SYNTHESIS OF HIGH PURITY 110 K PHASE IN THE Bi(Pb)-Sr-Ca-Cu-O SUPERCONDUCTOR BY THE SOL-GEL METHOD

Yang-Kook Sun*, In-Hwan Oh[†] and Wha Young Lee**

*Central Research Institute of Chemical Technology, Samsung Advanced Institute of Technology, Taejon 305-380, Korea
Division of Chemical Engineering, Korea Institute of Science and Technology, Seoul 136-791, Korea
**Department of Chemical Engineering, Seoul National University, Seoul 151-742, Korea

Abstract – $(BiPb)_2Sr_2Ca_2Cu_3O_x$ superconductor powders were synthesized by the sol-gel method using an aqueous solution of metal nitrates containing polyacrylic acid and tartaric acid as chelating agents. The conditions of the sol formation were determined and the thermal decomposition process of the gel precursor was examined. The effect of sintering temperature on the particle morphology was also investigated. High purity Bi(Pb)-Sr-Ca-Cu-O superconducting oxide powders with high-T_c phase could be obtained and they exhibited sharp superconducting transition with zero temperature of 105 K.

Key words: Bi(Pb)-Sr-Ca-Cu-O Superconductor, Sol-Gel, High- and Low-T_c Phase, Polyacrylic Acid, Tartaric Acid

INTRODUCTION

Since the discovery of the Bi-Sr-Ca-Cu-O system with a superconducting onset temperature above 110 K by Maeda et al. [1988], extensive works have been developed to increase its physicochemical properties. It is well known that the Bi-Sr-Ca-Cu-O superconducting oxide system has two superconducting phases, the so-called high-T_c phase (2223, $Bi_2Sr_2Ca_2Cu_3O_x$) with T_c around 110 K and the low-T_c phase (2212, $Bi_2Sr_2CaCu_2O_x$) with T_c around 80 K [Takayama-Muromaci et al., 1988; Tarascon et al., 1988]. However, one of the problems with the Bi-Sr-Ca-Cu-O superconducting oxide system is the difficulty in obtaining a single phase of the high-T_c phase superconductor since the high-T_c phase is less stable than the low-T_c phase. A low oxygen partial pressure sintering process [Endo et al., 1988; Lee et al., 1989], prolongation of the sintering time [Kobayashi et al., 1989], the partial substitution of Pb for Bi [Takemura et al., 1989; Liang et al., 1989] and the addition of excess calcium and copper to the stoichiometric composition of the high-T_c phase [Endo et al., 1989] have been found to increase the volume fraction of the high-T_c phase.

Superconducting properties are much affected by synthetic methods [Sata, 1995]. Superconducting oxides are usually prepared by solid state reaction which utilizes metal oxides and carbonates. This method, however, has several disadvantages: inhomogeneity, nonuniformity of particle size and shape, high impurity content, lack of reproducibility, high porosity of the sintered sample, necessity of repeated processings, and higher temperature and longer period for sintering. Several solution methods, such as the sol-gel method [Xu et al., 1990; Nozue et al., 1991], the citrate process [Aoki, 1990; Liu et al., 1989; Wang et al., 1989], spray pyrolysis [Chen and Tsen, 1990] and

freeze drying [Song et al., 1990], have been developed to overcome these problems. Particularly, the citrate process and the sol-gel method have many advantages over others, including highly homogeneous mixing, good stoichiometric control, and the production of active submicron-size particles in a relatively shorter processing time and lower temperature. Also, ceramic fibers and thin film can be produced from sol-derived gel precursors with such shape by adjusting pH, temperature, aging time and viscosity of the solutions. However, when the citrate process or the sol-gel method was used for the preparation of $(Bi, Pb)_2Sr_2Ca_2Cu_3O_x$, it was almost impossible to obtain sol-gel from the solution and thus the high-T_c phase because of the low solubility of bismuth salt and the great difference in the solubilities of the metal salts. Recently, Sun and Lee [1993] have reported that the modified citrate process produced much more high-T_c phase than the citrate process and its transition temperature, 108 K, was much higher. Using the sol-gel method, the authors have successfully demonstrated the preparation of $YBa_2Cu_3O_{7-x}$ superconducting powders [Sun and Oh, 1996] and $LiCoO_2$ powders for the cathode materials of lithium secondary batteries and fuel cells [Sun et al., 1996].

