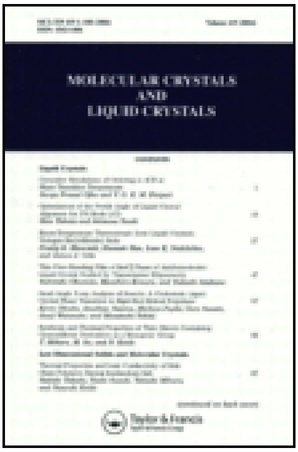

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THE GROWTH OF $Nd_{2-x}Ce_xCuO_4$ SINGLE CRYSTALS BY THE TSFZ METHOD

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Abstract Phase diagrams of the Nd_2O_3-CuO and $(Nd,Ce)_2O_3$-CuO systems were investigated by differential thermal analysis. It was found that Nd_2CuO_4 and $Nd_{2-x}Ce_xCuO_4$ melt incongruently at 1270±5 °C and 1315±5 °C respectively, and the solids of Nd_2CuO_4 and $Nd_{2-x}Ce_xCuO_4$ exist in equilibrium with the liquid of 79-91 mol% CuO, respectively. On the base of these results, $Nd_{1.86}Ce_{0.14}CuO_4$ single crystals were grown by the traveling solvent floating zone (TSFZ) method. The as-grown crystals were 5 mm in diameter and 50 mm in length with a lusterless black, and had a few subgrains. The Meissner signal was not observed from the as-grown crystals, but it was observed below 19 K from the crystals annealed in N_2 at 900 °C for 70 hours.

INTRODUCTION

The new type superconductors of $Nd_{2-x}Ce_xCuO_4$ had been discovered recently [1]. $Nd_{2-x}Ce_xCuO_4$ is a compound substituted Ce^{4+} for Nd^{3+} in Nd_2CuO_4, so that the carriers are not holes but electrons in the $Nd_{2-x}Ce_xCuO_4$ superconductors. For clarification of the superconducting mechanism of $Nd_{2-x}Ce_xCuO_4$, it is desired to obtain high quality and sizable single crystals of $Nd_{2-x}Ce_xCuO_4$. Growth of $Nd_{2-x}Ce_xCuO_4$ single crystals have been performed by the self-flux method, the top-seeded solution method and the traveling solvent floating zone method (TSFZ method) [2-4]. However, high quality and sizable single crystals of $Nd_{2-x}Ce_xCuO_4$ had not yet been obtained. We had already grown high quality and sizable single crystals of $La_{2-x}Sr_xCuO_4$ by the TSFZ method [5-6]. In this study, the phase diagrams in the systems of Nd_2O_3-CuO and $(Nd,Ce)_2O_{3+\delta}$ -CuO were determined, and the $Nd_{2-x}Ce_xCuO_4$ single crystals were grown by the TSFZ method on the base of these phase diagrams. Also, the grown crystals of $Nd_{2-x}Ce_xCuO_4$ were investigated about magnetic properties.

EXPERIMENTAL PROCEDURE

The phase diagrams in the systems of Nd_2O_3-CuO and $(Nd,Ce)_2O_{3+\delta}$ -CuO were investigated by differential thermal analysis with thermal gravity analysis (TG-DTA). Mixture of Nd_2O_3, CeO_2 and CuO was calcined at 850 °C for 24 hours in air, and then used as the sample for TG-DTA measurement. TG-DTA experiments were performed between room temperature and 1300 °C at the heating and cooling rates of 5 °C/min in oxygen flow of 0.1 MPa. The samples after the TG-DTA measurement were analyzed by the powder XRD method and an electron probe microanalyzer (EPMA).

The feed rods and the solvents for crystal growth were prepared as follows. The raw materials of Nd_2O_3, CeO_2 and CuO were mixed with stoichiometric composition of $Nd_{2-x}Ce_xCuO_4$ (x=0.15), and calcined at 850 °C for 24 hours in air. The pre-heated powder was formed into a cylindrical shape of 5 mm in diameter by 60 mm in length, and pressed at a hydrostatic pressure of about 100 MPa. The rod was sintered at 1000 to 1200 °C for 12 hours in oxygen, and then used as a feed rod. The solvents, in which the compositions were CuO content between 80 and 90 mol% CuO and Ce content of x=0.15, were prepared in the same way as preparation of the feed rods.

