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ScienceDirect
Journal of Physics and Chemistry of Solids 68 (2007) 1390–1395
JOURNAL OF PHYSICS AND CHEMISTRY OF SOLIDS
www.elsevier.com/locate/jpcs

Superconductivity and calorimetric studies of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ under different annealing conditions

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Received 18 November 2006; received in revised form 5 February 2007; accepted 22 February 2007

Abstract

Polycrystalline samples of electron-doped $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ have been prepared under different annealing conditions and investigated by means of X-ray-diffraction, oxygen content analysis, electrical resistivity, magnetic susceptibility and low temperature specific heat measurements. X-ray-diffraction patterns show that samples contain a single T′ phase. The superconducting transition temperatures T_{cm} taken with the onset of diamagnetism in magnetic-susceptibility measurements are 20 and 19.5 K for sample annealed in flowing Ar gas and in vacuum ($\sim 10^{-3}$ torr), respectively. The data of the samples, which are annealed in flowing Ar gas, show clear evidence for an αT^2 term at zero magnetic field in superconducting electronic specific heat, and are consistent with *d*-wave superconductivity. However, this behavior is not observed in the other sample, which is annealed in vacuum. These results indicate that different heat treatments affect the oxygen content, homogeneity, superconducting transition temperature T_c, superconducting volume fraction, and the superconducting pairing symmetry of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$.

Keywords: A. Superconductors; D. Specific heat

1. Introduction

Rare-earth cuprates of composition R_2CuO_4 (R = Pr, Nd, Sm and Eu) with the tetragonal T′ structure play a unique role among cuprates, becoming the so-called electron-doped superconductors when Ce or Th is doped and the oxygen content of sample is reduced by proper heat treatment [1–4]. In order to improve the quality of sample, the correlation between the preparation of sample and superconducting properties in $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ has been extensively investigated by different annealing conditions [5]. In the past years, the great discussion over pairing symmetry in the hole-doped cuprates has been resolved, and is in favor of predominantly *d*-wave orbital order parameter symmetry for hole-doped (p-type) high-T_c superconductors [6–11]. However, the symmetry of the superconducting pairing state in the electron-doped (n-type) cuprates remains controversial [12–16]. Since the concentration range of Ce in $Pr_{2-x}Ce_xCuO_{4+\delta}$ in which superconductivity occurs is much narrower ($0.1 \leqslant x \leqslant 0.18$) than that of the hole-doped $La_{2-x}Sr_xCuO_{4-y}$ system ($0.05 \leqslant x \leqslant 0.3$) [17], and the oxygen content of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ is very sensitive to annealing condition [5], the superconductivity and the determination of pairing symmetry of electron-doped $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ may strongly depend on the sample quality and preparation. In our previous work [18], we had found some evidences from low temperature specific heat (LTSH) measurements for *d*-wave pairing symmetry in $Pr_{1.85}Ce_{0.15}CuO_4$. However, the heat treatment effect on superconductivity and the pairing symmetry of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ are not clear. In this study, several polycrystalline samples $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ have been prepared under different annealing conditions and investigated by means of X-ray-diffraction, oxygen content analysis, electrical resistivity,

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0022-3697/$ - see front matter
doi:10.1016/j.jpcs.2007.02.037

magnetic-susceptibility and LTSH measurements. These results enable us to clarify the heat treatment effect on the superconductivity and the observation of pairing symmetry using LTSH experiments in the electron-doped $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$. Furthermore, we compare the results of T_c (superconducting transition temperature) for electron-doped $Pr_{1.85}Ce_{0.15}Cu_{1-x}M_xO_{4.065}$ and hole-doped $La_{1.6}Sr_{0.4}Cu_{1-x}M_xO_4$ (M = Ni and Zn) to provide possible explanations for these behaviors observed in LTSH of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$.

