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Polymeric Precursors for the Preparation of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$

TENG-MING CHEN AND Y. H. HU

Institute of Applied Chemistry, National Chiao-Tung University, Hsinchu, Taiwan 30050, Republic of China

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The Pechini process has been used to prepare bulk Bi(Pb)–Sr–Ca–Cu–O superconductors by employing the polymeric citric acid/ethylene glycol (CA/EG) derived precursors. With appropriate heat treatment these precursors can be converted into a pure $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ superconductor with T_c in the range of 100–110 K and with good stoichiometry control and uniform grain size. The chemistry involved in the materials processing leading to the formation of the superconductor and the results of X-ray diffraction, infrared spectroscopy, thermal analysis (DTA/TGA), and SEM morphological studies obtained in our investigations on the precursors as well as the oxide superconductors are presented.

Introduction

Over the last decade there has been great emphasis placed on preparation processes to produce homogeneous and fine particulate specialty ceramics including, in recent years, high temperature oxide superconductors. As a result, many preparation techniques such as sol–gel, freeze-drying, coprecipitation, and organometallic synthesis followed by drying and final calcination have been developed. Among various precursor methods the Pechini process (*1*) now appears to be more versatile and efficient than Pechini originally suggested. This process calls for forming a chelate between mixed cations (dissolved as salts) with a hydroxy carboxylic acid (e.g., citric acid) in an aqueous solution which is then mixed with a poly(hydroxyl alcohol) (e.g., ethylene glycol) and stirred while heating stepwise at moderate temperatures to cause a condensation reaction. The principle and applications of Pechini and related precursor processes have been described in a review article by Lessing (*2*). Anderson and co-workers have used this method in the preparation of over 100 different highly dispersed perovskites, spinels, and related complex oxides, including $LaMnO_3$ and $BaTiO_3$ (*3, 4*). Essentially, this method is able to provide soluble metal-organic and polymeric precursors which have been used for production of oxide powders with excellent homogeneity, uniform grain size, and good stoichiometry control at relatively low temperatures (*2*).

Recently, the preparation of $YBa_2Cu_3O_{7-x}$ superconducting powders and thin films was reported (*5*) using precursors from citric acid/ethylene glycol (CA/EG)-derived polyester and mixed metal cations. Furcone *et al.* (*6*) have reported citrate-derived spin-on films of high T_c $YBa_2Cu_3O_{7-x}$ and $Bi_4Sr_3Ca_3Cu_4O_{16+x}$ superconductors. To our knowledge, there has not been any report

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regarding the preparation of Bi(Pb)–Sr–Ca–Cu–O superconductors using this method. In this paper we report the preparation of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ superconductors (2223 phase) using CA/EG precursors and describe the materials characterizations. Furthermore, preliminary investigations on the effect of processing conditions on the phase stability and microstructure of this oxide superconductor are also discussed.

Experimental

Synthesis and Pyrolysis of Polymeric Precursors

Nitrates or corresponding oxides of Bi, Pb, Sr, Ca, and Cu with 1.5 : 0.5 : 2 : 2 : 3 molar ratio were first dissolved in conc. HNO_3 solution, which was then mixed with an aqueous solution of citric acid (CA) and ethylene glycol (EG) with various CA : EG ratios, i.e., 2 : 1, 1 : 1, 1 : 2, 1 : 4, and 1 : 10, respectively. Following mixing, these solutions were stirred vigorously while heating at 80 to 110°C for several hours until a green-bluish viscous material remained with the evolution of NO_x noted. Further heating to moderate temperatures (150–250°C) caused a condensation reaction beween chelated citric acid and ethylene glycol forming a bluish glassy and gel-like material. Drying and charring of this material carried out in an alumina crucible at 350–400°C in the air for 24 hr resulted in a dark brown material that was further ground, pelletized, and pyrolyzed in an alumina boat at 800 and 860°C, respectively, for 2 days under a flow of oxygen. During the pyrolysis, heat generated from the combustion of the hydrocarbon portion of the polymer backbone speeded up the reaction, and most of the residual hydrocarbon in the materials was simultaneously oxidized and removed by oxygen flow. Pellets of the 2223 phase for resistivity measurements were obtained by sintering the above pyrolyzed products at 860°C for 60 hr then cooling slowly in the air or quenching in liquid nitrogen.

