

Preparation of Bi₂O₃-PbO-SrO-CaO Coating Sol for Wiring and Superconductivity and Its properties

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Abstract Cu-free multi-component sol, of which final oxide composition becomes Bi_{1.9}Pb_{0.35}SrCaO, Bi_{1.8}Pb_{0.2}SrCaO and Bi_{1.5}SrCaO, respectively, was prepared through sol-gel route and coated on a bare Cu substrate. Starting materials were metal-alkoxides as follows.; [Bi(OC₂H₅)₃, Pb(OⁱC₃H₇)₂, Sr(OⁱC₃H₇)₂, Ca(OC₂H₅)₂] as a reagent grade. Transparent light yellowish sol was obtained in the case of Bi_{1.9}Pb_{0.35}SrCaO and Bi_{1.8}Pb_{0.2}SrCaO composition and Bi_{1.5}SrCaO composition's sol was light greenish. Each sol was repeatedly dip-coated on Cu substrate four times and pre-heated at 400°C and finally heat-treated in the range of 740~900°C. In the results, crystalline phases confirmed by XRD were (2201) orthorhombic and monoclinic phases. However, only Bi_{1.9}Pb_{0.35}SrCaO_x composition showed pseudo-superconductive behavior after heat-treatment at 900°C for 12 seconds and then onset temperature was 77 K, even though it did not exhibit zero resistance below T_c.

Key words Cu-free precursor, Thin Film, Bi2201 Superconductor, copper tape.

1. Introduction

Many works have been paid to the wiring technique of high temperature superconductor since its discovery. As already well known, the electric resistance of superconductor becomes zero below the critical temperature and the electric current loss sustain without loss. Until now, the worldwide active research for wiring has been advancing and it is anticipative that its application will come true in near future.¹⁾ For the present, many works about the high T_c superconductor are mainly concentrated on Yttrium and Bismuth oxide system. Yttrium based system superconductor is weak to the moisture and its wiring process is difficult because it shows anisotropic growth and heat-treatment temperatures is higher than melting temperature (960.5°C) of Ag, which is commonly used as sheath. Accordingly, in this study, we focused to the Bi-system super-conductor for improving mechanical quality and increasing critical electric current density.

Meanwhile, alternative method for Bi-containing superconductive wiring is to coat the precursor on Cu

wire and induce in-situ superconductive phase formation by heat-treatment. In the previous works, the metal acetate as raw materials for Bi-Sr-Ca-Cu-O system sol has been mainly used and coated on Yttria-stabilized zirconia substrate (YSZ). After heat-treatment, coated thickness became to 20 μm and (2212) superconductive crystal phase could be obtained.²⁾ Another report for Bismuth system(Bi : Sr : Ca : Cu = 2 : 2 : 2 : 3) using sol-gel process, showed the results that coated thickness was 10 μm and superconductive crystal phase was obtained after heat-treatment at 860°C for 15-70h.^{3,4)} However, in these works, there were two drawbacks. Firstly, their precursor composition had to contain Cu source precursor for formation a superconductive crystal phase after heat-treatment. Secondly, when metal acetate is used as raw materials, much heats evolved at the decomposition temperature might cause the micro-cracks within the coated film.

Accordingly, in this work, we prepared Cu-free Bi-(Pb)-Sr-Ca-O precursors without chemical additives such as chelating agents used in sol-gel process of the previous works,²⁻⁶⁾ and tried to induce the superconductive crystal phase formation on Cu substrate directly by dip-coating and investigated the properties.

