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Superconductivity and structural characteristics of ceramic Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ prepared by ambient pressure synthesis using citrate pyrolysis method

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Abstract

Sintered material of Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ (Pr247) was synthesized at ambient pressure condition by using citrate pyrolysis precursor method, and the superconductivity caused by oxygen reduction treatment has been confirmingly observed and examined.

By resistivity and magnetization experiments, it has been found that the critical temperature T_c of the reduced samples could reach about 10 K higher than previously reported data for pure Pr247. Besides, from TEM observations, the present material was found to be heterogeneous system containing Pr247, Pr124 and novel stacking structure phases rich in CuO single chains. These results have suggested that oxygen–reduction at such region rich in the CuO single chains may affect the superconductivity of the adjacent crystal region containing CuO double chains, and might enhance the superconductive critical temperature.
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1. Introduction

As known for Y-base high-T_c superconductors, there are three different crystalline phases, YBa$_2$Cu$_4$O$_8$, Y$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ and YBa$_2$Cu$_3$O$_{7-\delta}$, which are distinguished by layered pattern of two types crystalline blocks with CuO double chain structure and with single chain one [1]. It has been also recognized that Pr substitution for Y sites restrains the superconductivity on the CuO$_2$ planes, while the other rare earth elements can replace the sites without any distinct change of T_c [1,2]. Very recently, however, Pr$_2$Ba$_4$Cu$_7$O$_{15-\delta}$ (Pr247), which has alternative structure of CuO double chain block and single chain one, was found

to show superconductivity by the conductive CuO double chains when the sintered specimen was reduction-treated [3,4], and then Pr247 has been regarded as an essential studying material of the cuprate oxide superconductor series.

Besides, the authors have just succeeded in ambient pressure synthesis of Pr247 by our developed method [5] using citrate pyrolysis precursor [6]. As a characteristic of this method, the chemical reaction to Pr247 is completed by the first calcination process, and so the sintering temperature (lower than that in high pressure case) does not concerns chiefly with the reaction. On the other side, the calcination temperature condition for Pr247 formation is in a tight range, so that mixture of the other structures, Pr124 or Pr123, tends to occur [5]. In the present work, then, superconductive behaviors caused by oxygen reduction for such Pr247 ceramic material are studied, chiefly by tracing change in the electric resistivity along

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the duration of the reduction treatments. And further, possible new natures relating to the structural peculiarity of our material will be discussed with the help of magnetization measurements and atomic scale observations by transmission electron microscopy (TEM).

2. Experimental

2.1. Sample preparation and structural characterization

The applied synthetic procedure was as already reported [5]. In this method, the optimum calcination temperature for Pr247 formation is 885 °C, which is only ~1 °C distant from both higher side of Pr124 formation condition and lower side of Pr123 formation one [5]. Considering inevitable temperature gradient in the calcination device, at least one of such impurity structures is included necessarily. In the present work, then, the calcination temperature was decided at 884 °C so as to avoid 123-phase formation but permit a little 124 formations. Thus calcined products were grinded, sieved and pressed to form a disk pellet, and then were sintered at 883 °C for 48 h in atmospheric O_2. Some cut pieces of the sintered pellet were heat treated at 400 °C in vacuum, to be reduced samples. The treatment duration was varied in four values from 3 h to 36 h.

Both the calcined products and the as-sintered samples were checked by X-ray diffractometer analyses, and to be confirmed that a little $BaCuO_2$ phase and 15–30 wt% of Pr124 phase are included in the Pr247 sample, while Pr123 phase is not found.

High-resolution transmission electron microscopy (HRTEM) was also carried out for such samples. A tiny part of the sample was grinded in ethanol and the particles were dispersed on Cu grids with a carbon-coated holey film, to be observed with a JEM-2010/SP microscope operated at 200 kV.