In this study, high purity Bi(Pb)-Sr-Ca-Cu-O superconducting oxide powders were synthesized by the sol-gel method using polyacrylic acid (PAA) and tartaric acid, $C_4H_6O_6$, as chelating agents at considerably lower temperature and shorter time. The mechanism of this method is similar to the Pechini method [Lessing, 1989], where citric acid and ethylene glycol are used as chelating agents, but we used different chelating agents of PAA and tartaric acid which have more functionalities.

EXPERIMENTAL

The Bi(Pb)-Sr-Ca-Cu-O superconductor with a high-T_c phase was synthesized according to the procedure as shown in Fig. 1.

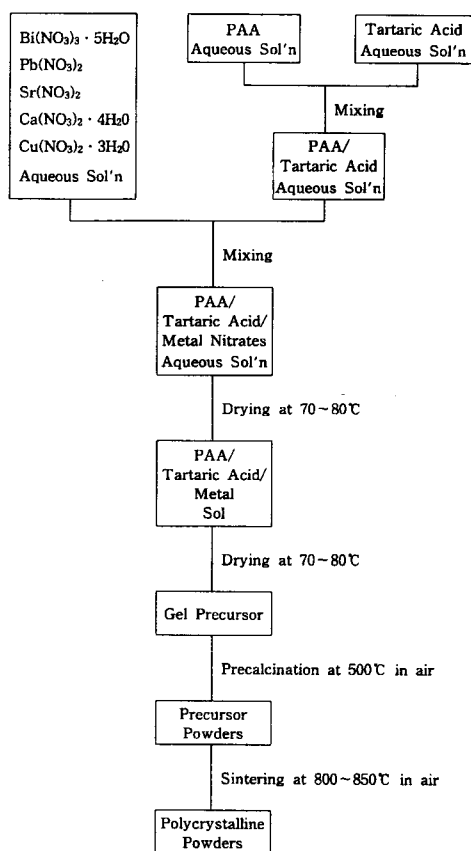[†]To whom all correspondences should be addressed.

Fig. 1. Flowsheet of the preparation procedure for $(BiPb)_2Sr_2$-$Ca_2Cu_3O_x$ powders by the sol-gel method.

As starting reagents, $Bi(NO_3)_3 \cdot 5H_2O$, $Pb(NO_3)_2$, $Sr(NO_3)_2$, $Ca(NO_3)_2 \cdot 4H_2O$ and $Cu(NO_3)_2 \cdot 3H_2O$ were used. All the reagents with high-purity were purchased from the Aldrich Chemical Co. A stoichiometric amount of each nitrate salts with a cationic ratio of Bi : Pb : Sr : Ca : Cu being equal to 1.85 : 0.35 : 1.9 : 2.1 : 3.1 was dissolved in distilled water and mixed well with an aqueous solution of PAA and tartaric acid. The mixed solution was evaporated at 70-80 °C for 1 day until a viscous transparent sol was obtained. To remove water further, the viscous transparent sol was heated at 70-80°C while it was mechanically stirred with a magnetic stirrer. During the evaporation of water from the sol solution, the gel could be formed even if stirring was not applied. But stirring might facilitate the evaporation rate in addition to the advantage in the homogeneity of the gel formed. As the evaporation of water proceeded, the sol turned into a viscous transparent gel. The gel precursors obtained were decomposed at 500°C for 10 hours in air to eliminate organic contents. The decomposed powders were ground for a minute, followed by calcination at 800°C for 10 hours or at 820-850°C for 40 hours. For the measurement of DC electrical resistance, the powders obtained were pelletized and air-sintered at 850 °C for 40 hours.

The thermal decomposition behaviour of the gel precursor was examined by means of thermogravimetry/differential thermal analysis (TG-DTA 2000, MAC Science) and the crystalline phase of the materials calcined at the various temperatures was identified by the powder X-ray diffraction (Rint-

2000, Rigaku) patterns using $CuK\alpha$ radiation. The surface morphology of the material was studied using scanning electron microscope (S-4100, Hitachi). To examine the superconducting properties of the materials prepared, DC electrical bulk resistance was measured as a function of temperature by the four-probe method.

