴⁰⁾ the most common solvents used in the alkoxide sol-gel process. Therefore, in order to make homogeneous solutions, it is necessary to use other soluble copper salts or find solvents which dissolve copper alkoxides.

Copper acetylacetonate and copper acetate are soluble in alcohol. However, blue precipitates are formed, when a solution consisting of $\text{Ba}(\text{OC}_4\text{H}_9)_2$ and $\text{Y}(\text{OC}_4\text{H}_9)_3$, and an alcoholic solution of the above copper salts are mixed. This precipitation is assumed to arise as a result of ligand exchange between barium or yttrium alkoxide and copper salt, leading to the formation of insoluble copper alkoxide.

The present authors have found that copper alkoxides are soluble in triethanolamine and have prepared homogeneous solutions consisting of Y, Ba and Cu alkoxides.³⁷⁾ 0.866 g Ba metal is dissolved in 100 ml methanol under reflux in N_2 to make a barium methoxide solution. Separately, 7.26 ml xylene solution of 0.44 mol/l $\text{Y}(\text{OC}_4\text{H}_9)_3$ (Hokko Chemical Industry Co. Ltd.) is added to the mixture of 38 ml methanol and 5 ml triethanolamine, and the resultant solution is added to the barium methoxide solution. 1.199 g $\text{Cu}(\text{OCH}_3)_2$ synthesized by the reaction of LiOCH_3 with CuCl_2 ⁴¹⁾ is added to the resultant solution under stirring to obtain a dark blue solution. A high basicity of a nitrogen atom in triethanolamine may produce partially or completely amine-coordinated copper, which makes the copper alkoxide soluble in the solution.

3. CONVERSION OF ACETATE-DERIVED GEL TO $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ CERAMICS

When heated, the acetate derived gel pieces bloat vigorously in the temperature range $200^\circ\text{--}300^\circ\text{C}$ and the porous nature of the product remains up to higher temperatures as shown in Fig. 3. Corresponding weight loss of the gel is seen in the thermogravimetric analysis curve (see Fig. 4), where the loss of ammonium ion and water is detected in the infrared absorption spectra.³⁴⁾

Each metal compound is found to be separately precipitated from the gel in

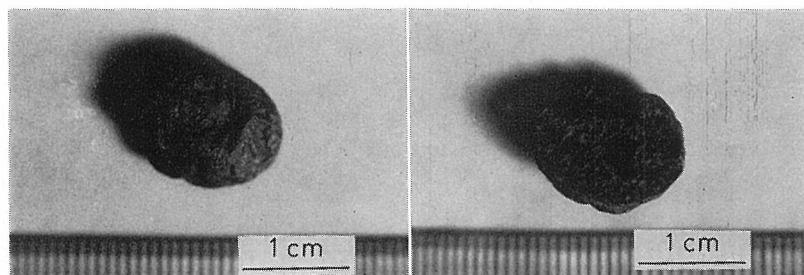


Fig. 3. Appearance of the gel-derived sample heated to 910°C at a rate of $5^\circ\text{C}/\text{min}$ on a Pt plate. (a) upper side. (b) bottom side.

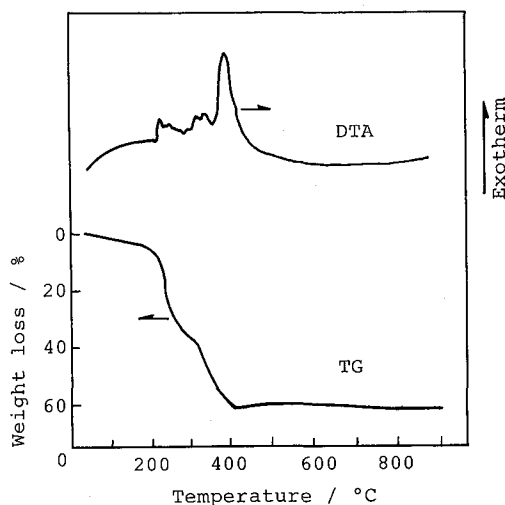


Fig. 4. DTA and TG curves of the acetate-derived gel powder. A heating rate of 10°C/min was used for measurement.

Table 1 Phases identified by X-ray diffraction analysis for gel-derived products heated at a rate of 5°C/min.

