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Protected Vacuum Annealing Effect on Single Crystals of $Pr_{1-x}LaCe_xCuO_4$ in the Overdoped Regime

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Abstract. We report the effect of protected vacuum annealing on the superconducting (SC) and magnetic properties of $Pr_{1-x}LaCe_xCuO_4$ (PLCCO) single crystals in the overdoped regime (x = 0.13 – 0.20). The powders and single crystals of PLCCO with all x were synthesized by the solid state reaction and grown by the travelling solvent floating zone (TSFZ) method, respectively. The powder x-ray diffraction (XRD) results analyzed by the Rietveld method have shown that there is a systematic decrease in the c-axis length with increasing x, suggesting the proper substitution of Ce for Pr in overdoped PLCCO up to x = 0.20. The so-called two-step annealing performed in the overdoped regime was essential for increasing the SC volume fraction estimated from the magnetic susceptibility measurements. Furthermore, the temperature dependence of the normal-state magnetic susceptibility for reduced crystals of PLCCO with all x has exhibited a Curie-Weiss-like behavior regardless of various steps of the protected vacuum annealing process.

1. Introduction

There are still open questions concerning the role of the oxygen reduction in the electron-doped high-T_c superconductivity. In the electron-doped cuprates with the so-called T'-structure, the superconducting (SC) regime in the generic phase diagram is quite narrow compared with the hole-doped ones [1, 2]. However, the recent investigation in thin films of T'-$(La,RE)_2CuO_4$ (RE = Sm, Eu, Gd, Tb, Lu, and Y) has revealed that they show Ce-free superconductivity [3]. This phenomenon is related to the role of the reduction annealing process for the occurrence of superconductivity in the T'-cuprates. The superconductivity in the T'-cuprates is very sensitive to the amount of excess oxygen at the apical site (O(3)) above or below the Cu site. The presence of the excess oxygen suppresses superconductivity

To achieve the optimum critical temperature (T_c) for the electron-doped T'-cuprates, it is necessary to find an optimum oxygen reduction process, as performed in T'-$Pr_{0.88}LaCe_{0.12}CuO_{4+\delta}$ single crystals [4]. An improved reduction technique has been used by Brinkmann *et al.* [5] to establish the superconductivity of $Pr_{2-x}Ce_xCuO_4$ over a wide doping-range between x = 0.04 and 0.17. They protected the single crystal surface with the polycrystalline pellets on the top and bottom having the same composition in order to overcome the destruction of the surface. Then, by employing a similar improved reduction annealing, named the protected vacuum annealing, we have obtained SC crystals with the T'-structure of $Pr_{1.3-x}La_{0.7}Ce_xCuO_{4+\delta}$ (x = 0.10) [6]. The difference from the technique by Brinkmann *et al.* [5] is that we have covered the crystal with polycrystalline powders of the same composition during the vacuum annealing process. Then, a so-called two-step annealing process has been developed by Krockenberger *et al.* [7] to achieve superconductivity of Ce-free thin films of Pr_2CuO_4. They claimed that the second-step annealing, performed at a lower temperature, provided "healing" of the defective CuO_2 plane by the oxygen rearrangement from the apical site to the regular in-plane site. The current paper reports the effect of protected vacuum annealing combined with the two-step annealing process on the SC and magnetic properties of single crystals of $Pr_{1-x}LaCe_xCuO_4$ (PLCCO) with x = 0.13 – 0.20.

2. Experimental

The polycrystalline powders and single crystals of PLCCO with x = 0.13 – 0.25 were synthesized by the solid sate reaction and the traveling solvent floating zone (TSFZ) method, respectively. The synthesized powders and the crystals prepared were characterized by the powder x-ray diffraction (XRD) to determine the crystal structure and the lattice constants. The quality and the composition of the crystals were checked to be good by the x-ray back-Laue photography and the inductively coupled plasma analysis, respectively. The reduction annealing was performed by combining the protected vacuum annealing and the two-step annealing process for all PLCCO crystals as described in Refs. [6] and [7], respectively. In order to determine T_c of the reduced samples, magnetic susceptibility measurements were performed as a function of temperature using a SC quantum interference device (SQUID) magnetometer.

