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Low-Temperature Synthesis of La_2CuO_4 with the T′-Structure from Molten Hydroxides

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The lanthanide cuprate with the general formula Ln_2CuO_4 (*Ln*: Lanthanide) crystallizes in three different structures, namely, K_2NiF_4-type (T), distorted K_2NiF_4-type (O) and Nd_2CuO_4-type (T′) structures, as schematically shown in Figure 1. The T-structure consists of single CuO_2 planes separated by *Ln*O−*Ln*O rock-salt layers, forming the corner-shared CuO_6 octahedra. The O-structure is essentially isostructural to the T-structure, but the CuO_6 octahedra are tilted because of the alleviation of the size mismatch between the larger O−Cu−O length in the CuO_2 plane and the smaller *Ln*−*Ln* one in the *Ln*O plane. The T′-structure consists of single CuO_2 planes separated by $Ln{-}O_2{-}Ln$ fluorite layers, forming CuO_4 squares instead of CuO_6 octahedra in the T-structure. It is understood that the T′-structure is derived from the T-structure through a shift of the so-called apical oxygen in the CuO_6 octahedra and that this shift causes enlargement of the fluorite layers due to the Coulomb repulsion between Ln^{3+} and Ln^{3+} and also between O^{2-} and O^{2-}, leading to the alleviation of the above-mentioned size-mismatch in the T-structure.

Recently, Tsukada et al.[1] successfully synthesized single-crystalline films of T′-$(La,Ln)_2CuO_4$ at 600 °C using the molecular beam epitaxy. Notice that T′-$(La,Ln)_2CuO_4$ films annealed in a vacuum show superconductivity below $T_c \approx$ 25 K without nominal carrier-doping. This is very unusual, because hole- or electron-doping is usually indispensable for the appearance of superconductivity in copper oxides including CuO_2 planes. Therefore, one may suppose that possible oxygen defects in the films supply the CuO_2 planes with electrons. The oxygen content in the films, however, is hard to be estimated. Accordingly, the synthesis of bulk samples of T′-$(La,Ln)_2CuO_4$ is essential in clarifying the origin of superconductivity in the non-doped T′-$(La,Ln)_2CuO_4$ films. It has been known that the crystal structure of La_2CuO_4 synthesized by the conventional solid-state reaction at an elevated temperature, ∼1000 °C, is the O-structure at room temperature because of the large size mismatch between the larger O−Cu−O length and the smaller La−La one. The size mismatch is relaxed with increasing temperature, because the thermal expansion of the ionic La−O bond is larger than that of the covalent Cu−O bond. As a result, a phase transition occurs at $T_{d1} \approx 250$ °C.[2] Here, T_{d1} is the structural phase transition temperature between the O-structure at low temperatures and the T-structure at high temperatures. On the other hand, Ln_2CuO_4 with Ln^{3+} ions smaller than La^{3+} ions, such as Pr^{3+}, Nd^{3+}, Sm^{3+}, Eu^{3+}, and Gd^{3+}, crystallizes in the T′-structure. Thus, La_2CuO_4 is situated near the borderline between T/O and T′-structures, so that several attempts to synthesize T′-La_2CuO_4 and T′-$(La,Ln)_2CuO_4$ have been reported so far. Takayama-Muromachi et al.[3] have obtained T′-$La_{1.8}Y_{0.2}CuO_4$ at 600 °C by the coprecipitation method. There, the T′-structure is stabilized because of both the low-temperature synthesis and the partial substitution of La^{3+} for Y^{3+} with the small ionic radius. T′-La_2CuO_4 has been prepared by the hydrogen reduction of O−La_2CuO_4 and the subsequent oxidation at 300−500 °C by Chou et al.[4] According to the powder X-ray diffraction patterns, however, these samples appear not to be crystallized well.