Temp./°C	Phases
90	Amorphous
230	Cu, Cu ₂ O
340	Cu, Cu ₂ O, Ba(OH) ₂
450	CuO, BaCO ₃ , Y ₂ O ₃
600	CuO, BaCO ₃ , Y ₂ O ₃
750	CuO, BaCO ₃ , Y ₂ O ₃ , YBa ₂ Cu ₃ O _{7-x}
910	YBa ₂ Cu ₃ O _{7-x}

the heat treatment. Table 1 shows the crystalline phases formed in the gel during heat treatment. It is seen that Cu and Cu₂O precipitate at around 200°C, and Ba(OH)₂ forms at around 300°C. Ba(OH)₂ turns into BaCO₃ at around 450°C, which is caused by the reaction between Ba(OH)₂ and CO₂, generated through thermal decomposition of the acetate ions. A large exothermic peak at 400°C attributed to decomposition of acetate ions is seen in the differential thermal analysis curve (see Fig. 4). Oxidation of Cu and Cu₂O and precipitation of Y₂O₃ occur at around 450°C.

Although the formation of YBa₂Cu₃O_{7-x} phase from the gel takes place through the reaction among Y₂O₃, BaCO₃ and CuO as in the case of the conventional powder-route, more intimate state of mixing in the gel-derived material allows the YBa₂Cu₃O_{7-x} formation at lower temperature. Figure 5 shows the X-ray diffraction patterns of the gel-derived materials heated at a rate of 5°C/min to 750°, 800° and 910°C, kept there for 19 h and cooled down to room temperature in the furnace. The pattern for the conventional powder-route sample prepared by mixing Y₂O₃, BaCO₃

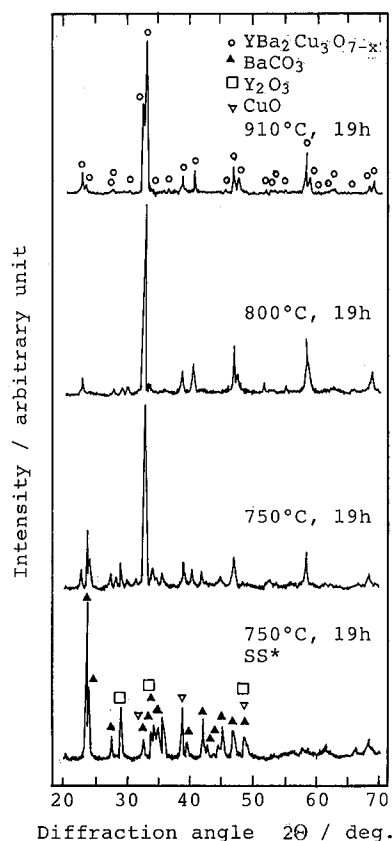


Fig. 5. X-ray diffraction patterns for the gel-derived products heated at a rate of 5°C/min to 750°, 800° and 910°C, kept there for 19 h, and cooled down in the furnace. *SS: prepared through the conventional powder-route method.

and CuO powders for 1 h, pressed isostatically under 750 kg/cm², and then heat-treated in the same manner as the gel is also shown in the figure. As seen from the figure, the $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ phase does not form at 750°C in the powder-route sample, but does form in the gel-derived sample. Heat treatment of the gel-derived sample at 800°C results in formation of $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ nearly in a single phase.

Repeated grinding or calcination is not required for obtaining superconductor of T_c higher than 90 K from the gel. Figure 6 shows the temperature dependence of the electrical resistance of the gel-derived products. Electrodes are set on the upper side surface of the sample. It should be emphasized that such a mild heat treatment in air as heating at a rate of 5°C/min, soaking at 910°C for 5 h and cooling down in the furnace gave rise to formation of a superconducting product with $T_{c(\text{end})}$ at 93 K. Such a rapid formation of high T_c superconducting materials cannot be expected in the conventional powder-route method. However, the product heat-treated at 800°C does not show superconductivity, although the main phase analyzed by X-ray diffraction is $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (see Fig. 5). The semiconducting behavior

