Low Temperature Synthesis of (La, Sr)$_2$CuO$_4$ —Preparation from Hydroxide—

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Abstract

The formation temperature of (La, Sr)$_2$CuO$_4$ prepared from mixed hydroxides was determined to be 750℃. This temperature was found to be 150℃ lower than temperatures of (La, Sr)$_2$CuO$_4$ synthesized from oxides/carbonates or nitrates. From the measurement of magnetic susceptibility, the volume fraction of superconductivity of the (La, Sr)$_2$CuO$_4$ prepared from mixed hydroxides was estimated to be about 5% at 5K. Our result indicates that the synthesis from hydroxides is useful in obtaining the LSCO bulk sample at low sintering temperature around 750℃.

1. Introduction

Since the discovery of cuprate superconductors, many processes were applied to prepare the superconductors. To obtain fully oxidized films of a desired layered structure, a low temperature growth method is favorable. An $YBa_2Cu_3O_y$ film with the (110) plane parallel to the substrate was grown epitaxially on $SrTiO_3$ (110) at a temperature as low as 530℃ by activated reactive evaporation[1]. A $Bi_2Sr_2CuO_y$ film was formed on a $SrTiO_3$ at a temperature of 300℃ by using NO_2 as an oxidizing agent[2]. However, less work has been done to lower sintering temperature for bulk samples. For a (La, Sr)$_2$CuO$_4$ (LSCO) sample, sintering temperature of 1000-1200℃ was reported[3-7].

We have recently reported that an [001] oriented $Ca(OH)_2$ film is formed on MgO substrate by a spray method[8]. By heating this film up to 600-800℃ in air for dehydration, a [111] oriented CaO film was formed. Since most of hydroxides change into the oxides between 100℃ and 600℃, the formation temperature of an oxide superconductor from hydroxides is expected to be 100-600℃. However, as far as we know, few works on formation of bulk oxide superconductors from hydroxides have been done.

The aim of this work is to clarify the formation temperature of the LSCO from hydroxides and to compare it with the formation temperature from other starting materials, *i.e.*, 1) La_2O_3, $SrCO_3$ and CuO, 2) La-, Sr- and Cu-nitrates and 3) chelate complex of La, Sr and Cu.

2. Experimental

2. 1 Preparation of starting materials and formation of LSCO samples

2. 1. 1 Hydroxide method

A mixed hydroxide was prepared by precipitation. La $(NO_3)_3 \cdot 8H_2O$ (99%, Kanto Chemical Co., INC.), Sr $(NO_3)_2$ (99%, Kanto Chemical Co., INC.) and Cu $(NO_3)_2 \cdot 3H_2O$ (99%, Kanto Chemical Co., INC.) with molar ratio of 1.85:0.15:1.00 were dissolved in water. By adding aqueous NaOH to the solution, mixed hydroxide was precipitated. After filtering the precipitation, it was washed with distilled water and dried in air at 90℃ for 12 hours.

2. 1. 2 Oxides and carbonate method

The powders of La_2O_3 (99.9%, High Purity Chemicals Co.), Sr $(CO_3)_2$ (96%, Kanto Chemical Co., INC.) and CuO (99.9%, Nihon Kagaku Sangyo Co., LTD.) with molar ratio of 1.85:0.15:1.00 were ground in an agate mortar.

2. 1. 3 Nitrate method

The powders of La $(NO_3)_3 \cdot 8H_2O$, Sr $(NO_3)_2$ and Cu $(NO_3)_2$ with molar ratio of 1.85:0.15:1.00 were dissolved in water. After evaporating water at 100℃, the specimen was ground and mixed in agate mortar.

2. 1. 4 Chelate method

The powders of La $(NO_3)_3 \cdot 8H_2O$, Sr $(NO_3)_2$ and Cu $(NO_3)_2$ with molar ratio of 1.85:0.15:1.00 were dissolved in water. By adding ethylenediaminetetraacetic acid (EDTA) to the solution, a mixed chelate of La, Sr and Cu was precipitated. After drying the solution at 100℃, the chelate complex was decomposed to oxide at 400℃.

2. 1. 5 Formation of the LSCO sample

All the powders prepared by the methods described above were pressed into pellets and sistered at 600-900℃ for 3-10 hours in air.

2. 2 Determination of crystal structure and chemical composition

The crystal structure of the samples was determined by the powder X-ray diffraction method (XRD). The atomic ratio of the samples were determined by atomic emission analysis of inductively coupled plasma (ICP-AES). The homogeneity of the samples were examined by energy dispersive electron probe (EPMA) method.

2. 3 Measurement of Tc

The critical temperature, Tc of the LSCO samples was determined by a SQUID (Quantum Desigh Co., MPMS) with field cooling under 20 Gauss.