The apparatus for crystal growth was an infrared heating furnace of the double ellipsoidal type with two 1.5 kW halogen lamps as the heat source. The growth conditions were the growth rate of 1.0 mm/h, the growth direction of the a-axis and the growth atmosphere of oxygen under the pressure of 0.2 MPa to prevent the vaporization of CuO from the molten zone.

The compositions of the $Nd_{2-x}Ce_xCuO_4$ phase and the inclusions in the grown crystals were analyzed by EPMA. The superconductive properties of the grown crystals were investigated by magnetization measurement with using a SQUID magnetometer.

RESULTS AND DISCUSSION

Phase diagrams in the systems of Nd_2O_3-CuO and $(Nd,Ce)_2O_{3+\delta}$ -CuO

Figure 1 shows the phase diagram of the $(Nd,Ce)_2O_{3+\delta}$ -CuO system. Nd_2CuO_4 and $Nd_{1.85}Ce_{0.15}CuO_4$ melted incongruently. The former decomposed to the Nd_2O_3 solid and the liquid at 1270±5 °C, and the latter decomposed to the $(Nd,Ce)_2O_{3+\delta}$ solid solutions and the liquid at 1315±5 °C. It was found that substitution of Ce^{4+} ions for Nd^{3+} ions in Nd_2CuO_4 raises the melting point. The composition of peritectic point of $Nd_{1.85}Ce_{0.15}CuO_4$ was 79 mol% CuO. The eutectic point of $Nd_{1.85}Ce_{0.15}CuO_4$ and CuO were the composition of 91 mol% CuO and the temperature of 1050 °C. However, when the mixture with a composition CuO-richer than $Nd_{1.85}Ce_{0.15}CuO_4$ was cooled after melted, it was molten partially below 1050 °C, and then solidified to $Nd_{2-x}Ce_xCuO_4$, CuO and Cu_2O completely at 1000 °C. Formation of Cu_2O was due to the following. When the mixture of $Nd_{2-x}Ce_xCuO_4$ and CuO was melted, some of the cupric ions in the liquid were reduced to cuprous ions with a vaporization of oxygen gas. Thus, Cu_2O was precipitated from the liquid during cooling.

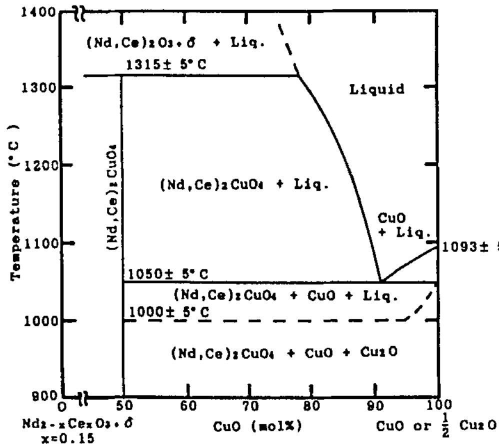

FIGURE 1 Phase diagram of $(Nd,Ce)_2O_{3+\delta}$ -CuO system.

Oka et al.[3] had reported the phase diagram of the Nd_2O_3-CuO system in air, which was similar to our results. However, the melting point of Nd_2CuO_4 reported by them was 1240 °C and was 30 degrees lower than our result. It seems that the melting point of Nd_2CuO_4 depends on oxygen partial pressure of the atmosphere gas and increases as oxygen partial pressure increases.

Crystal growth

The phase diagram of the $(Nd,Ce)_2O_{3+\delta}$ -CuO system indicates that it is possible to grow the single crystals of $Nd_{2-x}Ce_xCuO_4$ by the TSFZ method with using a solvent of the composition from 79 mol% CuO to 91 mol% CuO. Crystal growth of $Nd_{2-x}Ce_xCuO_4$ with Ce content of x=0.15 were attempted by the TSFZ method.