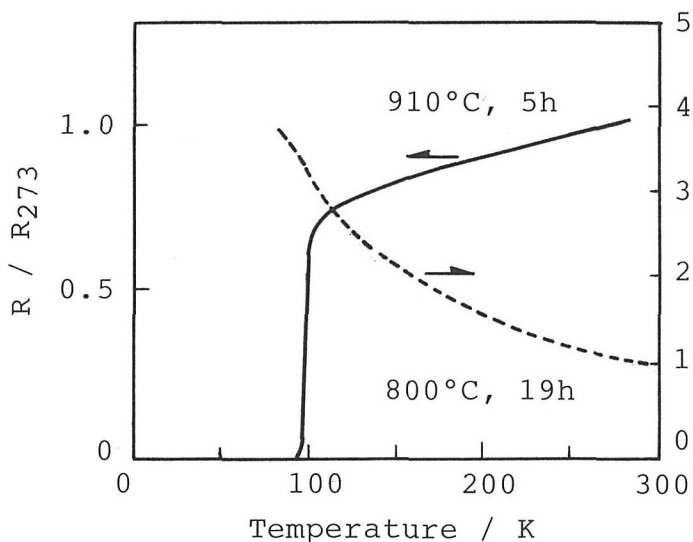


Fig. 6. Resistance vs. temperature for the gel-derived products heated at a rate of 5°C/min, heat-treated at 800°C for 19 h (----) or at 910°C for 5 h (—), and cooled down in the furnace.

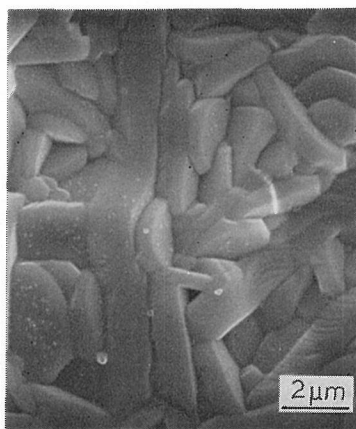


Fig. 7. Scanning electron micrograph of the upper side surface of the gel-derived product heated at a rate of 5°C/min to 950°C, kept there for 19 h, and cooled down in the furnace.

of this product may be related to the incomplete crystallinity revealed in the absence of the splitting in the main diffraction peak at 32.8° (see Fig. 5).

As mentioned before, the heat-treated products appear porous macroscopically, but microscopically, small crystals are densely arranged in the upper side surface of the products. Figure 7 shows the scanning electron micrograph of the gel-derived superconducting sample, where dense arrangement of crystals of the size 1–5 μm can be seen. $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ crystals of the size 10–50 μm, much larger than that observed here, are often reported in the products obtained by the powder-route method.

4. FIBERS

When concentrated, the pH-adjusted acetate solution turns into a viscous sol before gelation, and gel fibers of the diameter $5\mu\text{m}$ to 2mm can be drawn from the sol by putting a glass rod into the sol and drawing it up. Drawing gel fibers of more than 50cm in length is possible. Figure 8(a) shows the scanning electron micrograph of the gel fibers. Fibers with smooth surface and round-shaped cross-sections can be seen in the micrograph.

When heated on a substrate, the gel fibers soften and adhere to the substrate, so heat treatment of the gel fibers should be performed by suspending them from a ceramic rod, in order to keeping the fibers off the solid materials. As seen in Fig. 8(b), the smoothness of the gel fiber surface is lost and the fiber takes a hollow struc-

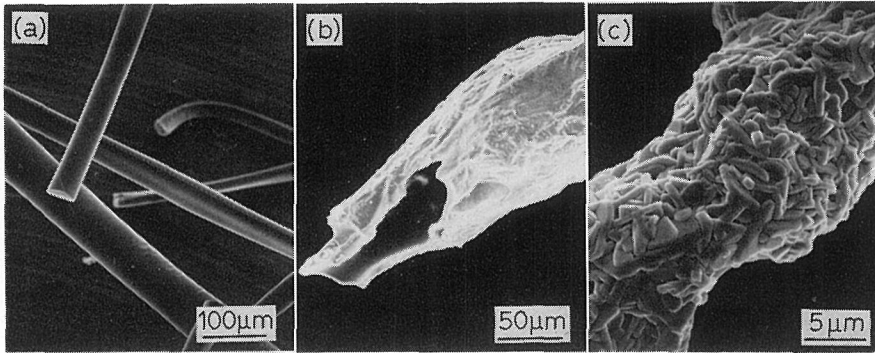


Fig. 8. Scanning electron micrographs of the Y-Ba-Cu-O fibers. Gel fibers (a) and fibers heated at a rate of $5^\circ\text{C}/\text{min}$ to 250°C (b) or 950°C (c).

