Preparation of Superconducting Compounds in Y-Ca-Sr-Cu-O System by Sol-Gel Method

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ABSTRACT

Superconductors in the Y-Ca-Sr-Cu-O system were obtained under atmospheric pressure through the sol-gel method. Disc samples, the nominal composition of which was Ca0.3Y0.7Sr0.3CuO2, showed superconductivity by contriving heating conditions under atmospheric pressure. The superconductivity was confirmed from both Meissner signal at about 70 K and zero electric resistivity at about 20 K. It is assumed that the superconductivity is due to orthorhombic Y(Sr,Ca)2Cu3O6 and K2NiF4-structure Y0.3Sr0.7Cu03-x.

KEY WORDS: Ca0.3-xYxSr0.7Cu1.0O2 composition, Y(Sr,Ca)2Cu3O6 superconductor, Y0.3Sr0.7Cu03-x superconductor, infinite-layered superconductor, sol-gel method

INTRODUCTION

For superconductors assumed to be formed in the Y-Ca-Sr-Cu-O system, Y0.3Sr0.7Cu03-x[1] in the K2NiF4 structure, YSr2Cu3O7-x[2] in the YBa2Cu3O7-x structure and infinite-layered (Y,Ca,Sr)CuO2[3] are candidates. However, the Y0.3Sr0.7Cu03-x and YSr2Cu3O7-x superconductors were not prepared in the phase equilibrium studies by Ikeda et al.[4] and Roth et al.[5]. Superconducting infinite-layered compounds have been synthesized only by the high pressure technique[6,7]. Superconducting compounds in the Y-Ca-Sr-Cu-O system have not been prepared at atmospheric pressure.

Previously, Ceramics of the Ca0.3-xYxSr0.7Cu2 nominal composition were prepared by the sol-gel method, and a sample showed a diamagnetic signal at about 50 K. Zero resistivity, however, was not detected[8]. In the present study, Ca0.3-xSr0.7Cu2 compounds showing both Meissner signal and zero resistivity have been prepared by the sol-gel method under atmospheric pressure.

EXPERIMENTAL PROCEDURE

Ca(OC2H5)2, Sr(OCH3)2, Y(OC2H5)3, and Cu(OCH3CH2)2 were used as starting materials. The solution of Ca(OC2H5)2 and Sr(OCH3)2 and the solution of Y(OC2H5)3 and Cu(OCH3CH2)2 were mixed to make a homogeneous non-aqueous solution. The nominal metal composition of the prepared mixture was Ca:Y:Sr:Cu = (0.3-X):X:0.7:1. The value of X ranged from 0 to 0.3. The homogeneous mixture was hydrolyzed and polycondensed under an acidic condition with acetic acid at about 80 °C to become viscous sol.

The sol was dried at 300 °C, and then calcined at 800 °C in air. The calcined powder was ground and compacted into discs 12 mm in diameter. The discs were heated for sintering with two different heating programs. That is, one was a heating program consisting of one step. In this program, the discs were heated at 800° and 1000 °C for 10 h in flowing pure oxygen. This heating program is named heat I in this paper. The other was a heating program consisting of two steps of process A and process B. This heating program is named heat II. For process A, heating temperature of 800°, 900°, and 950 °C, duration of 1 to 600 min, and concentration of oxygen in flowing gases, 0, 3 and 7%, were examined. Nitrogen was used as a base gas. In process B, the discs were heated at 1000° and 1050 °C for 10 h or 5 h in flowing gases with oxygen concentrations of 0, 3,
RESULTS AND DISCUSSION

Crystaline phases formed in the powder calcined at 800 °C were varied depending on whether it contained yttrium or not. In the powder containing no yttrium, $X_s$ of 0, a large amount of orthorhombic (Sr, Ca)CuO$_2$ (abbreviated to ortho-(Sr, Ca)CuO$_2$) and (Sr, Ca)$_2$CuO$_3$ formed. When yttrium was added, ortho-(Sr, Ca)CuO$_2$ almost disappeared and $Y(Sr,Ca)_2CuO_3$ was formed as a main phase. The phase identified as $Y(Sr,Ca)_2CuO_3$, may be $Sr_4Cu_2O_4$ containing calcium and yttrium. It was found that yttrium depresses the formation of ortho-(Sr, Ca)CuO$_2$. $Y_2O_3$ and a very small amount of CuO were also formed in the calcined powders containing yttrium. $Y_2O_3$ increased with the content of yttrium. When calcination was made at 700 °C, alkaline earth carbonates and CuO were formed in quantity.

XRD patterns of the disc samples heated at 1000 °C with heat I are shown in Fig.1. In the sample with $X_s$ of 0, besides a large amount of ortho-(Sr, Ca)CuO$_2$ which was already formed in calcination at 800 °C, (Sr, Ca)$_2$CuO$_3$ is formed. In the sample with $X_s$ of 0.1, ortho-(Sr, Ca)CuO$_2$, which was a trace phase in calcination, is grown to a main phase and $Y(Sr,Ca)_2CuO_3$, $Y(Sr,Ca)_2Cu_3O_7$ and Sr$Y_2O_4$ are formed. A trace of a phase which may be considered $Y_{0.3}Sr_{0.7}CuO_3$ in the K$_2$NiF$_4$ structure is also seen in the sample with $X_s$ of 0.1. Y($Sr,Ca)_2CuO_3$, Y($Sr,Ca)_2Cu_3O_7$, and Sr$Y_2O_4$ increase and ortho-(Sr, Ca)CuO$_2$ decreases as the content of yttrium increases.

Susceptibility-temperature curve of disc samples heated with heat I was measured. When heating was made at 800 °C, no samples showed the transition to diamagnetism. When heating temperature was raised to 1000 °C, the sample with $X_s$ of 0.3 did not show a diamagnetism, but the sample with $X_s$ of 0.1 exhibited a diamagnetic transition at about 50 K. The volume fraction of superconducting phases at 10 K was estimated at about 1%. The fact that a diamagnetic transition was not detected when the $X$ value increased suggests that the compound showing the diamagnetism is formed stably under the limited condition where the content of yttrium is about 0.1. The diamagnetism was assumed to be due to K$_2$NiF$_4$-structure $Y_{0.3}Sr_{0.7}CuO_3$.

The disc samples, the composition of which is $Ca_{0.2}Y_{0.1}Sr_{0.7}CuO_2$, having $X_s$ of 0.1, were examined in heat II consisting of process A and B.

Dependence of susceptibility of the samples on oxygen concentration of the flowing gas in process A is shown in Fig. 2. Process A was carried out at 950 °C and process B was made at 1000 °C for 10 h in the flow of O$_2$ gas. It is found that susceptibility increases with low concentration of oxygen. The oxygen concentration of less than 3% is especially effective in increasing susceptibility. Referring to this result, process A was carried out in the flow of N$_2$ gas after this examination.

Dependence of susceptibility on heating temperature on process A, and that on duration time of process A, were investigated. In this investigation, process B