Characterization of Precursors and Pyrolysis Products

IR absorption spectra of the mixed metal–CA/EG precursors were determined using a Nicolet FT-500 spectrometer on a pellet sample. DTA and TGA measurements of the precursors were carried out under an argon atmosphere using a Seiko SSC-5000 thermal analysis system with a heating rate of 20°C/min. X-ray powder diffraction data were obtained with a Shimadzu XD-5 diffractometer employing Cu$K\alpha$ radiation and a Ni filter. Morphological studies on the microstructure of the materials were carried out using a Hitachi S-570 scanning electron microscope. The temperature-dependent electrical resistivity measurements on the sintered Bi(Pb)-2223 sample were carried out by a conventional dc four-probe method, using a 10-mA dc current. The magnetic measurements under zero-field condition and with a 35 Gauss-field present (Meissner effect) were obtained, respectively, between 4.2 and 120 K with a fully automated SQUID magnetometer (MPMS system, Quantum Design).

Results and Discussion

The $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ precursors derived from the CA/EG mixture were bluish-green, homogeneous, and gel-like. This material is soluble in ethylene glycol, tetrahydrofuran, and 2-methoxyethanol, and can easily be fabricated into films by spin-coating on appropriate substrates, i.e., single crystal MgO or $SrTiO_3$.

The results of TGA/DTA studies on the precursors before pyrolysis are represented in Fig. 1. Weight losses in three distinct regions, namely, 160, 320–450, and 500–870°C, are clearly seen. The thermolysis of citric acid along with the loss of ethyl-

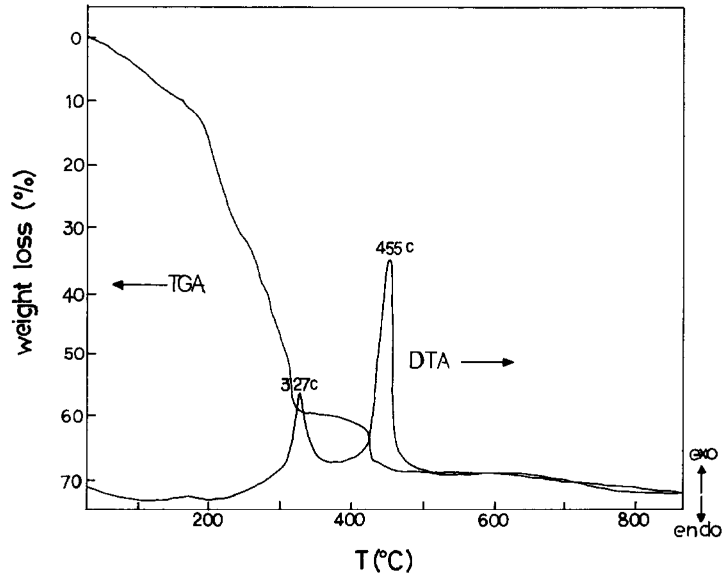

FIG. 1. The results of thermal analytical measurements (DTA/TGA) of the mixed metal-CA/EG precursors leading to the formation of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ superconductor.

ene glycol and the polymer formed from EG and CA occurs in the neighborhood of 330 and 450°C, respectively (7). The conversion of the organic component of the precursor to free carbon and the elimination of moisture are presumably responsible for most of the weight loss at temperatures below 450°C.

