Reduction annealing effects on crystal structural of T'-type cuprate

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Superconductivity in $RE_{2-x}Ce_xCuO_4$ (RE: trivalent rare earth element) with $Nd_2CuO_4(T')$ type structure is induced by the post-annealing procedure under the oxygen reduction atmosphere. It has been considered that the partially present excess oxygens at the apical site in the as-sintered compound suppress superconductivity. Then, the removal of excess oxygens due to annealing causes the superconductivity. Recently, superconductivity in the Ce-free compound was reported in the thin films and low-temperature synthesized powder samples [1, 2]. However, the structural analysis of the superconducting RE₂CuO₄ was lacking. Furthermore, the bulk compounds of RE₂CuO₄ sintered by the conventional solid-state reaction are known to remain method nonsuperconductor even after the annealing. Therefore, it is quite important to clarify the annealing effects on the crystal structure to understand the mechanism of superconductivity in RE_2CuO_4 .

To obtain the structural information (positional parameters and occupancy of each oxygen site), we conducted neutron diffraction measurements on La_{1.8}Eu_{0.2}CuO₄ (LECO) and Pr₂CuO₄ (PCO) at HERMES. The former exhibits superconductivity at ~20 K due to annealing, while the latter is an insulator, even the compounds were annealed. Thus. the comparison could yield clues for the mechanism of superconductivity in RE₂CuO₄.

Figure 1 shows the representative diffraction pattern measured at room temperature. We confirmed the absence of impurity phase for both as-sintered and annealed compounds. Then, the Rietveld refinement was performed by using FullProf. The amount of excess oxygen in assintered LECO and PCO is comparable, and that of removal oxygen due to annealing is also the same. Therefore, no significant structural difference in oxygen ions of the two systems was observed. The remarkable structural difference between LECO and PLC can be seen in the



Fig. 1. Neutron diffraction patterns of (a) assintered and (b) Ar-annealed Pr₂CuO₄. Blue and red solid lines represent calculated patterns by the Rietveld refinement and the difference patterns, respectively.

lattice constant. LECO with the larger average ionic radius of RE has longer in-plane and outof-plane lattice constants. Since the hopping parameter and charge transfer gap varies with the in-plane lattice constant, the different annealing effects on the physical properties in T^{*} -type RE_2 CuO₄ would be originated from the size of the lattice constant.

[1] O. Matsumoto, A. Utsuki, A. Tsukada, H. Yamamoto, T. Manabe, and M. Naito, Physica C **469**, 924 (2009).

[2] T. Takamatsu, M. Kato, T. Noji, and Y. Koike, Appl. Phys. Express **5**, 073101 (2012).

[3] M. Fujita *et al.*, J. Phys. Soc. Jpn. **90**, 105002 (2021).