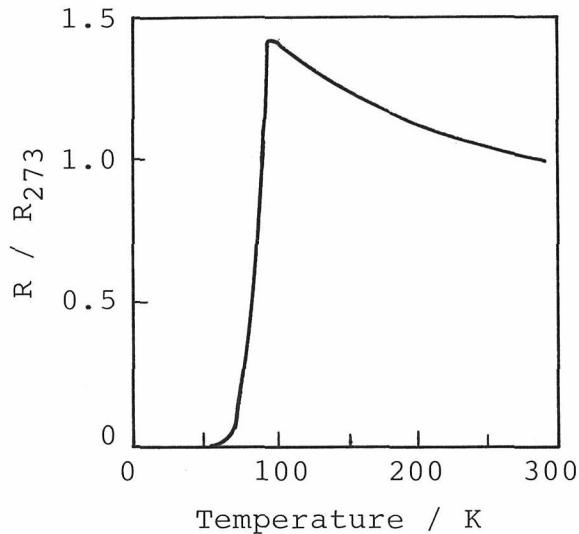


Fig. 9. Resistance vs. temperature for the fiber of 1mm in diameter, heated at a rate of $5^\circ\text{C}/\text{min}$ to 900°C , kept there for 8h , and cooled down in the furnace.

ture as a result of bloating at around 200°C. Such a structure of the fibers remains at higher temperatures where $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ is formed (see Fig. 8(c)), which gives rise to the fragile nature of the heat-treated fibers.

Figure 9 shows the temperature dependence of the electrical resistance of a fiber, 1 mm in diameter, heated at a rate of 5°C/min to 900°C, kept there for 8 h and cooled down in the furnace. The fiber shows superconductivity of $T_c(\text{onset})$ at 94 K and $T_c(\text{end})$ at 62 K. Superconducting transition at and above 60 K cannot be found in the fibers of the diameter less than several hundreds μm . The reason for such lower electrical qualities of the fibers than those of the bloated bulk products has not yet been found. It should be pointed out, however, that particularly for thinner fibers, orientation and arrangement of crystals within the fibers might have critical effects on the electrical conductivity, because conduction paths within the fibers would be greatly limited by anisotropic nature of the crystals in electrical behavior.⁽¹²⁾

5. COATING FILMS

The metal alkoxide solution prepared by the method mentioned in 2.2 has been used for making superconducting coating films. Figure 10 shows the procedure for making coating films. Zirconia (YSZ) rectangular plates of 21 mm×21 mm×0.5 mm in size serve as substrates. 0.2 ml of the alkoxide solution is placed on the substrate in 4 drops. After being dried on a hot plate, the coated substrate is heat-treated at 800°C for 5 min. This coating procedure consisting of the application of the solution and the subsequent heat treatment is repeated 5 to 10 times. The

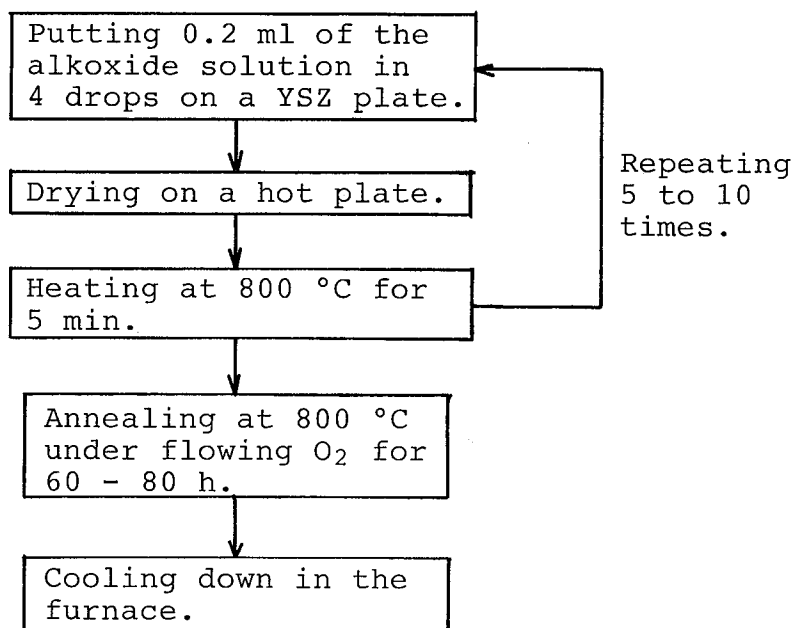


Fig. 10. Procedure for making superconducting coating films.

coating film thus obtained is annealed under the flow of O_2 at $800^\circ C$ for 60–80 h and then cooled down in the furnace to room temperature.

