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Growth and transport features of electron-doped superconductor $Pr_{1-x}LaCe_xCuO_{4-\delta}$ thin films*

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T′-phase electron-doped superconductor $Pr_{1-x}LaCe_xCuO_{4-\delta}$ (PLCCO) thin films are successfully prepared on $SrTiO_3$ (100) substrates by using the dc magnetron sputtering method. It is found that the films each have a highly oriented structure along the *c*-axis. For optimally doped films with $x \approx 0.10$, the superconducting transition temperature T_c is 23.5 K, which is similar to that of a single crystal. The quadratic temperature dependence of the resistivity is observed when $T > T_c$, which can be attributed to the two-dimensional Fermi liquid behaviour. Besides, the optimal conditions for preparing the T′-phase PLCCO thin films are also discussed in detail.

Keywords: electron-doped cuprate, $Pr_{1-x}LaCe_xCuO_{4-\delta}$, thin film, magnetron sputtering
PACC: 7475, 7430F, 8115G

1. Introduction

Recently, electron-doped cuprate superconductors have attracted much attention. Especially, the properties of the phase diagram, the transport, and other relevant mechanism of superconductivity are extensively addressed. The main investigations are focused on $Nd_{2-x}Ce_xCuO_4$ (NCCO),[1] $Pr_{2-x}Ce_xCuO_4$ (PCCO),[2] $La_{2-x}Ce_xCuO_4$ (LCCO),[3,4] $La_{2-x}Y_xCuO_4$(LYCO),[5] and recently on $Pr_{1-x}LaCe_xCuO_4$ (PLCCO).[6−10] Owing to the difficulty in preparing high quality single crystals or thin films, especially those of LCCO and PLCCO materials, further study is still required. For example, the LCCO single crystal has not been obtained yet due to its metastable phase in nature. Fortunately, superconducting LCCO thin films were successfully grown recently.[11−13] The PLCCO system has obvious advantages to the study on the mechanism of superconductivity. First, the superconductivity of PLCCO can be achieved in a wider doping region ($0.09 \leq x \leq 0.20$) than that of the PCCO system ($0.14 \leq x \leq 0.18$),[8] which is helpful for studying the competition between antiferromagnetic and superconducting phases. On the other hand, PLCCO materials have a smaller effect of rare-earth magnetic moments than the others, e.g. NCCO, which is more helpful for studying the intrinsic features of Cu^{2+} spins in the Cu–O plane. At present, PLCCO single crystals have been obtained and some important experimental results have been reported.[6−10] However, to our knowledge, no study of PLCCO thin films has been reported. For the further study of the superconductivity and the possible device development, the successful preparation of PLCCO thin films is of particular importance.

In the present work, the key problem in the PLCCO thin film deposition is solved. We change the thin film from T-phase into T′-phase by using a reduction treatment, i.e. by moving the apical oxygen from a CuO_6 octahedron in the T-phase into a CuO_4 plane in the T′-phase. The *c*-axis oriented PLCCO thin films with superconducting transition temperature $T_c = 23.5$ K (PLCCO single crystals with $T_c \approx 24$ K–26 K were reported in Ref.[14]) are synthesized. The transport measurement indicates clearly a two-dimensional Fermi liquid behaviour in the normal state of our PLCCO thin films.

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2. Experiment

The optimal electron-doped $x \approx 0.10$ PLCCO thin films were grown by using the dc magnetron sputtering method. For study, two targets of PLCCO were fabricated through conventional solid state reaction. The original components of Pr_6O_{11}, La_2O_3, CeO_2 and CuO powders were well mixed into two required atomic ratios of $Pr:La:Ce:Cu = 0.90:1.00:0.10:1.00$ (target I) and $Pr:La:Ce:Cu = 0.90:1.00:0.10:1.20$ (target II), separately, and each mixed powder was calcined under the same condition, specifically, at a temperature of 920–960 °C with several intermediate grindings. The powder was pressed into a disk with a diameter of 60 mm, and sintered at 960–980 °C for 24–36 h. Finally, it was cooled down to room temperature in a furnace.