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2. Experimental Procedure

Fig. 1 shows the processing procedure of $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$, $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ and $\text{Bi}_{1.5}\text{SrCa}$ precursor. At first, methyl alcohol of 60 ml as solvent and distilled water of 3 ml for hydrolysis were put into pyrex round flask at 50°C . And nitric acid of 0.17 mole (HNO_3 , purity 60%) as dispersing agent was added and stirred at 400 rpm. After adding nitric acid, bismuth tri-ethoxide [$\text{Bi}(\text{OC}_2\text{H}_5)_3$], lead di-isopropoxide [$\text{Pb}(\text{O}^i\text{C}_3\text{H}_7)_2$], strontium iso-propoxide [$\text{Sr}(\text{O}^i\text{C}_3\text{H}_7)_2$] and calcium ethoxide [$\text{Ca}(\text{OC}_2\text{H}_5)_2$], complying with intended composition were into the solvent one after another put. Subsequently, 2-methoxy-ethanol of 0.26 mole was added for dissolving lead di-isopropoxide and strontium iso-propoxide. After refluxing for 24 hours, yellowish transparent sol was obtained for the case of $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$ and $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ precursors and transparent greenish sol was obtained for $\text{Bi}_{1.5}\text{SrCa}$ case. The viscosity of complex precursors measured by viscometer (BROOKFIELD, Programmable Viscometer DV-II+, 61 spindle, 100 RPM) was about 1.25 cps. Finally, in order to abbreviate the number of dip-coating times and increase the coating thickness, PVB (Poly vinyl butyral-co-vinyl alcohol) was added to the above precursor sol. Then, the viscosity of $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$, the $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ and $\text{Bi}_{1.5}\text{SrCa}$ precursor sol increased to 11.3, 11.2 and 10.2 cps, respectively. Cu plate was pressed by 13 ton/cm^2 for 5 hours, chopped into the size of $18 \times 50 \times 1.0\text{ mm}$ and cleaned in ethanol solution by

using ultrasonic wave. After cleaning, each precursor sol was coated on Cu substrate by dip-coating (Withdrawal speed; 40 cm/min .) and dried at 100°C in thermostat. This coating procedure was repeated by 4 times. TG-DTA analysis (MAC Science, Model Mac-TGDTA 2000) was carried out for determining the decomposition and crystallization temperature of each coating film before the heat-treatment. As based on TG-DTA analysis results, each sample was put on a platinum boat, pre-heated for binder burn-out at 400°C for 4 hours in the muffle furnace and heat-treated for 20-300 seconds into tube furnace kept at various heat-treatment temperatures in the range of $740\text{-}870^\circ\text{C}$. X-ray diffraction (Shimadzu Model; XD-D1, Japan) after heat-treatment was carried out using Ni-filtered $\text{Cu-K}\alpha$ radiation for identifying the crystal formation. Their microstructure was observed by Scanning Electron Microscope (Topcon Model; ABT-32, Japan). Superconductive measurement was done by 4-probe method from room temperature to liquid He temperature.

3. Results and Discussion

The results of TG-DTA measurement in Fig. 2 show the decomposition temperature of organic component and the crystallization temperature for $\text{Bi}_{1.5}\text{SrCa}$, $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$, and $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ coating film depending on the heat-treatment temperature after 4 dipping times on Cu chip. As shown in Fig. 2, each sample shows similar tendency, that is, prominent thermo-gravimetric decrease starts from 200°C . And first exothermic peak around 256°C occurs owing to the decomposition of the remained organic components. Second exothermic peak is due to PVB (Poly vinyl butyral-co-vinyl alcohol-co-vinyl acetate). Another exothermic peaks at higher temperature are assigned to the crystallization peak occurred in coating film.

In the case of $\text{Bi}_{1.5}\text{SrCa}$ composition without containing Pb, the first crystallization and second one occurred at 675°C and 830°C , respectively [Fig. 2 (a)]. Meanwhile, the crystallization of the $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$ and $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ composition is observed at lower temperature, of which first crystallization peak is 599°C and 601°C , respectively, and each one at higher temperature is 806°C and 810°C , respectively [Fig. 2(b) and 2(c)]. All of these peaks are assigned to the (2201) crystal phase identified by X-ray diffraction meter [Fig. 3]. However, first crystallization peak at lower temperature is attributed to (2210)

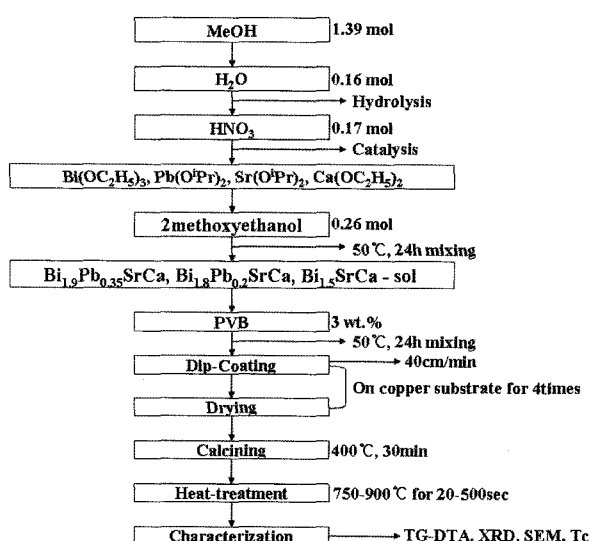


Fig. 1. Preparation procedure of $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$, $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ and $\text{Bi}_{1.5}\text{SrCa}$ precursor sol.