Repeated application of the solution is needed in order to make the film thickness sufficient for the film to exhibit superconductivity. When the thickness is insufficient, the coated film reacts with the substrate in the heat treatment to form non-superconducting phases. The film well adheres to the substrate. Application of a larger amount of the solution in a less frequent repetition fails to produce coating films which well adhere to the substrate.¹⁴⁾ Figure 11 shows the scanning electron micrograph of the fractured cross-section of the coating film made by annealing the coating film at $800^\circ C$ for 60 h in O_2 after 8 times repetition of the coating procedure. A coating film of $7\ \mu m$ in thickness composed of grains of $1\text{--}2\ \mu m$ in size can be seen in the micrograph.

Annealing the coating film under flowing O_2 is required for the formation of the superconducting orthorhombic phase of $YBa_2Cu_3O_{7-x}$ composition in the film. The temperature dependences of the electrical resistance of the coating films shown in Fig. 12 indicate that the film without annealing is of semiconducting nature and

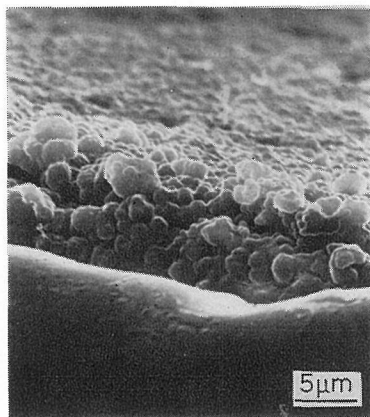
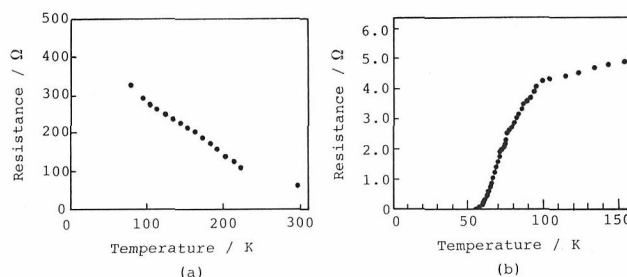


Fig. 11. Scanning electron micrograph of a $YBa_2Cu_3O_{7-x}$ coating film. The film was obtained through 8 times repetition of the coating procedure and annealing at $800^\circ C$ for 60 h under flowing O_2 .



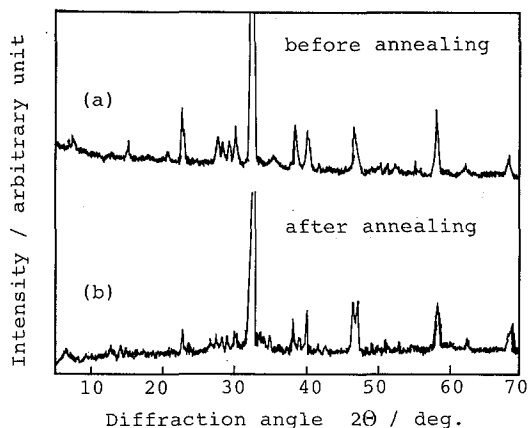


Fig. 13. X-ray diffraction patterns for the coating films derived from the metal alkoxide solution. Before (a) and after (b) annealing at 800°C for 60 h under flowing O_2 .

shows no superconducting transition, and the film with annealing treatment shows transition of $T_c(\text{onset})$ at 98 K and $T_c(\text{end})$ at 56 K. Figure 13 shows the X-ray diffraction patterns of the coating films before and after annealing. The patterns are taken by an X-ray apparatus equipped with an attachment for thin film X-ray diffraction. Either of the patterns correspond to a nearly single phase of $YBa_2Cu_3O_{7-x}$ composition. It should be noticed, however, that the splitting of the diffraction peak at about $2\theta=46^\circ$ is observed in the pattern taken after the annealing but not before the annealing. This indicates that the $YBa_2Cu_3O_{7-x}$ phase transforms from semiconducting tetragonal phase into superconducting orthorhombic phase¹¹⁾ through the annealing process.

