Crystal growth of $La_{2-x}Ce_xCuO_4$

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Abstract

Single crystals of $La_{2-x}Ce_xCuO_4$ have been successfully grown by the traveling-solvent floating-zone (TSFZ) method. The optimum condition of the atmosphere on the growth was determined. The effect of the annealing atmosphere and temperature was also studied. The characterization of the crystals by scanning electron microscopy-X-ray energy dispersion spectroscopy (SEM-EDS) and magnetic susceptibility measurement is reported. The structure of grown crystals is T-phase, different from other $Ln_{2-x}Ce_xCuO_4$ (Ln: La, Pr, Nd. Sm and Eu). Superconductivity is observed at 20-30 K in oxygen-annealed samples.

Key words: electron-doped cuprate; $La_{2-x}Ce_xCuO_4$; Traveling-solvent floating-zone method

1. Introduction

The electron-doped cuprate $Ln_{2-x}Ce_xCuO_4$ of the so-called T'-phase is difficult to be grown single crystal form and to become superconducting by the post-growth annealing treatment. Therefore, the research does not advance easily. The superconducting critical temperature T_c was reported to decrease as the atomic number of the host rare-earth element increases [1] and, it is known that the crystal growth is easy for La_2CuO_4. In this regard, La system seems to be a reasonable choice for trying to grow crystals. Although in sintering polycrystalline sample [2] and thin film [3] of T'-$La_{2-x}Ce_xCuO_4$, superconductivity has been observed, single crystal growth has not been reported so far.

2. Experimental technique

Single crystals of LCCO were grown by the TSFZ method using an infrared radiation-convergence type furnace with four 300-W halogen lamps and four ellipsoidal glass mirrors, as a radiation source and a condenser, respectively. The feed rod and starting materials were prepared from La_2O_3, Ce_2O_3 and CuO of 99.99 purity. The well-mixed powder with the required atomic ratio was first calcined at 900°C for 15h. Then after grinding and milling, it was formed into cylindrical shape of 6-8 mm in diameter and 10 cm in length by pressing at a hydrostatic pressure of about 2000 kg/cm^2 with cold isostatic pressing. The feed and starting materials rod were sintered in air for 15 h at 1100°C and 900°C, respectively. About 0.3-0.5 g of the starting material of $La_{1.85}Ce_{0.15}CuO_4$ and $La_{1.88}Ce_{0.12}CuO_4$ in the atomic ratio La:Ce:Cu= 1.85:0.15:8.0 and 1.88:0.12:8.0 were connected at the end of the feed rod. The growth was performed at a rate of 0.5mm /h. The feed rod and growing crystal were rotated at 15 rpm in opposite directions to each other. The composition of the grown crystal and the molten zone were analyzed by SEM-EDS with the acceletion voltage of 20 kV.

3. Results and discussion

Crystal boules grown by the TSFZ method have the dimension of 4-5 mm in diameter and 40-60 mm in

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Fig. 1. $La_{2-x}Ce_xCuO_4$ crystal boule grown by the TSFZ method.

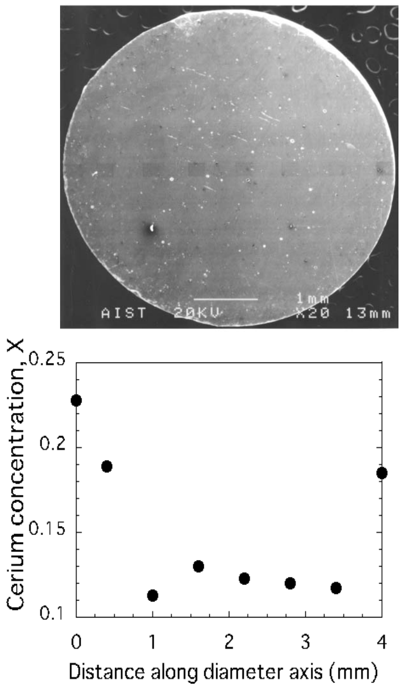

Fig. 2. An SEM micrograph and concentration profiles of Ce distribution in a cross-section parallel to the growth direction observed by EDS analysis of $La_{1.88}Ce_{0.12}CuO_4$ boule.

length as shown in Fig.1.

Several growth experiments were performed using different atmosphere in order to find optimum growth conditions. In this system, the as-grown crystals spontaneously broke into yellow pieces, when they were kept in air for over a week grown in argon atmosphere. The cerium-contained solvent tends to fall easily down onto the seed in oxygen and air atmosphere. However, the molten-zone remains stable in 0.1% and 1% oxygen mixed argon gas. SEM micrograph and concentrational profiles of Ce distribution in a cross-.section parallel to the growth direction observed by EDS analysis is shown in Fig 2. The EDS analysis showed that the TSFZ crystal has cerium homogeneously distributed inside the crystal. However, there is plenty of cerium in crystal surface part.

The as-grown crystal s were annealed in argon at

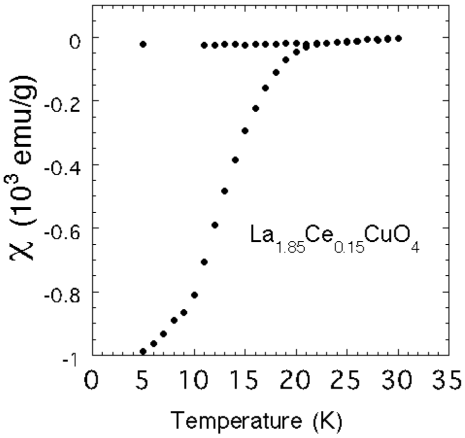

Fig. 3. Temperature dependence of magnetic susceptibility for $La_{1.85}Ce_{0.15}CuO_4$ annealed in oxygen.

900°C for 100 h and then in oxygen at 300°C for 20 h. As-grown and after argon annealed crystals were shown non-superconductor with T-phase structure. However, crystal showed superconductivity of 20-30 K after the oxygen annealing with T-phase structure. Fig.3 shows the magnetic susceptibility measurement in the oxygen annealed single crystal of $La_{1.85}Ce_{0.15}$ CuO_4.

4. Conclusion

In summary, we succeeded in preparing superconducting single crystals by the TSFZ method which show no superconducting and T-structure after argon annealing, but it show superconducting transition temperature with about 20-30 K after oxygen annealing. It is difficult to get the superconducting T'-LCCO crystal. The narrow condition for growing the LCCO crystal in which superconductivity coexists with T'-phase structure must be found out.

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