

Crystal Growth of the Electron-doped Single Layer Copper Oxide Superconducting System

Nobuhisa Kaneko

National Institute for Research in Inorganic Materials

Microscopic characters of electron-doped copper oxide superconductors have not been studied well in comparison with those of hole-doped because of the difficulty in large single crystal growth and its low superconducting transition temperature. Because the Fermi surface of an electron-doped single-CuO₂-layer superconductor leans at an angle of 45° against that of hole-doped, the former material has no nesting effect. If there is a nesting effect and/or there are some different Fermi surfaces that appear in multi-CuO₂-layer materials, it is difficult to interpret experimental results by comparison with the theoretical predictions and calculations. Therefore, microscopic studies on the dynamical characters of electron-doped materials might bring a solution to the mechanism of high temperature superconductivity. For this reason, the growth of single crystals of electron-doped materials, so large as to be able to use them for neutron scattering experiments, has recently become of great importance. The origin of incommensurate spin fluctuations in La_{2-x}Sr_xCuO₄ has already been investigated but is still not clear. In order to elucidate this problem, it is necessary to carry out similar experiments on electron-doped materials. Pr_{2-x}Ce_xCuO₄, which is electron-doped, was chosen to investigate the magnetic excitations and spin fluctuations using neutron scattering experiments because a Pr³⁺ ion has a very low background level in neutron scattering in comparison with other rare-earth ions. In this work, flux, Top Seeded Solution Growth (TSSG) and Traveling Solvent Floating Zone (TSFZ) methods were used to grow such crystals. Because the electron-doped materials must be deoxidized at high temperature in order to manifest superconductivity, optimized annealing conditions were carefully investigated. Crystal growth of Pr_{2-x}Ce_xCuO₄ was also compared to that of other electron-doped materials.

Replacing Pr³⁺ ions by Ce⁴⁺, Pr_{2-x}Ce_xCuO₄ shows superconductivity after reduction only when the doping rate x is within the range 0.14~0.17. The maximum transition temperature T_c is 25K when $x=0.14\sim 0.15$. This study revealed that the peritectic temperature of Pr_{1.85}Ce_{0.15}CuO₄ system is lower by 120°C than that of the non-doped ($x=0$) system. This behavior is opposite to the case of a Nd_{1.85}Ce_{0.15}CuO₄ system in which the peritectic temperature is higher by 45°C than that of non-doped Nd₂CuO₄. The peritectic temperatures of Pr₂CuO₄ and Nd₂CuO₄ are almost equal (1270°C), and their primary phase region is of 15mol% in the CuO flux scale (here, the scale is written by a mole percentage of CuO in the Pr(or Nd)₂CuO₄-CuO system) and of 230°C in the temperature scale. The primary phase region of Nd_{1.85}Ce_{0.15}CuO₄ is of (20mol% ; 285°C), i.e. wider than that of the non-doped compound. Whereas, when $x=0.15$ in the Pr-system, the region is of (~ 20mol% ; ~ 100°C), therefore narrower than in the non-doped system. It means that crystal growth of Pr_{1.85}Ce_{0.15}CuO₄ is more difficult than that of the similar Nd-compound.

The method of crystal growth was chosen according to the desired crystal composition. The flux and TSSG methods were used to obtain low doping rates ($x < 0.14$), because the distribution coefficient is low compared to that of highly doped materials ($x \sim 0.15$). Thus, the Ce distribution in a crystal is expected to be comparatively uniform, the disorientations of the crystallographic

axes within the crystal is smaller and it is easier to grow large crystals. It is important to choose the crucible used for the flux and TSSG methods considering problems such as the contamination of crystals by the crucible, creeping out of the melts and so on. Many types of crucibles were tested in order to find the most suitable for these methods.

Non-doped crystals having a volume of about 4cm^3 were grown by the flux method in Pt crucibles. Dendrites that crystallized on the wall of the crucible on the surface of the melt were identified as Pt_2Cu , using Electron Probe Micro Analysis (EPMA). The disorientations of the axes of these crystals were measured by neutron scattering experiments as $\sim 0.4^\circ$ (c-axis) and $\sim 0.5^\circ$ (a,b-axis). The temperature dependence of the magnetic Bragg peak intensities were also measured and Néel temperature was defined as $T_N=255\text{K}$.

In low doping region, we used MgO crucibles and BaCO_3 as an additive in the CuO flux. Previous to growth, CuO was melted in the MgO crucible in order to induce a reaction between the flux and the crucible, thus reducing such a reaction during the actual growth. This enabled to develop a method that hardly causes any problem of contamination from either the crucible or the additive in long-time growth. A $\text{Pr}_{1.93}\text{Ce}_{0.07}\text{CuO}_4$ crystal of about 1cm^3 in volume and having an almost constant Ce-distribution (error by $\pm 3\%$) is obtained with this method. Mg contamination from crucibles was not detected by EPMA and was less than 2% by Inductively Coupled Plasma emission spectrometry (ICP). Ba contamination from the additive was observed neither by EPMA nor by ICP. The disorientations of the axes was derived by neutron scattering experiments as $\sim 0.3^\circ$ (c-axis) and $\sim 0.5^\circ$ (a,b-axis). Dendrites that crystallized on the surface of a melt were identified as Mg_2CuO_x , or $(\text{Mg,Cu})\text{O}_x$ using EPMA.

It is observed, in flux and TSSG methods, that the surface of the melt easily reacts to the crucible leading to the dissolution of the crucible of the melt surface/crucible interface. Without seed-cooling in TSSG method, the melts easily crept up the seed, the seed-holder was dissolved and the seed (with part of the holder) eventually fell down. In both cases, these severe reactions were due to the oxygen atmosphere. Optimizing of cooling conditions of the seed should be efficient in solving this problem, however suitable conditions were not obtained in this study.

TSFZ method was used for materials with superconducting composition to avoid contamination and to obtain samples with uniform Ce-concentration. FZ furnaces were improved in this study to form a sharp focus and to adjust the focus of mirrors with 2 or 4 lamps precisely. Crystals were grown according to the conditions of a flux growth, and using the data on crystallization of secondary phases and stability of melts. The crystal showed superconducting transition at $T_c=24\text{K}$, but it was composed of several grains that have a preferential c-axis orientation. It is difficult to grow large single crystals because $(\text{Pr,Ce})_4\text{O}_{7+\delta}$ crystallized, thus hindering the growth of a dominant grain. Contrarily to the non-doped case, here the melt zone composition easily and partially leaves the $\text{Pr}_{1.85}\text{Ce}_{0.15}\text{CuO}_4$ primary phase region, the (composition ; temperature) range of which is narrower. Therefore, secondary phases crystallize. The amount of secondary phases and the mechanism of crystallization were investigated.

The annealing conditions required in order to show superconductivity was optimized ; at first, annealing in argon gas at 950°C for 10 hours, and next, annealing in oxygen gas at 950°C for 10 hours (this treatment destroys superconducting character), finally annealing in argon gas at 950°C for 10 hours. After these treatments the sample showed a superconducting transition at 24K (18K, after the first annealing step) and ΔT_c got narrower. The mechanism of these changes of T_c and ΔT_c versus the annealing steps was also examined.