To gain further insight into the coordination of various cations and to confirm the formation of metal–chelated polyester precursors, we have measured the FTIR spectrum of the polyester derived from EG and CA (shown in Fig. 2a). The spectrum of the polyester precursor showed a sharp absorption at 1740 cm^{-1} corresponding to the C=O stretching mode (*8*), and two strong peaks observed near 1150 and 1050 cm^{-1}, respectively, can be assigned to the assymmetric stretching of the C–O (OR) in the ester (*8*). This may indicate all of the COOH group had reacted with ethylene glycol to form esters. In the spectrum of the mixed metal–chelated EG/CA precursors (shown in Fig. 2b), a new peak at 1640 cm^{-1} was observed in addition to the ester C=O and C–O peaks at 1740 and 1220 cm^{-1}, respectively. The new absorption can presumably be attributed to the formation of $-COO^-$ groups coordinated in a monodentate fashion to metal ions as reported by Kirschner and Kiesling (*9*). In addition, the absorptions occurred at 1090 and 810 cm^{-1} are assigned respectively to the O–H (in-plane) and C–H (out-of-plane) deformations of excess ethylene glycol present in the precursors (i.e., the EG/CA ratio was 4). A temperature-dependent IR study on the pyrolysis products of the metal coordinated precursors is currently under investigation to monitor the coordination of various cations during the heat treatment.

The XRD patterns of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ prepared from EG/CA (4 : 1) precursors as described in the Experimental section and under slow-cooling or quenched conditions, respectively, are represented in Fig. 3. Samples obtained from the same

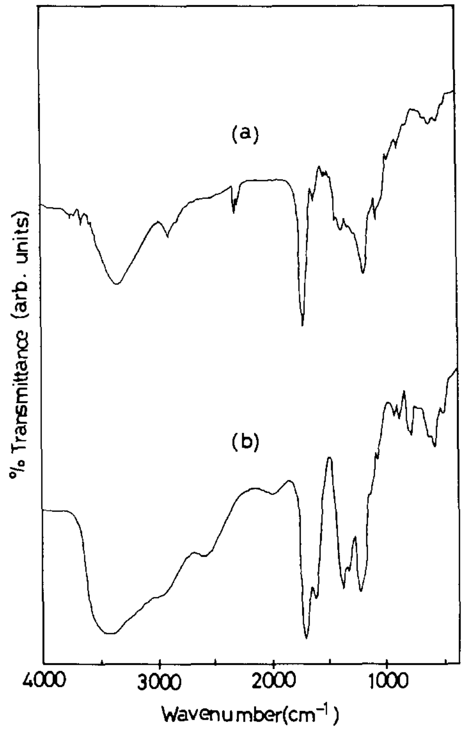

FIG. 2. The FTIR absorption spectra of (a) EG/CA (4 : 1) polymeric precursors and (b) mixed metal-chelated EG/CA precursors, respectively, prior to pyrolysis.

batch of preparation and quenched with liquid N_2 gave a nearly pure 2223 phase (Fig. 3b). In contrast, those obtained by slow-cooling gave a mixture of both 2212 and 2223 phases based on X-ray diffraction data.

To confirm superconductivity of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ phase we have investigated the temperature-dependent resistivity and magnetic susceptibility of this oxide derived from EG/CA precursors, and the results of both measurements are represented in Figs. 4 and 5. The temperature dependences of resistivity for $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ phase prepared under both slow-cooling and liquid-N_2 quenched conditions, respectively, are shown in Fig. 4. The liquid-N_2 quenched sample (Fig. 4b) showed a sharp transition with T_c (onset) = 110 K and T_c (zero) = 100 K indicating the presence of 2223 phase, whereas that obtained under slow-cooling conditions (Fig. 4a) clearly revealed that two transitions occurred at ca. 107 and 80 K, respectively, with a nonzero residual resistance of 4 × 10^{-5} ohm at 15 K. The effect of final heat treatment on the phase formation and stability, as shown by the XRD and resistivity data, is not clear. Presumably, the lead-containing 2223 phase partially disproportionated into 2212 phase and some Pb–Ca–O phase(s) (e.g., Ca_2PbO_4) during the cooling process (*10*), and this observation requires further investiga-