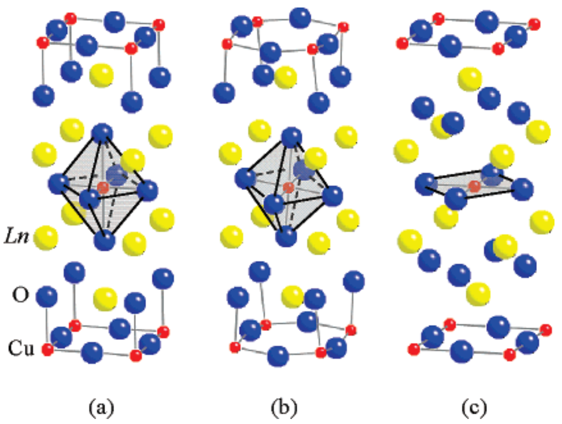

Figure 1. Schematic crystal structures of Ln_2CuO_4. (a) K_2NiF_4-type (T-structure), (b) distorted K_2NiF_4-type (O-structure), and (c) Nd_2CuO_4-type (T′-structure).

In this paper, we report that well-crystallized bulk samples of T′-La_2CuO_4 have been successfully synthesized at a temperature as low as 350 °C by the direct precipitation from the molten KOH/NaOH eutectic mixture. Because alkaline metal hydroxides have relatively low melting points and dissolve metal oxides, the direct reaction becomes possible at significant low temperatures. In fact, superconducting oxides such as T−La_2CuO_4,[5] $EuBa_2Cu_4O_8$,[6] and $(Ba,K)BiO_3$[7] have been synthesized at temperatures as low as 250−450 °C by the direct precipitation from molten hydroxides.

Polycrystalline bulk samples of T′-La_2CuO_4 were synthesized as follows. Stoichiometric amounts of La_2O_3 and Cu

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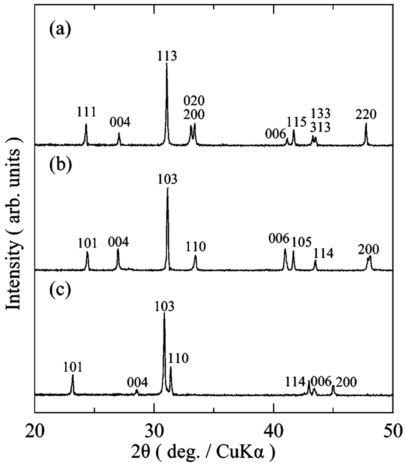

Figure 2. Powder X-ray diffraction patterns at room temperature using Cu Kα radiation for bulk samples of La_2CuO_4 obtained by (a) the conventional solid-state reaction method at 900 °C in air, (b) the direct precipitation from the molten KOH/NaOH eutectic mixture including La_2O_3 and CuO powders as starting material at 350 °C in air, and (c) the direct precipitation from the molten KOH/NaOH eutectic mixture including La_2O_3 and Cu powders as starting materials at 350 °C in flowing Ar gas.

powders were mixed, ground, and put in an alumina crucible together with KOH and NaOH. Typical amounts were 30 g of KOH, 22 g of NaOH, 6.3 g of La_2O_3, and 1.2 g of Cu. The crucible was kept at 350 °C in flowing Ar gas for 2 weeks. The melt was quenched to room temperature by removing the alumina crucible from the furnace. A black polycrystalline powder was isolated by dissolving the hydroxides with distilled water and drying at 150 °C in air. For comparison, polycrystalline bulk samples of La_2CuO_4 were also synthesized by the conventional solid-state reaction method and by the direct precipitation from the molten KOH/NaOH eutectic mixture including La_2O_3 and CuO powders as starting materials in air at 350 °C for 4 days. The structural analysis was carried out by powder X-ray diffraction using Cu Kα radiation. Magnetic susceptibility measurements were performed using a SQUID magnetometer.

