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Impact of annealing on the electron-doped cuprate superconductors studied by X-ray core-level photoemission spectroscopy

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1 Introduction

Although doping electrons in the T'-type cuprates by substituting Ce^{4+} for Ln^{3+} (Ln: rare earth) has long been considered to be indispensable for the superconductivity, superconductivity has recently been realized in thin films and powdered samples without Ce substitution and only by post annealing to remove excess oxygen atoms [1,2]. The development of the annealing method has also enabled us to realize superconductivity with very low Ce concentration even in bulk single crystals [3]. In order to understand the nature of the superconductivity without Ce doping, it is crucial to understand the effect of the post annealing on the electronic structure. For this purpose, we have performed X-ray core-level photoemission measurements on single crystals of the T'-type cuprates $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ with varying both Ce concentration x and annealing conditions.

2 Experiment

Single crystals of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ (x = 0, 0.05, 0.10) were synthesized by the floating zone method. As-grown and annealed samples were prepared for each composition. The sample with x = 0.10 was annealed at 800 °C for 24 hours. To x = 0 and 0.05, two-step annealing [4] was applied: first annealed at 800 °C for 24 hours, and then 400 °C for 48 hours. As a result, annealed samples with x = 0.05 and 0.10 showed superconducting transitions at 26 K and 27 K, respectively, and x = 0 was metallic but non-superconducting, while all the as-grown samples were insulating.

X-ray photoemission spectroscopy (XPS) measurements were performed at beamline 2A of Photon

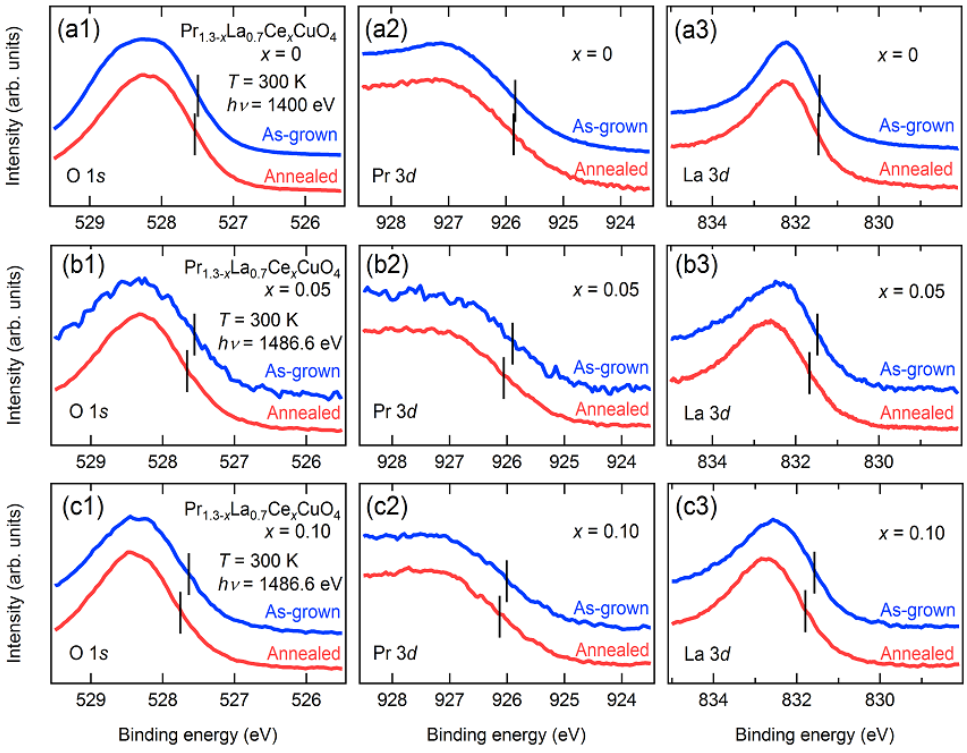

Fig. 1. XPS core-level spectra of as-grown and annealed $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ samples. (a1)-(a3) O 1*s*, Pr 3*d*, and La 3*d* spectra of samples with x = 0, respectively. (b1)-(b3),(c1)-(c3) The same plots as (a1)-(a3) for samples with x = 0.05 and 0.10, respectively.