The PLCCO thin films were deposited on (100) $SrTiO_3$ (STO) substrates under the following conditions: the background vacuum was $\leq 1 \times 10^{-4}$ Pa and the substrate temperature was in a range of 770–835 °C. After deposition, a reduction treatment was carried out at a temperature 650 °C in vacuum ($< 1 \times 10^{-4}$ Pa) for 30–40 min. The sputtering current was about 200–220 mA and the deposition rate was about 2.5–3.0 nm/min. The thickness of each PLCCO film was around 100 nm.

X-ray diffraction (XRD) was carried out with an x-ray generator (MXP18A-HF) to examine the structure of the thin films. Temperature dependence of resistivity was measured by using a four-terminal SQUID magnetometer (MPMS-5).

3. Results and discussion

Figure 1 shows the x-ray diffraction (XRD) patterns of the PLCCO thin films deposited with target I at temperatures of 770, 780, 800, 820, and 835 °C, separately. It is found that the XRD patterns clearly show the competition between the non-superconducting T- phase and superconducting T′-phase, which is similar to the scenario observed in the LCCO thin films.[13] The c-axis lattice constant is about 1.314 nm for the T-phase structure and around 1.256 nm for the T′-phase structure estimated from the XRD data. We should mention here that the deposition temperature is a crucial factor to change the PLCCO thin films from T-phase into T′-phase. In a range of 770–835 °C, when the deposition temperature is increased, the PLCCO thin films tend to be of T-phase, and when the deposition temperature is decreased the PLCCO thin films tend to be of T′-phase. The PLCCO films of pure T′-phase can be achieved when the deposition temperature reaches 770 °C. These films are the best films under these conditions, and their superconducting transition temperature T_c is roughly 15.4 K. However, this value is much lower than that of PLCCO single crystals.[7,8] To obtain high-T_c PLCCO thin films, further study is necessary.

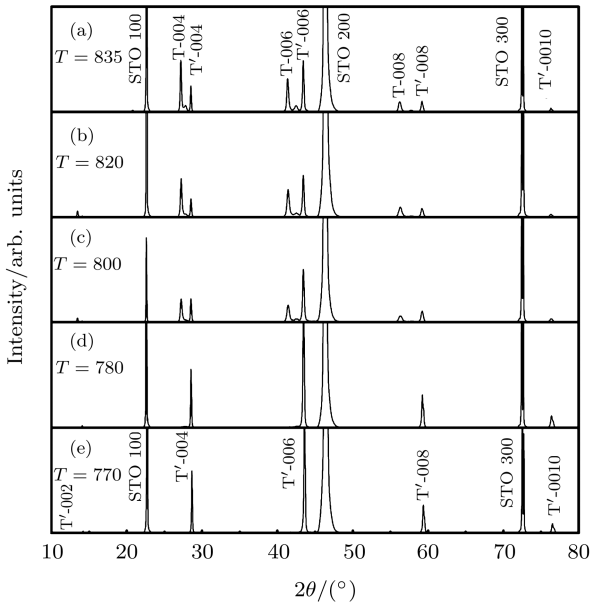


Fig.1. XRD patterns of $Pr_{1-x}LaCe_xCuO_{4-\delta}$ thin films deposited with a stoichiometric target at temperatures ranging from 770 to 835 °C and a 35-min reduction treatment at 650 °C, showing clearly the competition between T- and T′-phases.