Figure 2 shows the powder X-ray diffraction patterns at room temperature for bulk samples of La_2CuO_4 obtained by different processes. By the conventional solid-state reaction at 900 °C in air, the O−La_2CuO_4 with $a = 5.36 \pm 0.01$ Å, $b = 5.40 \pm 0.01$ Å, and $c = 13.15 \pm 0.01$ Å has been obtained, as shown in Figure 2a. By direct precipitation from the molten KOH/NaOH eutectic mixture including La_2O_3 and CuO powders as starting materials at 350 °C in air, T−La_2CuO_4 with $a = 3.79 \pm 0.01$ Å and $c = 13.19 \pm 0.01$ Å has been obtained, as shown in Figure 2b. This result is in good agreement with the previous report by Ham et al.[5] In this case, it is understood that the large size-mismatch between the larger O−Cu−O length and the smaller La−La one in the T-structure expected at 350 °C is alleviated not through the formation of the O-structure but through the decrease in the Cu−O bond length, which is probably due to hole-doping into the CuO_2 planes, namely, the high Cu valence caused by the excessively incorporated oxygen, so that the T-structure becomes stable. Our sample of T−La_2CuO_4 shows superconductivity with $T_c \approx 27$ K in the measurement of magnetic susceptibility. The lattice parameters and T_c are consistent with those of electrochemically oxygenated $La_2CuO_{4.044}$.[8] In the synthetic method using the molten hydroxides, it is known that superoxides and peroxides produced by the reaction of the melt of hydroxides with the atmospheric oxygen are responsible for stabilizing high oxidation states of cation. In fact, the *c*-axis length larger than that for the sample obtained by the conventional solid-state reaction method suggests the incorporation of excess oxygen, namely, the increase of the Cu valence.[9] Finally, by the direct precipitation from the molten KOH/NaOH eutectic mixture including La_2O_3 and Cu powders as starting materials at 350 °C in flowing gas of Ar, T′-La_2CuO_4 has been obtained, as shown in Figure 2c. All the peaks can be indexed on the basis of the tetragonal lattice with $a = 4.02 \pm 0.01$ Å and $c = 12.49 \pm 0.01$ Å. Compared with the lattice parameters in O− and T−La_2CuO_4, the *a*-axis length is large and the *c*-axis length is small, indicating the formation of the T′-structure. Moreover, all the peaks are as sharp as those in Figure 2a, suggesting that the well-crystallizing T′-La_2CuO_4 has been obtained. In this case, it is understood that the alleviation of the size mismatch is realized through the shift of the apical oxygen as mentioned above, because no high valence state of Cu can be expected for the synthesis in flowing Ar gas. It has been found that the O-structure with the distorted K_2NiF_4-type structure is never crystallized. That is to say, the size mismatch in the T-structure is alleviated by the formation of the T-structure with the high oxidation state of Cu or the T′-structure without the apical oxygen.

The obtained samples of T′-La_2CuO_4 were annealed in vacuum at 635 °C for 150 h, but they were still insulating unlike the superconducting $(La,Ln)_2CuO_4$ films.[1] To clarify the reason for the difference between non-superconducting bulk samples and superconducting films, the optimization of the annealing condition for the removal of excess oxygen and the detailed characterization of the bulk samples are under way.

In conclusion, we have successfully synthesized well-crystallized bulk samples of T′-La_2CuO_4 by the direct precipitation from the molten KOH/NaOH eutectic mixture at a temperature as low as 350 °C in flowing Ar gas. Unlike superconducting $(La,Ln)_2CuO_4$ films, however, T′-La_2CuO_4 exhibits no superconductivity. This reaction temperature is significantly low for the synthesis of bulk samples. The reason why T′-La_2CuO_4 has been obtained at a temperature as low as 350 °C is guessed that the large size-mismatch between the larger O−Cu−O length and the smaller La−La one in the T-structure is alleviated in the T′-structure. It has also been found that the distorted La_2CuO_4 with the O-structure is never crystallized. In addition, the technique using molten hydroxides has been found to be very useful for the synthesis of well-crystallized bulk samples at low temperatures.

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