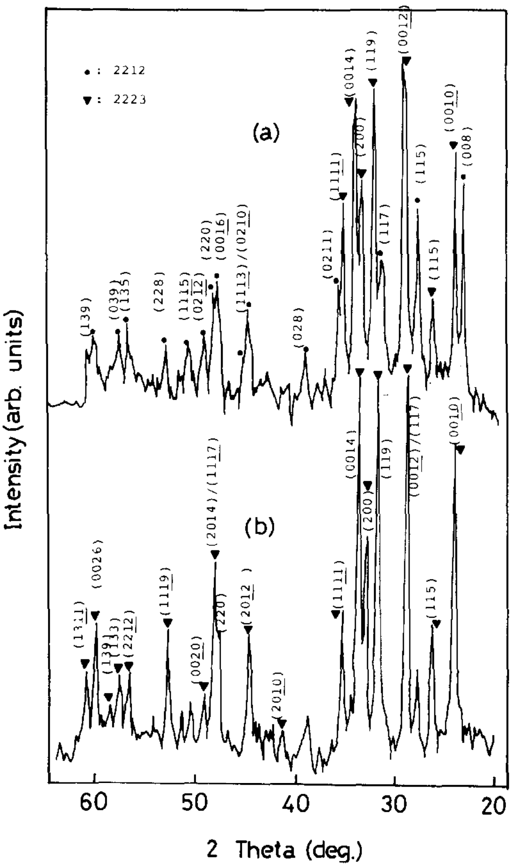

FIG. 3. The X-ray diffraction patterns of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ obtained after final sintering and under (a) slow-cooling and (b) liquid-N_2 quenched conditions, respectively.

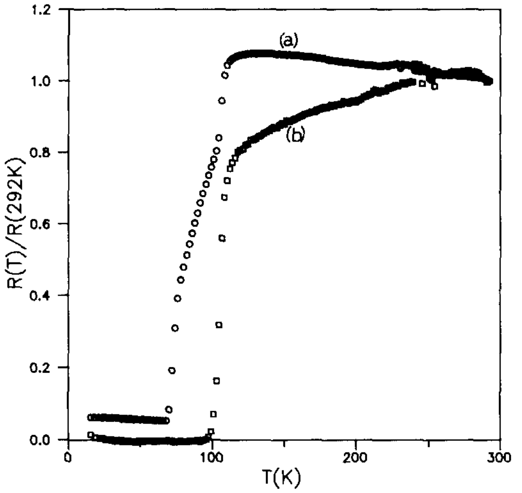

FIG. 4. Temperature dependences of reduced resistivity of the $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ phase under (a) slow-cooling and (b) liquid-N_2 quenched conditions, respectively.

tions. To ensure that superconductivity was a bulk property of the samples, magnetization measurements under zero-field-cooled (flux exclusion) and field-cooled (flux expulsion) conditions were carried out and are represented in Fig. 5, where superconducting onset temperature around 107 K is in good agreement with the resistance data. The Meissner fraction of $-4\pi\chi$ was estimated to be ca. 40% at 5 K from the field-cooled sample, indicating bulk superconductivity of the samples.

Scanning electron microscopic studies on $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ phase prepared by the precursor method showed clearly the lamellar feature of the grains obtained under quenched conditions (Figs. 6a and 6b). Step growth behavior due to stacking of plate-like grains is clearly observed in the bottom right corner of the micrograph (Fig. 6a). However, the sizes of the plate-like grains were estimated to be ca. in the range of micrometers.

The residual carbon trapped and remained in the final oxide superconductors, particularly those derived from the metal–organic precursors, has been quantitated and reported to be related to porosities in the materials and to the lowering of T_c of the superconductors (*11*). We, however, did not observe any deterioration of superconductivity of our lead-containing 2223 phase prepared by the precursor method. In addition, the effect of composition of polymeric precursors (i.e., the EG/CA ratio in the Pechini process) on the variation of the final agglomerate morphology and microstructure of the sintered oxide superconductors (e.g., the size of the grains and the impurities present in the grain boundaries), presumably closely related to superconducting properties, has been noted and is under investigation in our laboratories.