Factory with $h\nu$ = 1400 eV, and laboratory-based equipment using the Al $K\alpha$ line ($h\nu$ = 1486.6 eV). The samples were cleaved *in-situ* under ultra-high vacuum of 1 × 10^{-10} Torr at Photon Factory and 3 × 10^{-9} Torr in laboratory, and measured at T = 300 K.

3 Results and Discussion

Annealing dependence of XPS spectra of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ samples are shown in Fig. 1. For x = 0.05 and 0.10, peak shifts toward higher binding energies were clearly observed for the O 1*s*, Pr 3*d*, and La 3*d* core levels after annealing while the shift was much smaller for x = 0.

The amount of the peak shifts is summarized in Fig. 2(a). The fact that the three core levels were shifted in the same direction by nearly the same amount for each sample suggests that the shifts are mainly due to changes in the chemical potential. By taking the average of the shifts of the three core levels, we estimated chemical-potential shifts as shown in Fig. 2(b). The chemical-potential shifts observed in the as-grown samples of ~ 0.015 eV per Ce concentration x is consistent with a previous XPS study on $Nd_{2-x}Ce_xCuO_4$ [5] and certainly reflects electron doping by Ce substitution. For x = 0.05 and 0.10, chemical-potential shifts larger than 0.1 eV were observed by annealing. Assuming that 1 % electron doping shifts the chemical potential by 0.015 eV, doped electrons in the annealed x = 0.10 sample amount to 0.20, which is considerably larger than the Ce concentration. This large electron doping to T'-cuprates by annealing has also been observed in a recent angle-resolved photoemission study [6]. It is possible that annealing in a heavily reducing atmosphere removed not only impurity oxygen at the apical site but also regular oxygen (from CuO_2 planes and/or LnO layers), and led to the large electron doping.

In conclusion, we have performed XPS measurements on the T'-type cuprates $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ and observed large chemical-potential shifts by post annealing, which is possibly related to reduced oxygen stoichiometry.

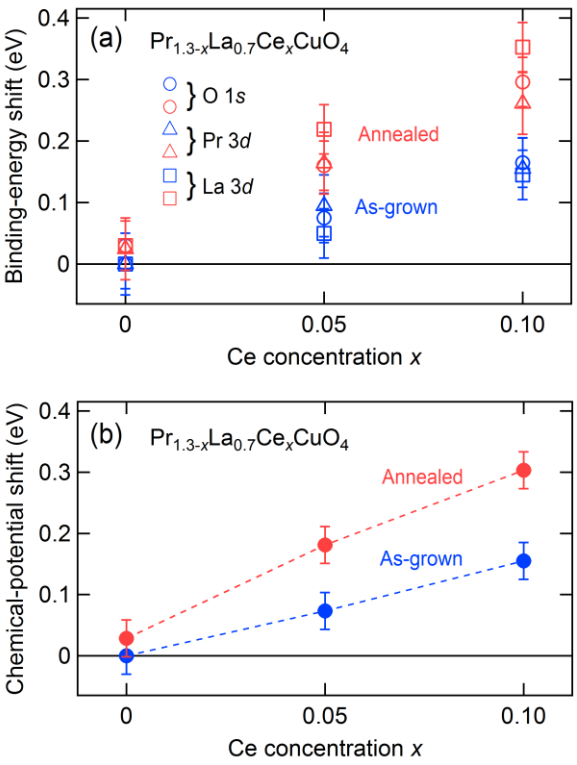

Fig. 2. Core-level shifts of $Pr_{1.3-x}La_{0.7}Ce_xCuO_4$ observed by XPS measurements. (a) Shifts of the binding energies of the O 1*s*, Pr 3*d*, and La 3*d* core levels. (b) Chemical-potential shifts estimated from the average shifts of the three core levels plotted in (a).

Acknowledgement

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References

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