orthorhombic crystalline phase and second one at higher temperature is assigned to (2201) monoclinic phase as shown in Fig. 4. As Pb quantity increases, each peak temperature decreases. This means that the addition of Pb to the Bi_{1.5}SrCa composition lower the reaction temperature between coating film and Cu substrate because Pb functions as flux and it may cause the crystallization easily. Meanwhile, thermo-gravimetric weight of all samples steadily increased until 900°C after first crystallization. It means that the oxidation of Cu substrate and the reaction with the coating film concurred.

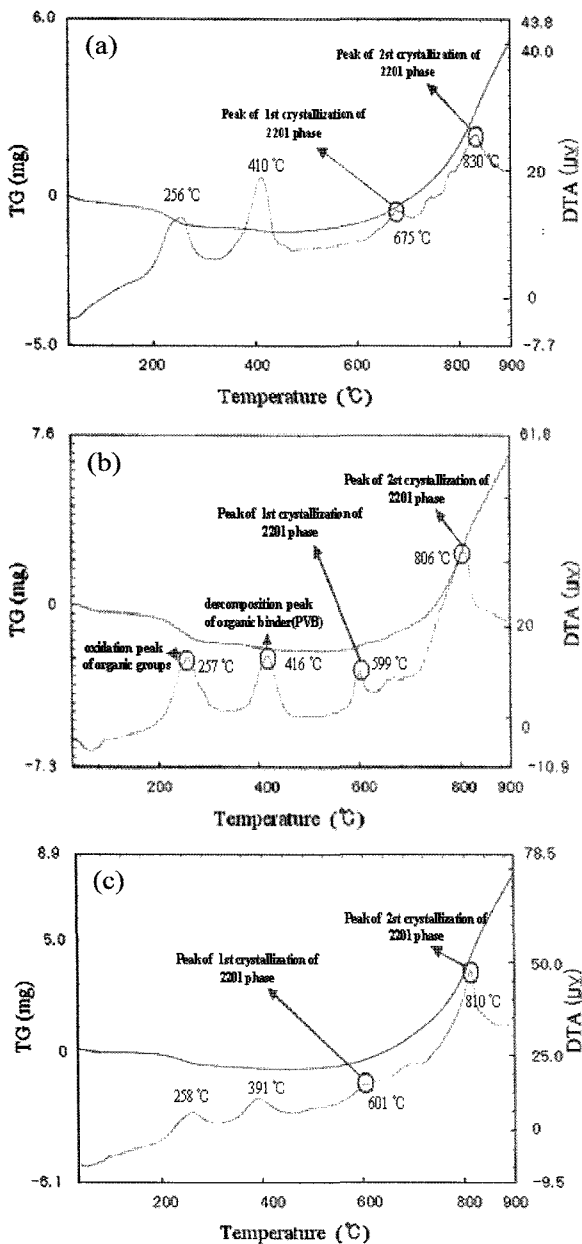


Fig. 2. TG-DTA data of (a) Bi_{1.5}SrCaO_x, (b) Bi_{1.8}Pb_{0.2}SrCaO_x, (c) Bi_{1.9}Pb_{0.35}SrCaO_x coating film on Cu substrate.

Fig. 3 shows the results of XRD diffractometer for Bi_{1.5}SrCa, Bi_{1.8}Pb_{0.2}SrCa and Bi_{1.9}Pb_{0.35}SrCa coated film after heat-treatment at 800°C for 20 seconds. In Fig. 3, typical superconductive (2212) crystal phase (Bi₂Sr₂Ca₁Cu₂O_x phase) was not shown. At present, it isn't clear why (2212) crystal phase did not form and crystal phase containing Ca component couldn't be detected in samples in this XRD results after heat-treatment. However, (2201) orthorhombic phase (Bi₂Sr₂Cu₁O_x phase), which seems to be more preferential to show superconductivity than (2201) monoclinic phase, was observed in all samples. Meanwhile, in the case of Bi_{1.9}Pb_{0.35}SrCa composition, (2201) monoclinic phase also occurred. Anyway, under these heat-treatment conditions, each sample didn't show superconductivity.