3. Results and Discussion

In Fig. 1 (a), an XRD pattern for the raw material of mixed hydroxide is shown. Broad peaks of La $(OH)_3$ and CuO_x were observed, suggesting that a part of Cu $(OH)_2$ is dehydrated into CuO even before sintering. In fact, it is known that the Cu $(OH)_2$ is unstable in

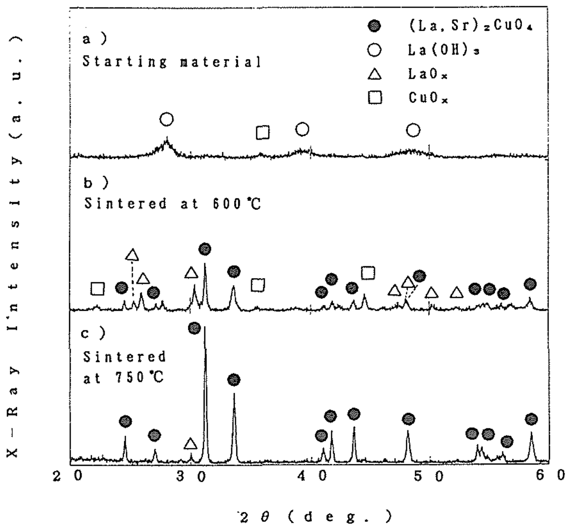

Fig. 1 XRD patterns of a) a raw material of hydroxides mixture, b) a specimen sintered at 600℃, and c) a specimen sintered at 750℃

the air and changes into CuO. As shown in Fig. 1 (b), by sintering the starting material at 600℃,LSCO, LaO$_x$ and CuO$_x$ were formed.

By sintering the material at 750℃, almost a single phase of LSCO was obtained as shown in Fig. 1 (c). The atomic radio of the sample shown in Fig. 1 (c) was measured by the ICP-AES, indicating that La:Sr:Cu = 1.88:0.16:1.00. From the EDX experiment, no variation of the atomic ratio was observed throughout the sample, indicating the composition of the sample is homogeneous. Therefore, formation temperature of the LSCO from mixed hydroxides was found to be 750℃.

In Fig. 2 (a), an XRD pattern for the starting material of mixed oxides and carbonate is shown. Peaks from both LaO$_x$ and CuO$_x$ were observed. As shown in Fig. 2 (b), by sintering the starting material at 600℃, LSCO, LaO$_x$ and CuO$_x$ were formed. With raising the sintering temperature to 900℃, almost a single phase of LSCO was prepared, as shown in Fig. 2 (c). Therefore, formation temperature of the LSCO from oxide/carbonate is estimated to be 900℃.

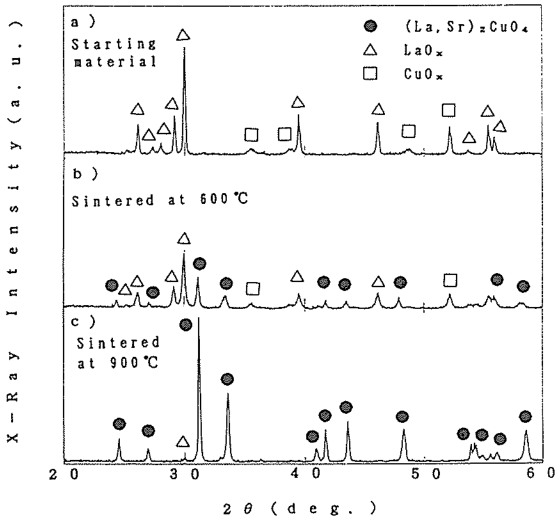

Fig. 2 XRD patterns of a) a raw material of oxide/carbonate mixture, b) a specimen sintered at 600℃, and c) a specimen sintered at 900℃

In Fig. 3 (a), an XRD pattern of mixed nitrates is shown. Together with peaks from La (NO$_3$)$_3$, those from an unknown phase was observed. As shown in Fig. 3 (b), by sintering the starting material at 600℃, LaO$_x$ and CuO$_x$ were observed with weak peaks of the LSCO. With raising the sintering temperature to 900℃, almost a single phase of LSCO was prepared as shown in Fig. 3 (c). Therefore, formation temperature of the LSCO from nitrates is determined to be 900℃.