RESULTS AND DISCUSSION

In a sol-gel process where PAA is used as a chelating agent, carboxylic acid group (-COOH) of PAA forms a chelate with mixed cations, resulting in a sol. The utility of PAA in the sol-gel process comes from the chemical bonding of cations onto the polymer chains. The most important thing during the sol formation process is to distribute the cations atomistically throughout the polymeric structure and not to cause a cation segregation and thereby a precipitation. The severity of the segregation largely depends on the solubility of the cations in solution as a function of pH [Lessing, 1989]. Heating the sol to moderate temperature causes a condensation reaction between -COOH groups through dehydration due to the concurrent formation of a water molecule. As the most of the excess water is removed, the sol turns into a gel, and an extremely high viscosity polymeric resins are developed. The gel can be either cross-linked or not, depending on the stoichiometry of the ratios of reactants. Since PAA has more functional groups than citric acid which is the conventional chelating agent, it should greatly aid the formation of a cross-linked gel and the cross-linked gel may provide more homogeneous mixing of the cations and less tendency for segregation during calcination.

Although PAA has been successfully employed to synthesize ultrafine $LiCoO_2$ powders [Sun et al., 1996], a sol could not be formed when only PAA was used as a chelating agent in this study. To examine the effect of PAA on the sol formation, the molar ratio of PAA to total metal ions was firstly set to 3 since the theoretical minimum amount of PAA needed to bind all the metal ions was 2.2, and then the amount of PAA was varied. As the PAA quantity used increased, the appearance of the dried materials derived from the solution changed from gel precursor with precipitate to one with crystal. This is believed to be due to the fact that the carboxylic groups on the PAA could not form the chemical bonding of the cations onto PAA's polymer chains because of the low solubility of bismuth salt and the great difference in the solubilities of the metal salts. However, it was found that application of tartaric acid, HOOC-CHOH-CHOH-COOH ($C_4H_6O_6$), as a complementary chelating agent in addition to PAA, allowed us to obtain the sol-gel precursor. Since tartaric acid has -COOH groups as well, chelates with the cations can be formed and dehydration between tartaric acids and PAA may occur. Furthermore, -OH groups in tartaric acid may facilitate the condensation reaction with -COOH groups in PAA via polyesterification during the evaporation process.

Table 1 summarizes the appearance of the gels derived from the solutions of the different $C_4H_6O_6$/Cu molar ratios with the molar ratio of PAA to total metal ions being fixed at 3. Sol formation was possible only in a limited tartaric acid content of the solution. It was found that dark blue transparent gel was ob-

Table 1. Appearance of the gels from the solutions at the different $C_4H_6O_6$/Cu molar ratios when the molar ratio of PAA to total metal ions was 3

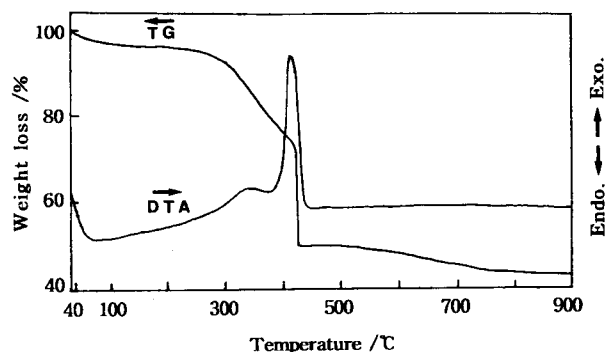| $C_4H_6O_6$/Cu	Appearance of the gels
0	transparent gel with 35% precipitate
1	transparent gel with 15% precipitate
2	transparent gel with 10% precipitate
4	transparent gel

Fig. 2. Thermogravimetric and differential thermal analysis of the gel precursors at an air flow rate of 40 cc/min and a heating rate of 5 °C/min.
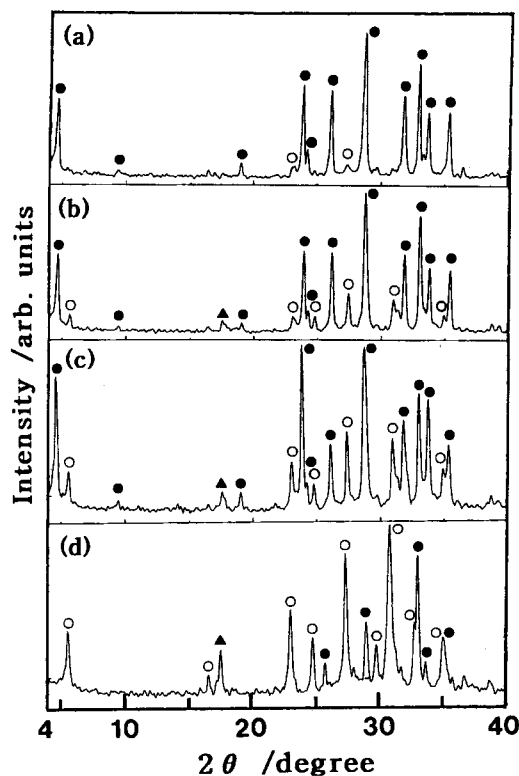