Fig. 4 shows X-ray diffraction patterns of Bi_{1.9}Pb_{0.35}SrCaO_x coating films heat-treated at different temperatures and times. As shown in Fig. 4, after heat-treatment at 740°C for 50 seconds, monoclinic crystalline phase was only confirmed in the samples. In the samples heat-treated over 800°C, both of monoclinic and orthorhombic crystal

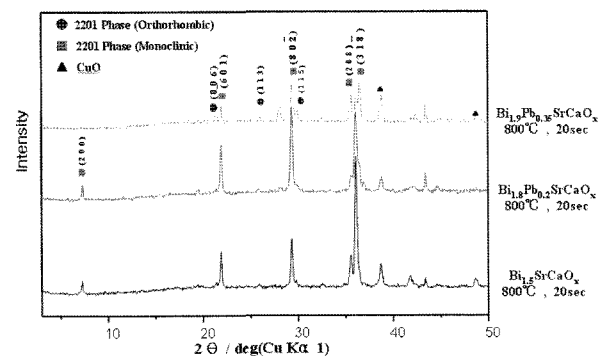


Fig. 3. XRD patterns of coating films after heat treated at 800 °C for 20 seconds.

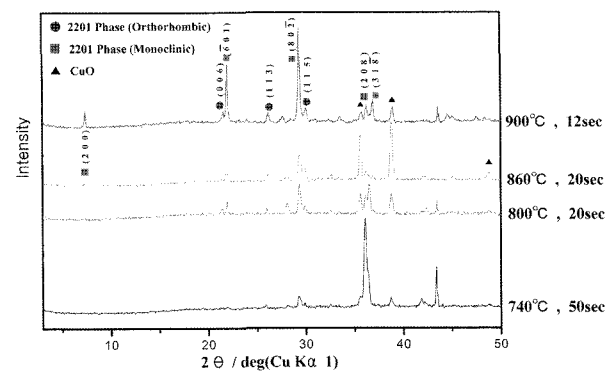


Fig. 4. XRD patterns of Bi_{1.9}Pb_{0.35}SrCaO_x coating films heat treated at different temperatures and times.

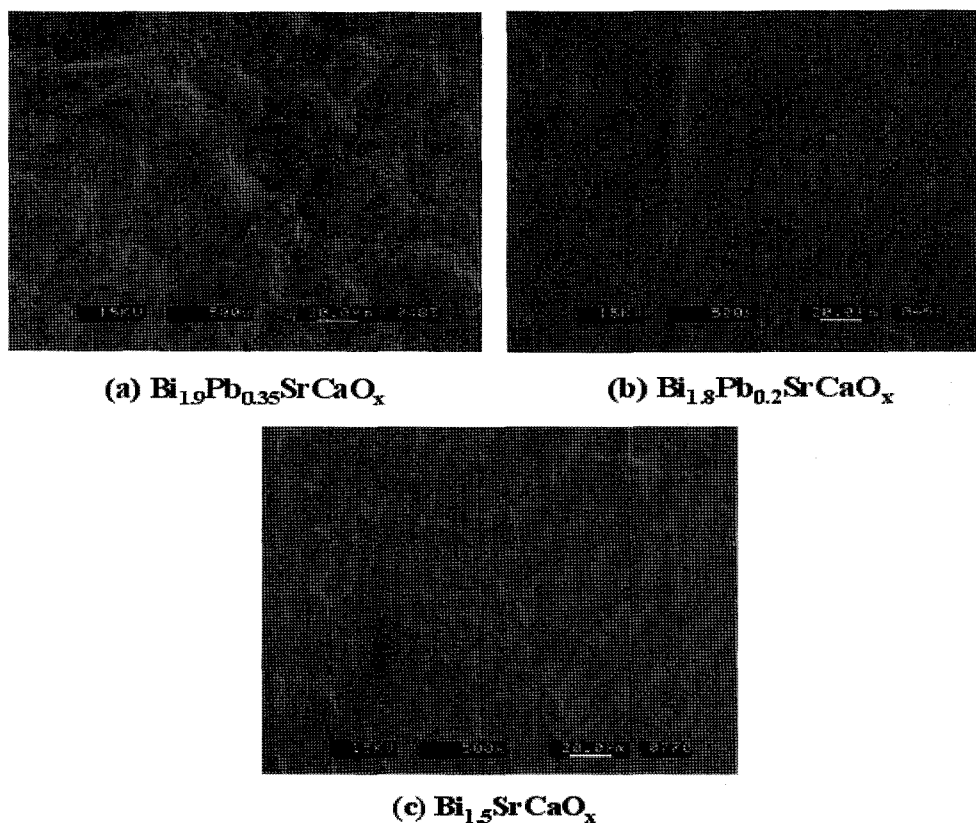


Fig. 5. SEM Image for the surface of coating films after heat-treated at 860°C for 20 seconds.