6. CONCLUDING REMARKS

Sols and gels derived from an aqueous solution of metal acetates and from a metal alkoxide solution containing triethanolamine have been prepared as precursors for the high temperature superconducting oxide $YBa_2Cu_3O_{7-x}$. It has been shown that $YBa_2Cu_3O_{7-x}$ phase is formed at lower temperatures in the acetate-derived gel than through conventional powder-route method, and superconducting products of $T_c(\text{end}) > 90$ K can be obtained through heat treatment in air without repeated grinding and calcination. Fabrication of superconducting fibers has been performed by drawing gel fibers from the acetate-derived viscous sol and heating the gel fibers. It has been shown that repeated application of the metal alkoxide solution to a zirconia substrate and annealing the film under flowing O_2 results in the formation of superconducting film of 7 μm in thickness.

REFERENCES

- (1) M. K. Wu, J. R. Ashburn, C. J. Torng, P. H. Hor, R. L. Meng, L. Gao, Z. J. Huang, Y. Q. Wang and C. W. Chu, *Phys. Rev. Lett.*, **58**, 908 (1987).

- (2) M. J. Cima and W. E. Rhine, *Adv. Ceram. Mater.*, **2**, 329 (1987).
- (3) M. H. Kayser, B. Borglum, G. Antony, S. G. Syu and R. C. Buchanan, *Mat. Res. Soc. Symp. Proc.*, **99**, 159 (1988).
- (4) C. T. Wang, L. S. Lin, J. H. Lin, J. Y. Su, S. J. Yang and S. E. Hsu, *Mat. Res. Soc. Symp. Proc.*, **99**, 257 (1988).
- (5) J. A. Voigt, B. C. Bunker, D. H. Doughty, D. L. Lamppa and K. M. Kimball, *Mat. Res. Soc. Symp. Proc.*, **99**, 635 (1988).
- (6) Y. Yoshisato, T. Yokoo, T. Ikemachi and Y. Kuwano, *J. Ceram. Soc. Japan*, **96**, 459 (1988).
- (7) R. S. Liu, J. H. Kung, P. T. Wu and C. T. Chang, in "High Temperature Superconductors II", D. W. Capone II, W. H. Butler, B. Batlogg and C. W. Chu Ed., Materials Research Society, Pittsburg, 1988, P. 129-132.
- (8) K. Kaneko, H. Ihara, M. Hirabayashi, N. Terada and K. Senzaki, *Jpn. J. Appl. Phys.*, **26**, L734 (1987).
- (9) T. Kawai and M. Kanai, *Jpn. J. Appl. Phys.*, **26**, L736 (1987).
- (10) Y. Oka, N. Yamamoto, Y. Tomii, H. Kitaguchi, J. Takada, A. Osaka, Y. Miura and M. Kiya-ma, *J. Japan Society of Powder and Powder Metallurgy*, **34**, 590 (1987).
- (11) I.-W. Chen, S. Keating, C. Y. Keating, X. Wu, J. Wu, R. E. Reyes-Morel and T. Y. Tien, *Adv. Ceram. Mater.*, **2**, 457 (1987).
- (12) M. Kanai and T. Kawai, *J. Ceram. Soc. Japan*, **96**, 378 (1988).
- (13) M. J. Cima, R. Chiu and W. E. Rhine, *Mat. Res. Soc. Symp. Proc.*, **99**, 241 (1988).
- (14) S. Sakka, in "Treatise on Materials Science and Technology", M. Tomozawa and R. H. Doremus Ed., Academic Press, New York, 1982, P. 129-167.
- (15) J. D. Mackenzie, in "Ultrastructure Processing of Ceramics, Glasses and Composites", L.L. Hench and D. R. Ulrich, Ed., John Wiley, New York, 1986, P. 15-26.
- (16) M. Hirabayashi, *Bull. Japan Inst. Metals*, **26**, 943 (1987).
- (17) C.-T. Chu and B. Dunn, *J. Am. Ceram. Soc.*, **70**, C375 (1987).
- (18) E. C. Behrman et al., *Adv. Ceram. Mater.*, **2**, 539 (1987).
- (19) E. J. A. Pope and J. D. Mackenzie, in "High Temperature Superconductors II", D. W. Capone II, W. H. Butler, B. Batlogg and C. W. Chu Ed., Materials Research Society, Pittsburg, 1988, P. 97-100.
- (20) K. Wu, S. Kramer and G. Kordas, *Mat. Res. Soc. Symp. Proc.*, **99**, 395 (1988).
- (21) F. Uchikawa, H. Zheng, K. C. Chen and J. D. Mackenzie, in "High Temperature Supercon-ductors II", D. W. Capone II, W. H. Butler, B. Batlogg and C. W. Chu Ed., Materials Re-search Society, Pittsburg, 1988, P. 89-92.
- (22) H. Zheng, K. C. Chen and J. D. Mackenzie, in "High Temperature Superconductors II", D. W. Capone II, W. H. Butler, B. Batlogg and C. W. Chu, Materials Research Society, Pit-tsburg, 1988, P. 93-96.
- (23) T. Kumagai, H. Yokota, K. Kawaguchi, W. Kondo and S. Mizuta, *Chem. Lett.*, **1987**, 1645 (1987).
- (24) H. Nasu, S. Makida, T. Imura and Y. Osaka, in "High Temperature Superconductors II", D. W. Capone II, W. H. Butler, B. Batlogg and C. W. Chu Ed., Materials Research Society, Pittsburg, 1988, P. 101-104.
- (25) W. W. Davison, S. G. Shyu and R. C. Buchanan, *Mat. Res. Soc. Symp. Proc.*, **99**, 289 (1988).
- (26) C. E. Rice, R. B. van Dover and G. J. Fisanick, *Appl. Phys. Lett.*, **51**, 1842 (1987).
- (27) M. E. Gross, M. Hong, S. H. Liou and P. K. Gallagher, *Mat. Res. Soc. Symp. Proc.*, **99**, 731 (1988).
- (28) P. Barboux, J. M. Tarascon, B. G. Bagley, L. H. Greene, G. W. Hull, B. W. Meagher and C. B. Eom, *Mat. Res. Soc. Symp. Proc.*, **99**, 49 (1988).
- (29) E. I. Cooper, M. A. Frisch, E. A. Giess, A. Gupta, B. W. Hussey, E. J. M. O'Sullivan, S. I. Raider and G. J. Scilla, *Mat. Res. Soc. Symp. Proc.*, **99**, 165 (1988).
- (30) Y.-M. Chiang, S. L. Furcone, J. A. S. Ikeda and D. A. Rudman, *Mat. Res. Soc. Symp. Proc.*, **99**, 307 (1988).
- (31) S. Kramer, K. Wu and G. Kordas, *Mat. Res. Soc. Symp. Proc.*, **99**, 323 (1988).
- (32) S. Shibata, T. Kitagawa, H. Okazaki, T. Kimura and T. Murakami, *Jpn. J. Appl. Phys.*, **27**,