2.2. Measurements

AC electric resistivity measurements were done by 4-wire method for the cut rectangular pieces (cross section about 1–2 mm^2) of the reduced samples and the as-sintered one in temperature range 6–300 K. For the ac measurements, fundamental in-phase voltage response $V'_{1\omega}$ to ac excitation current $I \cdot \sin \omega t$ ($\omega/2\pi = 8.0$ Hz) was derived by FFT analysis, and specific resistivity was estimated taking the measure of the samples into account. For one typical sample that showed superconductivity, dc magnetization behavior of the ceramic bulk piece was observed with a SQUID magnetometer, in order to discuss the superconductive critical temperature.

3. Results and discussion

AC resistivities for three reduced samples with the treatment time of 3 h, 12 h and 24 h and for as-sintered one are plotted against temperature up to 300 K in Fig. 1. While a
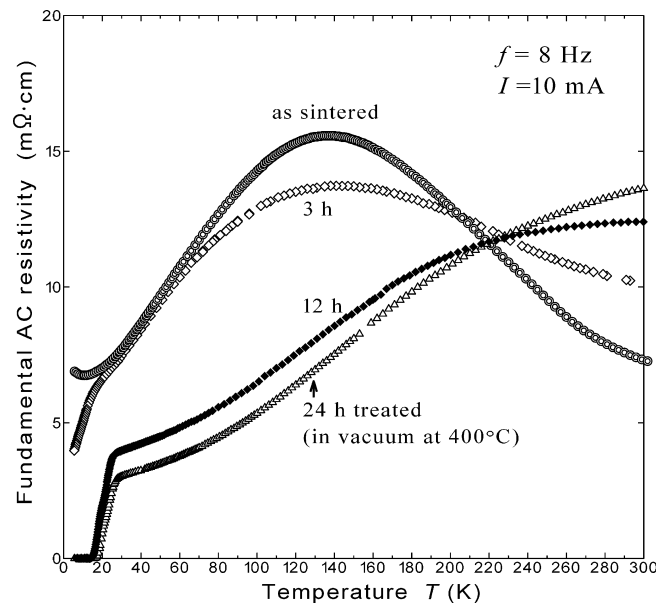

Fig. 1. Temperature dependences of ac resistivities for three reduced samples with the treatment time of 3 h, 12 h and 24 h and for as-sintered one. Excitation current density amplitudes are in the range of 0.36–0.56 A cm^{-2}.

gentle maximum is seen simply around 136 K for the as-sintered sample, an abrupt change around ~15 K appears on such a curve for the 3 h reduced sample. As the treatment time increases to 12 h or over, metallic resistivity decrease below 300 K and also superconductive abrupt drop below ~30 K are revealed. These behaviors are quantitatively similar to already reported results [3,4], but some quantitative differences are also noticed.

Detailed behaviors around the superconductive transitions for 12 h and 24 h reduction-treated samples (and referential data of 3 h treated one) are shown in Fig. 2, for which smaller current density conditions (0.04, 0.08, 0.2 A cm^{-2}) have been applied. Around the onset regions of resistivity dropping, each onset temperature point can be estimated as a cross point of the asymptotic lines from normal-conducting side and from lower temperature side, to be 25.0 K for 12 h reduced sample and 26.5 K for 24 h reduced sample. As for zero-resistivity attainment temperature, each lies at about 10–11 K lower than the onset temperature, while it somewhat depends on current density value. And seeing the middles of the dropping resistivity, change in curve feature is notices. Additionally, resistivity curve for the 36 h reduction-treated sample is almost same as that for 24 h treated sample, meaning that the oxygen reduction effect almost saturates after 24 h treatment duration.

The transition behaviors are reflected by a series of dc magnetization data: M_{ZFC} in heating process after zero-field cooling, M_{FC} in field cooling process and M_r the thermoremanent magnetization in heating process after field cooling. Such typical results for the 24 h reduction-treated sample are shown in Fig. 3. The observed M_{FC} reflecting