It is known that both Ce and O concentrations are two important factors for high quality Ce-doped thin films. The former is determined mainly by the target composition and the later by the reduction treatment condition. During the sputtering deposition, Cu atoms are easily lost in the CuO_2 plane since the atomic weight of Cu is small compared with that of other cations of Pr, La and Ce in the PLCCO materials. So the low T_c problem may be caused by the concentration of Cu, which has been also found in the preparation of LCCO thin films.[13] It can be understood that a lack of Cu will influence the growth of the CuO_2 plane in the film, thereby leading to the deterioration of superconductivity, or even the domination of T′-phase in the sample. To avoid the loss of the Cu concentration in PLCCO thin films, we

have tried to add more CuO into target II of PLCCO and found that an excess of 20% Cu atoms is suitable. The PLCCO thin films deposited by target II are highly improved. During the deposition, temperature is fixed at 810 °C and the reduction treatment is performed at 650 °C for 35 min. As a result, we obtain PLCCO thin films in pure T′-phase. Figure 2(a) shows the x-ray diffraction patterns, in which the *c*-axis lattice parameter is about 1.234 nm. It is smaller than 1.256 nm of the thin films deposited by target I without excessive Cu atoms. The small width of half maximum (FWHM) is 0.33°, which is obtained from a rocking curve of (006) XRD peak of PLCCO thin film as shown in Fig.2(b). Above all, the T_c of PLCCO thin films is enhanced obviously up to 23.5 K.

It should be emphasized that the time of reduction treatment is a very critical condition for the formation of pure T′-phase in preparation, no matter what stoichiometry of Cu is used in the targets. In addition, the oxygen concentration is also important. We have found that the 35-min reduction treatment is the best choice for about 100 nm thickness films: treatment times shorter than e.g. 30 min or longer than e.g. 40 min will cause the thin film quality to degrade.

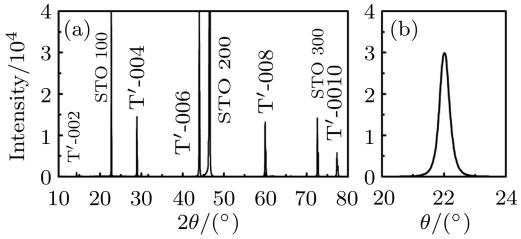


Fig.2. (a) XRD patterns of pure T′-phase in $Pr_{1-x}LaCe_xCuO_{4-\delta}$ thin film deposited with a target with an excess of 20% Cu atoms at temperature 810 °C and a 35-min reduction treatment at 650 °C, and (b) rocking curve of (006) peak for the same PLCCO thin film.

Figure 3 shows the temperature dependence of the resistivity of PLCCO thin films obtained at three different reduction times and a reduction treatment temperature of 650 °C. First, in contrast to the general linear temperature dependence of resistivity in hole-doped cuprates, for example $YBa_2Ca_3O_7$,[15−17]

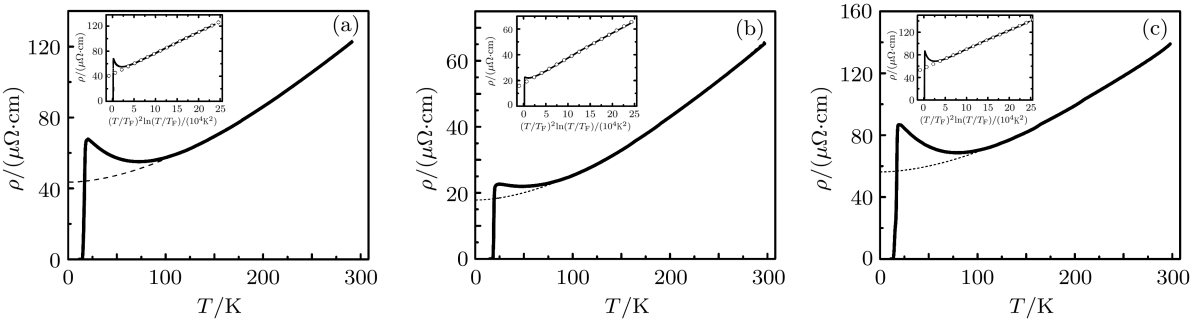


Fig.3. Resistivity $\rho(T)$ for PLCCO thin films deposited under the same condition as that described in Fig.2 but with different reduction treatment times: (a) 30, (b) 35, and (c) 40 min, where the dashed lines are the fitting curves by Eq.(1), showing linear dependence of ρ vs $T^2\ln(T/T_F)$ with $T_F = 4800$ K (see the inset in the figure).

