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Preparation of Silver Doped High Temperature Superconductors by the Controlled Double-Jet Precipitation

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PREPARATION OF SILVER DOPED HIGH TEMPERATURE SUPERCONDUCTORS BY THE CONTROLLED DOUBLE-JET PRECIPITATION

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Abstract Chemical precursors of high temperature superconductors were prepared by the controlled double-jet precipitation of their oxalates to obtain suspensions with submicron average crystal size,narrow crystal size distribution, desired chemical composition and internal structure.To improve mechanical and electrical properties of HTSC layers the chemical precursors of HTSC were doped by silver oxalates using the same method. This technique enables to achieve better mixing of reagents in compare with mixed oxide processing. The suspensions were coagulated, washed, and coated on various substrates.During carefully controlled heat treatment the grains readily sintered and formed HTSC layers. The layers prepared by this technique showed some improvements in mechanical and electrical properties. When coated on silver substrate, high density layer and a strong bond between the HTSC layer and substrate were achieved.

INTRODUCTION

The intensive efforts continue to prepare chemical precursors of high temperature superconductors (HTSC) by precipitation from solutions to produce chemical precursor of HTSC with submicron average crystal size,narrow crystal distribution, desired chemical composition, internal structure, morphology. However, crystallization by precipitation from solutions is a rather difficult process because of complexity of steps simultaneously and uncontrolled occuring during or after precipitation : nucleation, crystal growth,Ostwald ripening, recrystallization, coagulation and agglomeration. To overcome a traditional characterization of precipitation from solutions as a mysterious unit operation it is necessary to open the door for controlling of processes occuring during or after precipitation[1] and to develop a convenient technique to achieve the desired properties of HTSC.

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CONTROLLED DOUBLE-JET PRECIPITATION

It is now well-known that to obtain a desired product via oxalate route the reaction conditions have to be controlled: pH, anion or cation concentration[2], solubility, contamination, type and amount of a convenient lyophilic polymer to prevent coagulation and agglomeration,to by-pass filtration or centrifugation because of recrystallization etc. On the other hand the mixing/stirring conditions play also an important role and some considerations have to be fulfilled to avoid many difficulties.In order to solve these problems we have introduced a method of the controlled double-jet precipitation as a promising method for the preparation of chemical precursors of HTSC.[3]

In modern precipitations of some sparingly soluble salts, such as silver halides[4], the cation and anion solutions are simultaneously separately introduced to the crystallizer with a stirred solution of a lyophilic polymer under conditions, where the temperature, excess of anions or cations in the crystallizer, pH, presence of solvent,growth restrainer or modifier, reactant addition rates and mixing/stirring conditions are tightly controlled. While the reactants are added at balanced addition rate in separate jets, the reaction is referred to as controlled double-jet precipitation.

An interesting characteristic of double-jet precipitation is that the observable nucleation stage ends rather early and the only growth occurs, i.e. further addition of reactants causes only growth of crystals already present. During the growing stage the nucleation may be eliminated, recrystallization and Ostwald ripening can be minimized by controlling of supersaturation in the crystallizer.The presence of protective agents prevents coagulation and agglomeration of microcrystals. After precipitation the suspension is coagulated and the by-products are washed while the surface of microcrystals is protected by growth inhibitors to prevent recrystallization. The next step is coating.

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EXPERIMENTAL

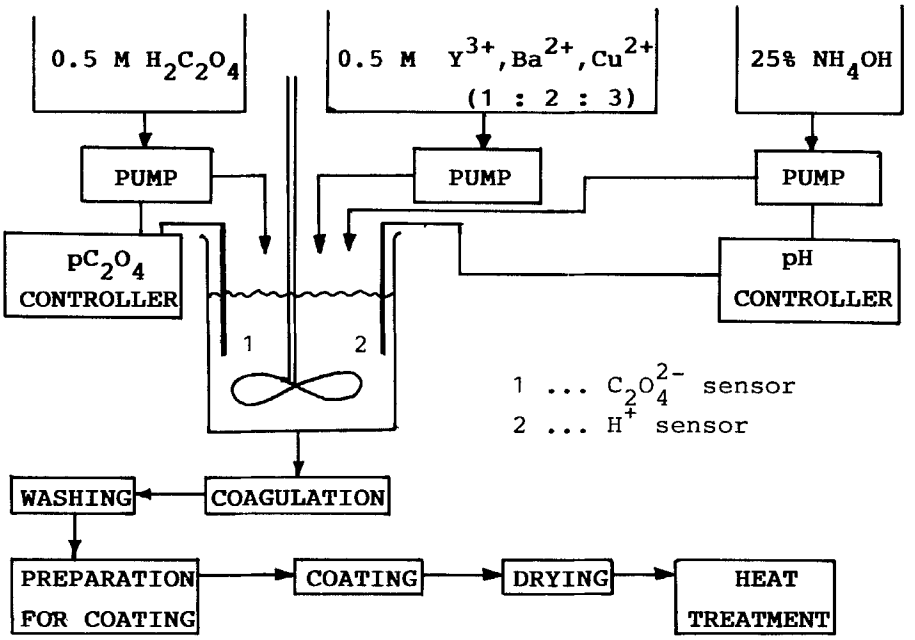

FIGURE 1 Procedure for preparation of HTSC layers via the controlled double-jet precipitation