phase were observed and CuO crystal peaks were also shown. It means that oxidation of Cu substrate continued after crystallization such as confirmed in Fig. 2. However, after heat-treated at 900°C for 12 seconds, the intensity of (2201) orthorhombic crystal phase increased. This means that excessive Pb addition might be more effective to formation crystallization of (2201) orthorhombic crystalline phase.

In Fig. 5, scanning electron microscopic photographs of $\text{Bi}_{1.5}\text{SrCa}$, $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCa}$ and $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$ coating film after heat-treatment at 860°C for 20 seconds were shown. As shown in fig. 5(a), $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$ coated film shows rougher surface than any other composition's one. It reveals that crystallization of (2201) orthorhombic crystal phase preferentially occurred between coating film and Cu substrate. This results from that excess Pb addition leads to form liquid phase and make the (2201) orthorhombic phase crystallization easily compared to the other composition.^{7,8)} And excessive Cu oxidation seems to depress the formation of superconductive (2212) crystal phase.

Under these experimental conditions, the only

$\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCa}$ precursor coating film heat-treated at 900°C for 12 seconds shows the pseudo superconductivity. As shown in Fig. 6, onset temperature is 77 K and its resistance decreases to 17 K, even though it doesn't exhibit zero resistance below T_c . However, this result suggests the possibility that Cu-free Bi-system precursor by using sol-gel method can be used to fabricate the superconductive wiring.

4. Conclusions

Non-aqueous Cu-free precursor with $\text{Bi}_{1.5}\text{SrCaO}_x$, $\text{Bi}_{1.8}\text{Pb}_{0.2}\text{SrCaO}_x$, and $\text{Bi}_{1.9}\text{Pb}_{0.35}\text{SrCaO}_x$ composition could be successfully prepared by using sol-gel process. This non-aqueous precursor sol is stable without change of viscosity for one year. By adding excessive Pb to $\text{Bi}_{1.5}\text{SrCaO}_x$ composition, crystallization of $\text{Bi}_2\text{Sr}_2\text{CuO}_x$ (2201) orthorhombic crystal phase occurs at lower temperature. At the same temperature, orthorhombic (2201) crystal phase and monoclinic (2201) crystal phase occur earlier than other composition as Pb quantity is increased. It is assumed to be more effective to generate

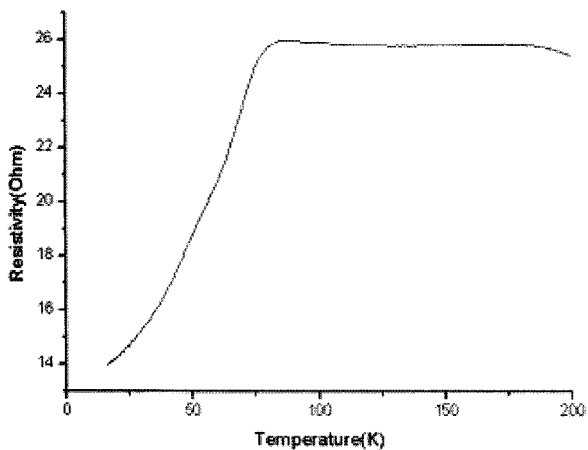


Fig. 6. Temperature dependence of resistance of Bi_{1.9}Pb_{0.35}SrCaO_x coating film after heat-treated at 900°C for 12 seconds.

superconductivity. Consequently, only Bi_{1.9}Pb_{0.35}SrCaO_x composition with mixed crystal phase such as orthorhombic and monoclinic phase showed pseudo superconductive behavior after heat-treatment at 900°C

for 12 seconds. This result suggests the possibility that Cu-free Bi-system precursor by using sol-gel method can be used to fabricate the superconductive wiring.

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