Fig. 3. Powder X-ray diffraction patterns of the gel-derived materials sintered at various conditions: (a) 850 °C, 40 hrs, (b) 840 °C, 40 hrs, (c) 820 °C, 40 hrs and (d) 800 °C, 10 hrs. ●=(BiPb)₂Sr₂Ca₂Cu₃Oₓ, O=(BiPb)₂Sr₂CaCu₂Oₓ and ▲=Ca₂PbO₄.

tained from the solution when the $C_4H_6O_6$/Cu molar ratio was equal to 4. On the other hand, precipitation occurred during the evaporation of water from the sol solution when the $C_4H_6O_6$/Cu molar ratio was less than this range. It is inferred from these results that tartaric acid, if an appropriate amount is used in addition to PAA, plays an important role in the formation of a cross-linked gel without precipitates of cations during the evaporation process via the chelating reaction between tartarate anions and metal cations and the condensation reactions such as dehydration or polyesterification as explained earlier.

Calcination of the gel in air or other gases causes a breakdown of the gel and charring at about 400 °C. Even as the chemical bonding of the cations with the polymeric chains is destroyed during pyrolysis, the high viscosity of the gel favors low cation mobility, which helps to prevent the different mixed cations from segregating. It is assumed during the calcination, therefore, that there is little segregation of the various cations that remain trapped in the char. Subsequently, the cations are oxidized to form crystallites of mixed cation oxides from 500 °C to 900 °C.

Fig. 2 shows the thermogravimetry (TG) and differential thermal analysis (DTA) of the gel precursors when the molar ratios of $C_4H_6O_6$/Cu and PAA/total metal ions were 4 and 3, respectively. It is seen that the weight loss of the gel precursors terminates at 760 °C and three discrete weight loss regions occur at 40-300 °C, 300-425 °C and 425-760 °C. The weight loss in the temperature range of 40 °C to 300 °C corresponds to the removal of water in the gel precursor, which is accompanied by an endothermic peak at 75°C in the DTA curve. The weight loss in the temperature range of 300 °C to 425 °C appears to be due to the combustion of organic constituents in the gel precursors such as PAA, tartaric acid and nitrate ions, which occurs with an exothermic peaks at 340°C and 420 °C. The weight loss in

this stage occupies 43 % of the total weight loss because of a violent oxidation-decomposition reaction. It appeared that PAA functioned as a fuel in the pyrolysis of the gel precursors, accelerating the decomposition of nitrate ions and tartaric acid. It was also observed during this pyrolysis stage that the gel precursors turned into fluffy dark brown powders after calcination. The weight loss in the temperature range of 425 °C to 760 °C corresponds to the oxidation of the remaining organic constituents.