2. Experimental

The polycrystalline samples of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ were prepared by the conventional solid-state reaction method. High-purity (99.99%) Pr_6O_{11}, CeO_2 and CuO powders were mixed and fired in air at 900 °C for 24 h, then furnace cooled down to room temperature. The resultant powders were pressed into pellets and heated at 1000 °C in air for 48 h, and then air quenched to room temperature. This process was repeated at least three times with intermediate grinding to ensure the homogeneity of samples. To study heat treatment effect on the superconducting properties of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$, samples were prepared under different annealing conditions. For oxygen reduction, samples were annealed under Ar atmosphere or vacuum ($\sim 10^{-3}$ torr). The annealing temperature is from 800 to 950 °C in intervals of 10 °C. For clarity and brief description, we only present typical data of four annealed samples in this paper: sample A was annealed at 850 °C for 12 h under Ar atmosphere and then furnace cooled down to room temperature. Sample B was annealed at 850 °C for 12 h under Ar atmosphere and then quenched to room temperature. Sample C was annealed in vacuum ($\sim 10^{-3}$ torr) at 850 °C for 9 h and then quenched to room temperature. Sample D was annealed at 900 °C for 12 h under Ar atmosphere and then quenched to room temperature. Structural analysis was carried out by powder X-ray diffraction. The oxygen content parameter δ in $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ was determined from standard iodometric titration method. The principle of this method is to determine the valence of Cu ions in the compound and thus we can calculate the oxygen content from electrical neutrality. Electrical resistivity measurement was made by means of a standard four-probe method with the data taken from 10 to 300 K. The DC magnetization was measured using a superconducting quantum interference device (SQUID) magnetometer in the temperature range of 5–30 K with a field of 10 Oe. Specific heat $C(T)$ was measured from 0.6 to 10 K with a ^{3}He relaxation calorimeter using the heat-pulse technique in zero magnetic field. The precision of the measurement in the temperature range is about 1%. To calibrate the calorimeter, $C(T)$ of a copper sample with mass 21.69 mg was measured. A fit of data below 7 K results in a linear term coefficient $\gamma = 0.698 \pm 0.002$ mJ/mol K^2 and the Debye temperature $\theta_D = 340$ K, both of which are consistent with the literature values [19] ($\gamma = 0.695$ mJ/mol K^2 and $\theta_D = 343$ K), and confirms the good calibration of the calorimeter.

3. Results and discussion

Fig. 1 shows the X-ray diffraction patterns of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$. It is found that samples A–C contain nearly a single T′ phase, and sample D has an impurity peak around $2\theta = 28.5°$. Conceicao et al. [5] prepared $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$ through three different precursors, and reported that the impurity $Pr_{1-x}Ce_xO_2$ peaks of samples made using conventional solid-state method occur at $2\theta = 28.6°$, 33.2°, and 47.6°. However, these $Pr_{1-x}Ce_xO_2$ peaks are not observed in Fig. 1 except for sample D at $2\theta \sim 28.5°$. Indeed, the impurity $Pr_{1-x}Ce_xO_2$ peaks appear

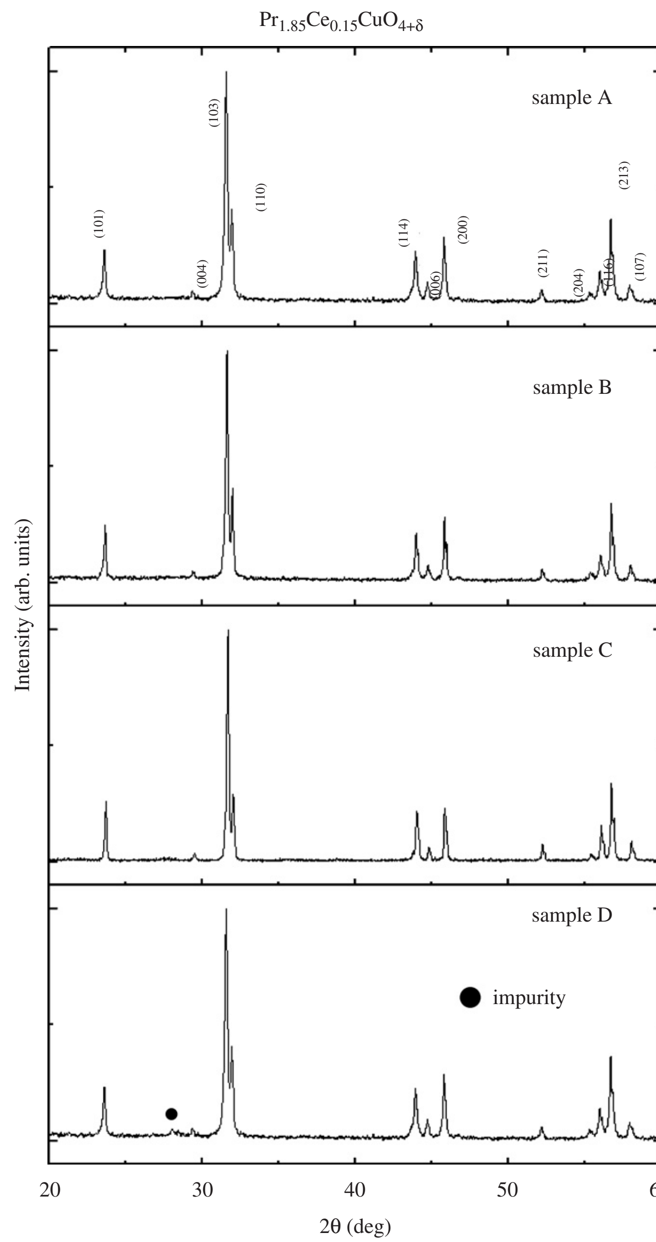

Fig. 1. X-ray diffraction patterns of $Pr_{1.85}Ce_{0.15}CuO_{4+\delta}$.