the quadratic behaviour of $\rho(T)$ in the normal state of PLCCO thin films is observed. These $\rho(T)$ curves indicate that for 30, 35, and 40 min reduction treatments, the values of superconducting transition temperature T_c reach 20.2, 23.5, and 18.8 K, respectively. Correspondingly, the values of residual resistivity ρ_0 for the three cases are 43.5, 17.7, and 56.1 $\mu\Omega$·cm, respectively. In comparison, the smallest upturn of the $\rho - T$ curve near T_c happens in the case of 35 min reduction treatment. All these results imply that the phase structure of PLCCO thin films deposited by target II under appropriate reduction treatment conditions is much better. The $\rho \propto T^2$ dependence of the present PLCCO thin films is also observed in many other electron-doped cuprates with optimal doping.[15] This phenomenon can be explained by electron-electron scattering.[18] Considering PLCCO as a two-dimensional system, the relation $\rho \propto T^2$ can be described by using the two-dimensional Fermi liquid model as[19,20]

$$\rho(T) = \rho_0 + A(T/T_F)^2 \ln(T/T_F), \qquad (1)$$

where ρ_0 is the residual resistivity, A is a coefficient, and T_F is the Fermi temperature. We fit the data by expression (1) and show the results in the insets of Figs.3(a)–3(c) with the dashed lines. The relation $\rho \propto$

$(T/T_F)^2\ln(T/T_F)$ is found in a wide temperature range with the best fitting parameter $T_F \approx 4800$ K. Under the 30-, 35-, and 40-min reduction treatments, the onset temperatures for the two-dimensional Fermi liquid behaviour are about 109, 90, and 112 K, respectively. The temperature range for $\rho \propto (T/T_F)^2\ln(T/T_F)$ is the largest in the case of 35 min treatment.

As discussed above, the reduction treatment should be a key process to remove the apical oxygen for the T′-phase, which is similar to the case of the LCCO thin film growth.[13] The present results imply that for PLCCO thin film preparation, a target with an excess of 20% Cu atoms is a must. The best conditions can be summarized as follows: the deposition and the reduction treatment temperatures are 810 and 650 °C respectively, and the treatment time is 35 min. The reduction treatment should be a successful method to remove the apical oxygen but retain the others for a pure T′-phase structure. In contrast, the 30-min treatment may not be able to completely remove the apical oxygen, and the 40-min treatment may induce more or less oxygen defects. Therefore we may explain why the upturn of the $\rho(T)$ curve of the PLCCO thin film near T_c with the 35-min reduction treatment is the smallest. The resistivity and the residual are also smaller than those in the cases of 30- and 40-min reduction treatments. $T_c \approx 23.5$ K is similar to that of the single crystal. So we may conclude that appropriate Cu and O concentrations as well as optimal Ce doping are very important to achieve perfect structure PLCCO thin films. Finally, it should be pointed out that the resistivity of PLCCO thin films is smaller than those of other optimal electron-doped cuprate superconducting thin films.[15]

4. Conclusions

We have synthesized superconducting T′-phase PLCCO thin films by magnetron sputtering on STO substrates. The optimal growth conditions are explored in detail and a superconducting transition temperature of the films up to 23.5 K is obtained. It is found that optimal Ce doping and appropriate Cu and O concentrations as well as a suitable deposition temperature and reduction treatment condition are necessary in order to achieve a perfect crystallization in PLCCO thin films. The films prepared under the optimal conditions have the highest T_c, smallest residual resistivity and display Fermi liquid behaviour in the largest temperature range. It should be noted that the resistivity of the PLCCO thin film is about 10^{-5} Ω·cm which is lower than those of other optimally electron-doped cuprate superconducting thin films, which indicates that the PLCCO thin films have an interesting physical feature and potential applications.

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