Fig. 3 shows the X-ray diffraction patterns of the gel-derived materials sintered at various temperatures when the molar ratios of $C_4H_6O_6$/Cu and PAA/total metal ions were 4 and 3, respectively. When a specimen was sintered at 800 °C, low-T_c (BiPb)₂Sr₂CaCu₂Oₓ and high-T_c (BiPb)₂Sr₂Ca₂Cu₃Oₓ became the main phases, containing a small amount of Ca₂PbO₄. A close look at this figure reveals that the ratio of the amount of the high-T_c phase to that of the low-T_c phase increased as the sintering temperature of the specimens increased. Particularly, the ratio of the characteristic (002) peak at $2\theta=4.7°$ representing the high-T_c phase to the characteristic (002) peak at $2\theta=5.8°$ representing the low-T_c phase increased with the raise of the sintering temperature, while the intensity of Ca₂PbO₄ peak at $2\theta=17.5°$ decreased. When a specimen was sintered at 850°C for 40 hours, the (002) peak at $2\theta=5.8°$ and Ca₂PbO₄ peak at $2\theta=17.5°$ completely vanished and a nearly pure high-T_c phase with a negligible amount of low-T_c phase formed. This may be ascribed to the fact that the PAA and tartaric acid-assisted gel
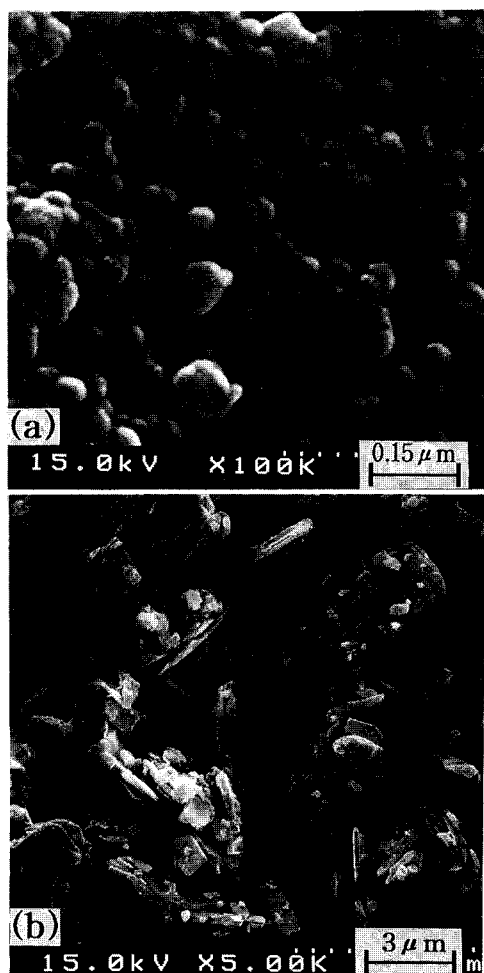
Fig. 4. Scanning electron micrographs of $(BiPb)_2Sr_2Ca_2Cu_3O_x$ powders sintered at (a) 500°C for 10 hrs and (b) 850°C for 40 hrs.

Fig. 5. Temperature dependence of DC electrical resistance for the pellet sintered at 850 °C for 40 hrs.

precursors are in atomic scale and homogeneously mixed with each other, and thus have high sinterability. Transformation from the low-T_c phase to the high-T_c one at the elevated temperature is quite consistent with the reaction mechanism of forming the superconducting phase in the previous study [Sun and Lee, 1993], where high-T_c $(BiPb)_2Sr_2Ca_2Cu_3O_x$ could be synthesized by the reaction of low-T_c $Bi_2Sr_2CaCu_2O_x$, CuO and Ca_2PbO_4, and in the other studies [Kijima et al., 1988; Uzumaki et al., 1989].

Scanning electron microscope (SEM) images of the free surfaces for the powders sintered at 500°C for 10 hours and 850°C for 40 hours are shown in Fig. 4. The surface of the powders calcined at 500°C consisted of monodispersed spherical fine particulates with an average particle size of about 50 nm, although some agglomerates were observed. As the sintering temperature increases, growth kinetics are favored and thus larger grains are observed. For the materials sintered at 850°C, it can be seen that plate-like grains were found, which were regarded as superconducting grains [Chen et al., 1990; Haung et al., 1989]. These plate-like grains grow in random directions each other and form a porous structure.

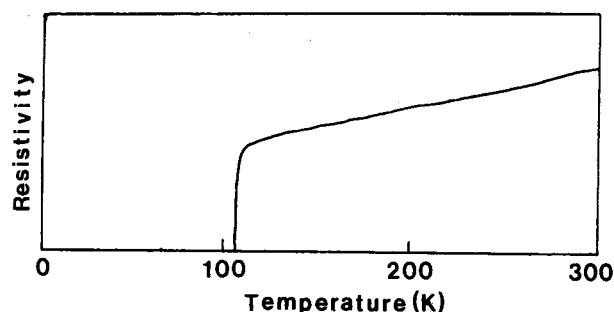Fig. 5 shows the temperature dependence of electrical resist-

ance for the pellet sintered at 850 °C for 40 hours. It is seen that the resistivity of the sintered pellets decreases linearly with decreasing temperature. The onset temperature and the zero temperature of the material are about 115 K and 105 K, respectively. The narrow transition temperature width, ΔT_c, must be due to the fact that the materials prepared by the sol-gel method exhibit excellent homogeneity and sinterability which are confirmed by the XRD and SEM results. It is notable that the sintering time and temperature necessary to obtain superconductors with the high-T_c phase in this study are less than those employed for the conventional solid state reaction method which requires long-term sintering and several intermediate grinding treatments. As an application of the materials prepared in this study, it is presumed that the transparent viscous sols can be used for the preparation of Bi(Pb)-Sr-Ca-Cu-O superconductor fibers, thin films and wires, since they shows very good spinnability.