The two solutions of cations and anions were added at the reactant flow rate 15 ml/min during 20 min to the crystallizer with the initial volume 500 ml(ethanol,water1:1)of 2% inert bone gelatin at 35° C, pH 5.0, pC_2O_4 2.0. After that the cation solution was replaced by 1.0 M $AgNO_3$ and the precipitation continued to add various amount of silver ions versus HTSC cations (from 1 to 30%). By the same technique the $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3$ oxalates were doped by silver ions. To decrease average crystal size under 100 nm, 100 mg of 8-hydroxy-quinoline was added prior the precipitation. When the precipitation was over another portion of oxine was added to inhibit recrystallization during washing. The suspension was prepared for coating and coated on various substrates in amount that the thickness of HTSC layer after heat treatment was about 20 μm. The properties of layers were measured by conventional techniques.

RESULTS AND DISCUSSION

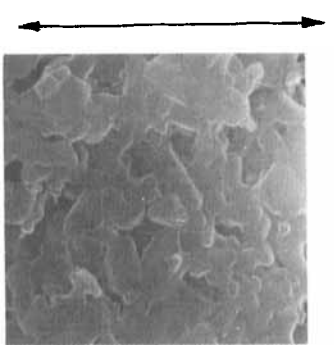

FIGURE 2 $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3O_x$ on $SrTiO_3$

FIGURE 3 $(Bi_2Pb_{0.5}Sr_2Ca_2Cu_3O_x)_9Ag_1$ on silver tape

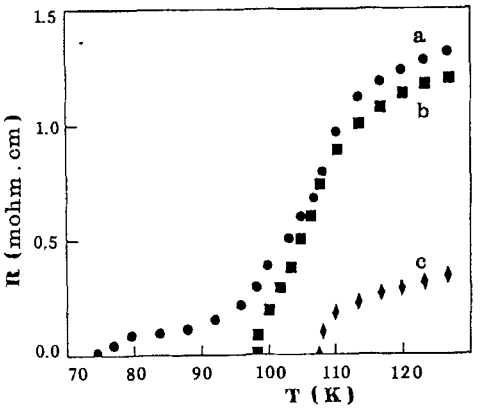

FIGURE 3 Resistivity-temperature curves for layers heated at 830°C
a) $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3O_x$
b) $Bi_2Pb_{0.5}Sr_2Ca_2Cu_3$ oxalates precursor precipitated in the prese of 100 mg oxine
c) $(Bi_2Pb_{0.5}Sr_2Ca_2Cu_3)_9Ag_1$ oxalates precursor precipitated in the presence of 100 mg oxine

Submicron oxalate grains were synthesized by the controlled double-jet precipitation. Thermogravimetric experiments showed that complete decomposition of the coprecipitated oxalates in the presence of an inert gelatin takes place till 800° C. To produce a powder with high sinterability, the precipitations were done in the presence of the growth restrainer of 100 mg of oxine.

The restrainer increases number of formed particles and decreases the average crystal size. On the other hand the restrainer stabilizes the particles against Ostwald ripening not only during the growth of particles but also during coagulation and washing of suspension.

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To further increase the sinterability of powder and thus overcome the grinding and mixing of oxides,the precursors of HTSC were doped by silver oxalate produced by the controlled double-jet precipitation to cover the surface of oxalates already present in the crystallizer. During the heat treatment it was observed that the powder started to sinter at about 800° C to form a high density layer.In the case that the layers were coated on a convenient metallic substrate,e.g. silver tape, the layers were strongly bounded to the substrate and the tape could be bent to shapes required for practical purposes without failure.

Other investigations of this sytems are underway.It is necessary to clarify if the silver dopant should cover individual grains to separate them or to form a net around the sintered HTSC grains.

CONCLUSION

Chemical precursors of Y-Ba-Cu-O and Bi-Pb-Sr-Ca-Cu-O HTSC were prepared by the controlled double-jet precipitation in the presence of inert bone gelatin. The precursors were doped by the silver oxalates to control silver doping on submicron level. If the precipitation were carried out in the presence of oxine, the powder with high sinterability formed layers with high density.

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