Conclusions

A polymeric EG/CA precursor process has been developed to prepare a pure $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ superconductor with T_c at ca. 107 K and with good stoichiometry and homogeneity control. We have investigated the materials chemistry involved in

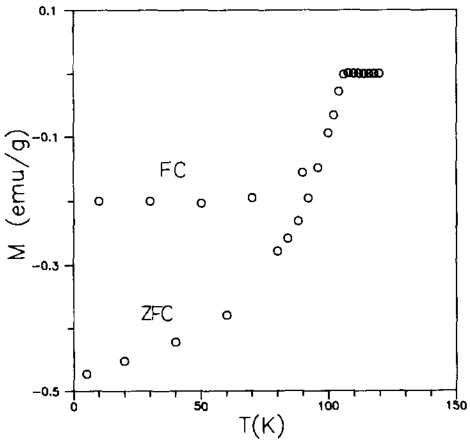

FIG. 5. Temperature dependences of dc magnetic susceptibility of superconducting $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ prepared under quenched conditions showing the Meissner (FC) and shielding (ZFC) effects.

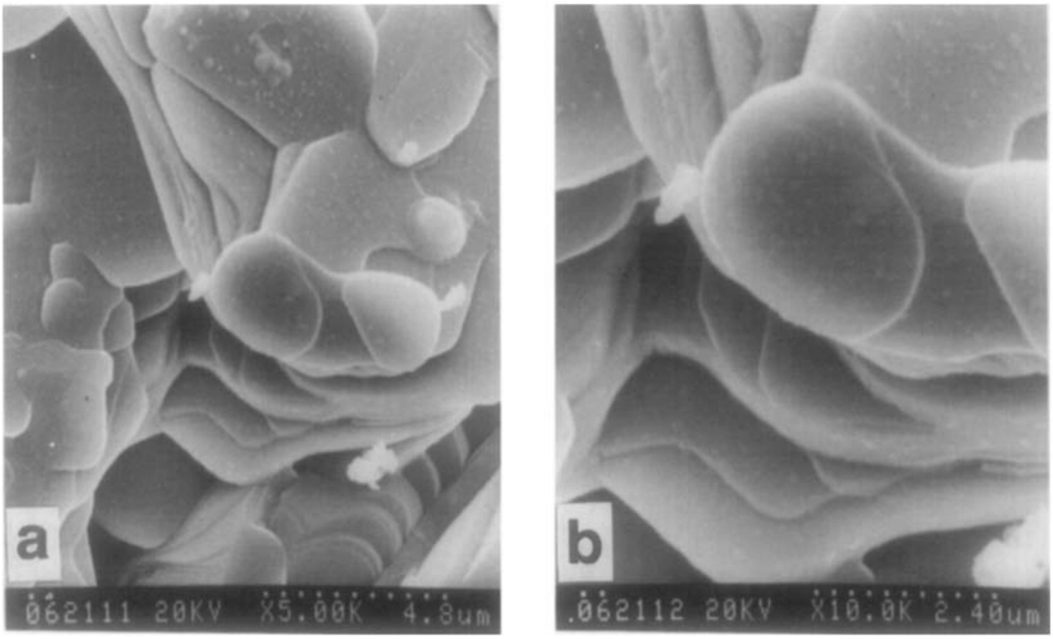

FIG. 6. Scanning electron micrographs of the superconducting $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$ showing the lamellar feature of the grains in this material.

the formation of high T_c bismuth superconductors. The IR absorption spectra indicate the formation of the highly viscous mixed metal–chelated polyester with various EG : CA ratios. On the other hand, the thermal behavior of the polymer precursor was monitored by both TGA and DTA analyses. We also found that the way final heat treatment was carried out during processing has a drastic effect on the formation of $Bi_{1.5}Pb_{0.5}Sr_2Ca_2Cu_3O_x$. The effects of EG/CA ratio in the precursors and the residual carbon content on the critical current density (J_c) and on the microstructure of the superconductor are noted and require further study.

Acknowledgments

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