CONCLUSION

High-T_c $(BiPb)_2Sr_2Ca_2Cu_3O_x$ superconductor powders were synthesized by the sol-gel method using an aqueous solutions of bismuth, lead, strontium, calcium, and cupric nitrates. When only PAA was used as a chelating agent, a sol could not be formed, but it was found that tartaric acid must be used as a complementary chelating agent in addition to PAA. Namely, transparent viscous sol was found to form when a molar ratio of tartaric acid to Cu was 4 and that of PAA to total metal ions was 3. Examination of the thermal decomposition process and analysis of the X-ray diffraction patterns reveal that the high purity Bi(Pb)-Sr-Ca-Cu-O superconducting oxide powders with the high-T_c phase could be obtained when the gel-derived material was sintered at 850°C for 40 hour in air. The material was seen to be composed of plate-like superconducting grains and they exhibited sharp superconducting transition with zero temperature of 105 K. This suggests that the sintering time and temperature necessary to obtain superconductor with the high-T_c phase in this study are less than those employed for the conventional solid state reaction method which requires long-term sintering and several intermediate grinding treatments.

REFERENCES

Aoki, A., "Preparation of High-Quality Bi-Pb-Sr-Ca-Cu-O Ox-

ide Precursor by the Citrate Gel Process", *Jpn. J. Appl. Phys.*, **29**(2), L270 (1990).

Chen, F. H., Koo, H. S. and Tseng, T. Y., "Synthesis of High-T_c Superconducting Bi-Pb-Sr-Ca-Cu-O Ceramics Prepared by an Ultrastructure Processing via the Oxalate Route", *J. Mater. Sci.*, **25**, 3338 (1990).

Chen, F. H. and Tsen, T. Y., "Formation of High-T_c Superconducting Bi-Pb-Sr-Ca-Cu-O Oxide Films by Spray Pyrolysis of an Oxalate Suspension", *J. Am. Ceram. Soc.*, **73**(4), 889 (1990).

Endo, U., Koyama, S. and Kawai, T., "Preparation of the High-T_c Phase of Bi-Sr-Ca-Cu-O Superconductor", *Jpn. J. Appl. Phys.*, **27**(8), L1476 (1988).

Endo, U., Koyama, S. and Kawai, T., "Composition Dependence on the Superconducting Properties of Bi-Pb-Sr-Ca-Cu-O", *Jpn. J. Appl. Phys.*, **28**(2), L190 (1989).

Haung, C. J., Tseng, T. Y., Heh, T. S., Chen, F. H., Jong, W. S., Fran, F. S. and Shiau, S. M., "Zero Resistance at 125 K Bi(Pb)-Sr-Ca-Cu-O Superconductor", *Solid State Commun.*, **72**, 563 (1989).

Kijima, N., Endo, H., Tsuchiya, J., Sumiyama, A., Mizuno, M. and Oguri, Y., "Reaction Mechanism of Forming the High-T_c Superconductor in Pb-Bi-Sr-Ca-Cu-O System", *Jpn. J. Appl. Phys.*, **27**(10), L1852 (1988).

Kobayashi, S., Saito, Y. and Wada, S., "The Effect of Sintering Conditions on the Formation of the High-T_c Phase in the Bi-Sr-Ca-Cu-O System", *Jpn. J. Appl. Phys.*, **28**(5), L772 (1989).

Lee, H. K., Lee, K. W., Ha, D. H., Park, K. and Park, J. C., "Effect of Oxygen Partial Pressure on the Transformation between High T_c and Low T_c in a Bi-Pb-Sr-Ca-Cu-O System", *Appl. Phys. Lett.*, **55**, 1249 (1989).

Lessing, P. A., "Mixed-Cation Oxide Powders via Polymeric Precursors", *Ceram. Bull.*, **68**(5), 1002 (1989).