- L53 (1988).
- (33) T. Goto, I. Horiba, M. Kada and M. Tsujihara, *Jpn. J. Appl. Phys.*, **26**, Suppl. 26-3, 1211 (1987).
 - (34) H. Kozuka, T. Umeda, J. S. Jin, F. Miyaji and S. Sakka, *J. Ceram. Soc. Japan*, **96**, 355 (1988).
 - (35) S. Sakka, H. Kozuka and T. Umeda, *J. Ceram. Soc. Japan*, **96**, 468 (1988).
 - (36) H. Kozuka, T. Umeda, J. S. Jin and S. Sakka, Presented in part at Materials Research Society, 1988 Spring Meeting, Reno, April, 1988.
 - (37) T. Monde, H. Kozuka and S. Sakka, *Chem. Lett.*, **1988**, 287 (1988).
 - (38) S. Doeuff, M. Henry, C. Sanchez and J. Livage, *J. Non-Crystal. Solids*, **89**, 206 (1987).
 - (39) S. Sakka and K. Kamiya, *J. Non-Crystal. Solids*, **48**, 31 (1982).
 - (40) D. C. Bradley, R. C. Mehrotra and D. P. Gauer, "Metal Alkoxides", Academic Press, New York, 1978.
 - (41) J. V. Singh, B. P. Baranwal and R. C. Mehrotra, *Z. Anorg. Allg. Chem.*, **477**, 235 (1981).
 - (42) T. R. Dinger, T. K. Worthington, W. J. Gallagher and R. L. Sandstrom, *Phys. Rev.*, **58**, 2687 (1987).