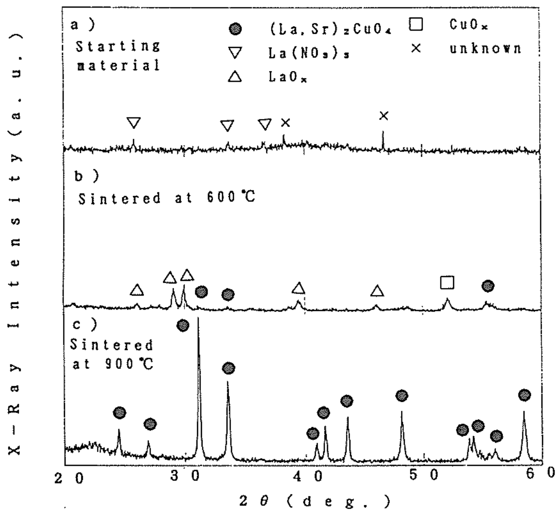

Fig. 3 XRD patterns of a) a raw material of nitrate mixture, b) a specimen sintered at 600℃, and c) a specimen sintered at 900℃

In Fig. 4 (a), an XRD pattern of the starting material of the mixed chelate complex is shown. No strong peaks were observed, suggesting that the chelate mixture has an amorphous structure. As shown in Fig. 4 (b), by sintering the starting material at 600℃, the LSCO was formed together with an unknown phase. As shown in Fig. 4 (c), by sintering at 700℃, almost a single phase of LSCO was obtained. Therefore, formation temperature of the LSCO from chelates is found to be 700℃.

From these experiments, it is found that the formation temperature of the LSCO by the hydroxide method is 150℃ lower than those by the oxide-and-carbonate method and nitrate method, and 50℃ higher than that of chelate method. The EDTA used by the chelate method is more expensive than the materials used by the hodroxide method. Therefore, it is to be noted that the hydroxide method is useful in obtaining the LSCO sample at low sintering temperature.

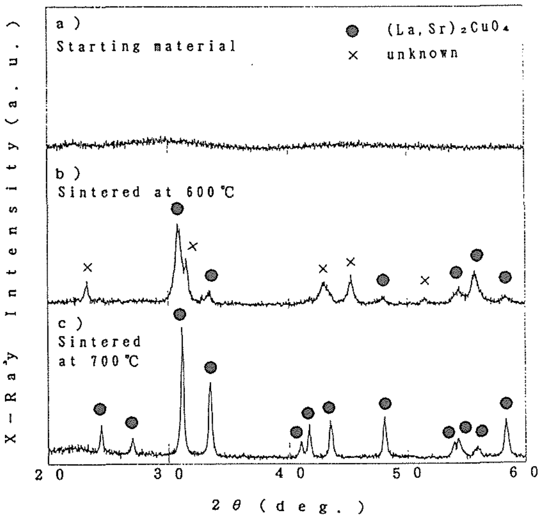

Fig. 4 XRD patterns of a) a starting material of chelate mixture, b) a specimen sintered at 600℃, and c) a specimen sintered at 700℃

For the specimens annealed at 600℃ and 750℃ from hydroxides, susceptibility was measured by SQUID. As shown in Fig. 5, the sample sintered at 750℃ from hydroxide showed a Tc of 27K, clearly indicating that it exhibits superconductivity, although the observed Tc is about 10K lower than that reported so far[9]. From the magnetic susceptibility at 5 K, the volume fraction of the superconductor was estimated to be about 5 %. The lower Tc and low volume fraction are probably due to the low density of the sample. In fact, the density of the sample was about 2.16g/cm^3, which correspnded to about 40% of the density of the ideal LSCO sample. The density will be increased by adding the press process during sintering.

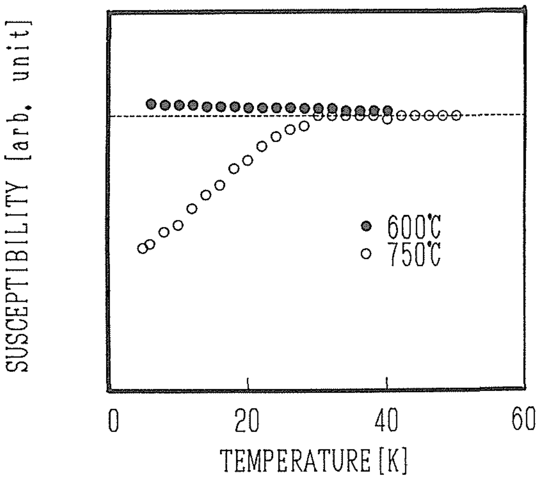

Fig. 5 Susceptibility vs. temperature for the LSCO sample prepared by the hydroxide method. While the solid circles represent the susceptibility of the sample sintered at 600℃, the open circles represent the susceptibility of that sintered at 750℃

Conclusion

A sintering temperature of 750℃ to prepare the single phase of LSCO was achieved by the hydroxide method. This temperature is 150℃ lower than those of the oxide-and-carbonate method and nitrate method, and 50℃ higher than that of chelate method. Our result indicates that the hydroxide method is useful in obtaining the LSCO sample at low sintering temperature.

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