3. Results and Discussion

XRD patterns displayed in Figure 1(a) indicate good quality of the crystals. Figure 1(b) shows the Ce-concentration dependence of the c-axis length for as-grown and reduced crystals of PLCCO. The c-axis length was estimated by analyzing the (00l) peak position of the powder x-ray diffraction pattern. It is found that the c-axis length decreases with increasing Ce-concentration up to $x \sim 0.20$, which is consistent with the former report [8]. This is because trivalent rare earth ions, in this case Pr^{3+}, are replaced by Ce^{4+} ions with a smaller ionic radius. For the a-axis length, it seems to increase slightly with increasing Ce-concentration. This can be understood as being due to the stretching of the Cu-O bonding owing to the increase in the number of electrons in the antibonding orbital. With increasing x above $x \sim 0.20$, the c-axis length tends to be saturated, meaning the solubility limit at $x \sim 0.20$.

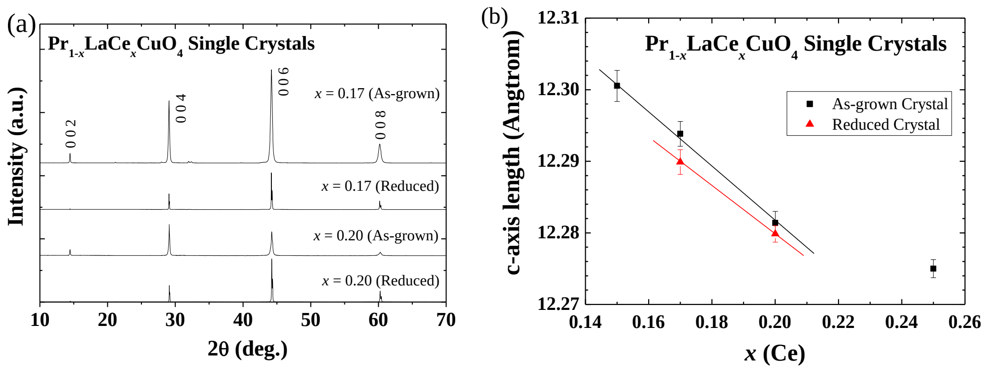

Figure 1. (a) XRD patterns and (b) Ce-concentration dependence of the c-axis length for both as-grown and reduced crystals of $Pr_{1-x}LaCe_xCuO_4$ (PLCCO). PLCCO with x = 0.17 was obtained by the two-step protected vacuum annealing, whereas PLCCO with x = 0.20 was obtained by the one-step protected vacuum annealing.

Through the reduction annealing, it is found that the c-axis length decreases, indicating a sufficient oxygen removal. In the as-grown crystals, there exists excess oxygen at some apical sites. The presence of the excess oxygen expands the c-axis lattice parameter. By removing the excess oxygen, the c-axis length is reduced. In fact, the oxygen removal occurs not only from the apical site but also from the CuO_2 plane being important for the appearance of superconductivity. Therefore, based on the results of PCCO thin films [7] and $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ single crystals [6], it is necessary to perform the two-step annealing for Ce-free and underdoped PLCCO crystals as well as PLCCO crystals in the overdoped regimes to recover the oxygen deficiency in the CuO_2 plane.

In this report, several annealing conditions were carried out to obtain the optimum T_c for reduced PLCCO crystals of $x = 0.17$ and 0.20. Figures 2(a) and 2(b) display the temperature dependence of the magnetic susceptibility for PLCCO with $x = 0.17$ and 0.20, respectively. It is found for $x = 0.17$ that the excess oxygen cannot be effectively removed at a low annealing-temperature. At a high annealing-temperature, however, the decomposition of the sample occurred. Therefore, the two-step protected annealing was necessary up to $x = 0.17$. The optimum T_c of $x = 0.17$ was obtained by the two-step protected vacuum annealing on the condition of the first annealing at 900 ºC for 12 h and the second annealing at 500 ºC for 12 h. Through this annealing, a sharp SC transition was observed at $T_c = 5.2$ K.

In PLCCO with $x = 0.20$ shown in Figure 2(b), behaviors different from those of $x = 0.17$ were observed. The optimum T_c was achieved only by the one-step annealing at a low temperature of 800 ºC for 24 h. Both a high annealing-temperature and a long annealing-time caused the decrease in the SC volume fraction due to the less-reduction and over-reduction, respectively. Moreover, the observed Meissner value of $x = 0.20$ at 800 ºC for 24 h is quite small. T_c in this case was lower than the measured lowest temperature 2 K in the present SQUID measurements. It is about 1/100 of Meissner signal of the reduced crystal of PLCCO with $x = 0.17$. Thus, the observed Meissner signal of $x = 0.20$ at 800 ºC for 24 h is due to filamentary superconductivity. Accordingly, the reduced crystal of PLCCO with $x = 0.20$ was considered to be almost non-SC. It has been found that the SC transition becomes broad with increasing x above $x = 0.17$, which is consistent with the former result [9], indicating the increasing hardness to obtain chemically homogeneous samples.