Liang, R., Ishii, H., Kawaji, H., Itoh, M. and Nakamura, T., "Synthesis of Superconducting 2223 Compound in the Lead-Added Bi-Sr-Ca-Cu-O System", *Jpn. J. Appl. Phys.*, **29**(8), L1412 (1989).

Liu, R. S., Wang, W. N., Chang, C. T. and Wu, P. T., "Synthesis and Characterization of High-T_c Superconducting Oxides by the Modified Citrate Gel Process", *Jpn. J. Appl. Phys.*, **29**(12), L2155 (1989).

Maeda, H., Tanaka, Y., Fukutoni, M. and Asano, T., "A New High-T_c Oxide Superconductors without a Rare Earth Element", *Jpn. J. Appl. Phys.*, **27**(2), L209 (1988).

Nozue, A., Nasu, H., Kamiya, K. and Tanaka, K., "Transport Characteristics Related with Microstructure of (Bi, Pb)-Sr-Ca-Cu-O Superconductor Prepared by the Sol-Gel Method", *J. Mater. Sci.*, **26**, 4427 (1991).

Sata, T., "Synthesis of 110 K Phase of Bi-Sr-Ca-Cu-O Superconductor Oxide by New Firing Method", *J. Ceram. Soc. of Jap.*, **103**(6), 541 (1995).

Song, K., Liu, H., Dou, A. and Soreii, C., "Rapid Formation of the 110 K Phase in Bi-Pb-Sr-Ca-Cu-O through Freeze-Drying Powder Processing", *J. Am. Ceram. Soc.*, **73**(6), 1771 (1990).

Sun, Y. K. and Lee, W. Y., "Preparation of High Purity 110 K Phase in the Bi(Pb)-Sr-Ca-Cu-O Superconductor Using the Modified Citrate Process", *Physica C*, **212**, 37 (1993).

Sun, Y.-K. and Oh, I.-H., "Preparation of Ultrafine $YBa_2Cu_3O_{7-x}$ Superconductor Powders by the Polyvinyl Alcohol-assisted Sol-Gel Method", *Ind. Eng. Chem. Res.*, **35**(11), 4296 (1996).

Sun, Y.-K., Oh, I.-H. and Hong, S.-A., "Synthesis of Ultrafine $LiCoO_2$ Powders by the Sol-Gel Method", *J. Mater. Sci.*, **31**, 3617 (1996).

Takayama-Muromachi, E., Uchida, Y., Ono, A., Izumi, F., Onoda, M., Matsui, Y., Kosuda, K., Takekawa, S. and Kato, K., "Identification of the Superconducting Phase in the Bi-Ca-Sr-Cu-O System", *Jpn. J. Appl. Phys.*, **27**(3), L365 (1988).

Takemura, Y., Hongo, M. and Yamajaki, S., "The Effect of Pb Substitution on the Bi-Sr-Cu-O Superconductor", *Jpn. J. Appl. Phys.*, **28**(6), L916 (1989).

Tarascon, J. M., McKinnon, W. R., Barbonx, P., Hwang, D. M., Bagley, B. G., Greene, L. H., Hull, G. W., Lepage, Y., Stoffel, N. and Giround, M., "Preparation, Structure, and Properties of the Superconducting Compound Series $Bi_2Sr_2Ca_{n-1}Cu_nO_y$ with n=1, 2, and 3", *Phys. Rev. B*, **38**(13), 8885 (1988).

Uzumaki, T., Yamanaka, K., Kamehara, N. and Niwa, K., "The Effect of Ca_2PbO_4 Addition on Superconductivity in a Bi-Sr-Cu-O System", *Jpn. J. Appl. Phys.*, **28**(1), L75 (1989).

Wang, N. H., Wang, C. M., Kao, H. C. I., Ku, H. C. and Lii, K. H., "Preparation of 95 K $Bi_2CaSr_2Cu_2O_{8+\delta}$ Superconductor from Citrate Precursors", *Jpn. J. Appl. Phys.*, **28**(9), L1505 (1989).

Xu, Q., Bi, L., Peng, D., Meng, G., Zhou, G., Mao, Z., Fan, C. and Zhang, Y., "Preparation of High-T_c Bi-Pb-Sr-Ca-Cu-O Superconductor by Using the Sol-Gel Method", *Supercond. Sci. Technol.*, **3**, 564 (1990).