Figure 3 displays the temperature dependence of the normal-state magnetic susceptibility in 1 T (H // c-axis) for reduced crystals of PLCCO with $x = 0.13 - 0.20$. A hump is observed around 100 K for all x, probably related to the Pr^{3+} moments included in the crystals [10]. At high temperatures above ~150 K, the temperature dependence of the magnetic susceptibility exhibits a Curie-Weiss-like behavior for all x. This result is similar to that in the hole-doped cuprates of $La_{2-x}Sr_xCuO_4$ (LSCO) in the overdoped regime [11], where the Curie-Weiss-like behavior of the magnetic susceptibility at high temperatures has been understood to be due to magnetic moments generally induced in the overdoped regime of hole-doped cuprates [12]. Additionally, it has been found that the behavior of the magnetic

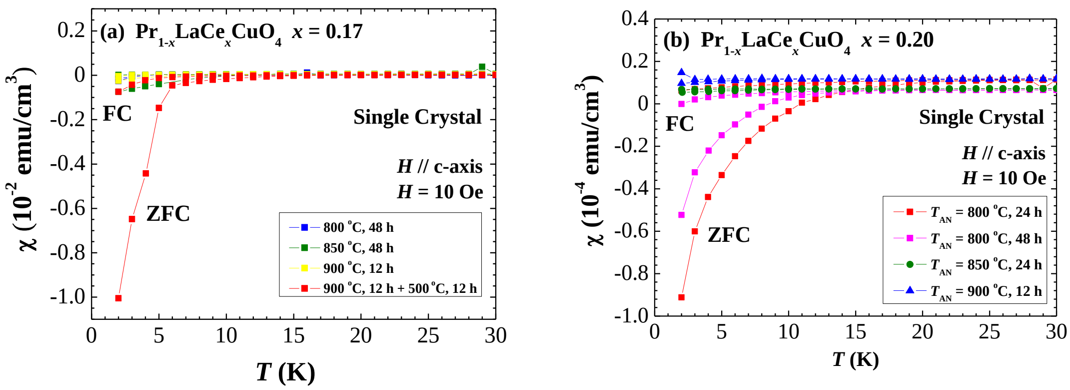

Figure 2. Temperature dependence of the magnetic susceptibility χ for $Pr_{1-x}LaCe_xCuO_4$ single crystals with (a) $x = 0.17$ and (b) $x = 0.20$ on various annealing conditions on both zero-field cooling (ZFC) and field cooling (FC).

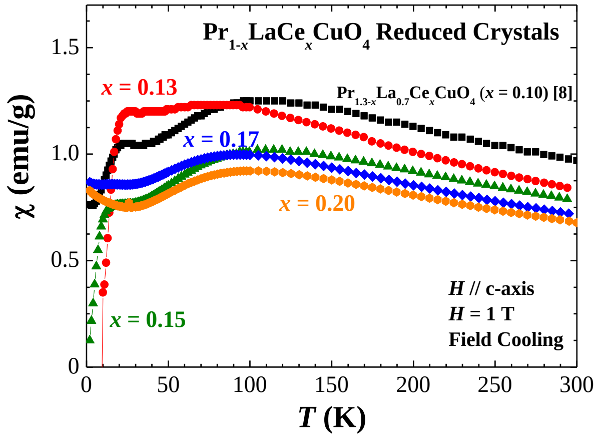

Figure 3. Temperature dependence of the normal-state magnetic susceptibility χ for reduced crystals of $Pr_{1-x}LaCe_xCuO_4$ with $x = 0.13 – 0.20$, together with $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ ($x = 0.10$) [6].

susceptibility is independent of various steps of the reduction annealing process in the overdoped regime of T'-PLCCO.

4. Summary

The effect of protected vacuum annealing on the SC and magnetic properties of PLCCO single crystals in the overdoped regime has been investigated. It has been found that a combination technique between the protected vacuum annealing and the two-step annealing process is very essential for achieving the optimum SC transition and increasing the SC volume fraction for both underdoped and overdoped T'-PLCCO. The normal-state magnetic susceptibility has been found to behave a Curie-Weiss-like dependence at high temperatures which is a general characteristic for both hole- and electron-doped cuprates in the overdoped regimes. Additionally, the magnetic behavior at high temperatures has been found to be independent of various steps of the reduction annealing process in the overdoped regime.

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