In the case of crystal growth with using a solvent of 80 mol%

CuO, the grown crystals of $Nd_{2-x}Ce_xCuO_4$ contained many inclusions of the $Nd_{1.48}Ce_{0.52}O_{3+\delta}$ solid solutions, and was brittle.

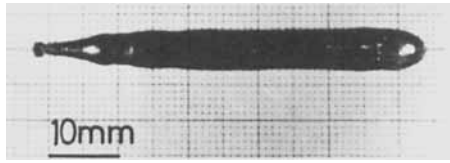

FIGURE 2 As-grown crystal of $Nd_{2-x}Ce_xCuO_4$.

Figure 2 shows an as-grown boule of $Nd_{2-x}Ce_xCuO_4$, which was grown by using a solvent of 85 mol% CuO. The as-grown boule was 5 mm in diameter and 50 mm in length with a lusterless black, and had a cleavage parallel to the *c*-plane. The grown crystals contained a few subgrains and some inclusions of CuO, but the single crystals with the size of about 2x3x5 mm^3 were obtained. The composition of the grown crystals was determined to be $Nd_{1.86}Ce_{0.14}CuO_4$, and was a little Ce-poorer than that of the $Nd_{1.85}Ce_{0.15}CuO_4$ feeds. Precipitation of CuO results from composition change of melt zone toward CuO-richer composition. Therefore, it is suggested that the optimum composition of the solvent may be between 80 mol% CuO and 85 mol% CuO.

Magnetic properties

The Meissner signal was not observed from the as-grown crystals of $Nd_{1.86}Ce_{0.14}CuO_4$. It had be reported that $Nd_{2-x}Ce_xCuO_4$ annealed under reduction condition became a superconductor [1], and also the single crystals of $Nd_{2-x}Ce_xCuO_4$ grown in the deoxidized atmosphere by the TSFZ method were superconductive below 10 K [3]. However, The single crystals of $Nd_{2-x}Ce_xCuO_4$ were grown in oxygen atmosphere to prevent vaporization of copper oxide, so that they were not superconductive. Thus, when the grown crystals of $Nd_{1.86}Ce_{0.14}CuO_4$ were quenched with using liquid nitrogen after annealed in N_2 at 900 °C for 70 hours, the Meissner signal was observed from them. Figure 3 shows the temperature dependence

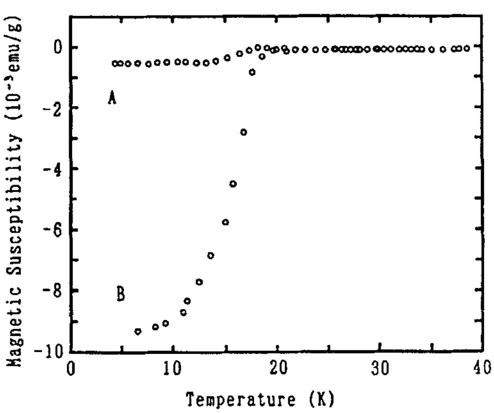

FIGURE 3 Temperature dependence of magnetization of $Nd_{2-x}Ce_xCuO_4$ annealed crystal : (A) and (B) are field and zero-field cooled magnetization at 1.3 Oe, respectively.

of the magnetization of the $Nd_{1.86}Ce_{0.14}CuO_4$ annealed crystals. The transition onset temperature of the annealed crystals was 19 K, and its value was lower than that of the $Nd_{2-x}Ce_xCuO_4$ ceramics reported previously [1]. The low transition temperature may be caused from precipitation of CuO in the grown crystals and the annealing conditions.

CONCLUSIONS

The phase equilibriums in the systems of Nd_2O_3-CuO and $(Nd,Ce)_2O_{3+\delta}$ - CuO were determined by TG-DTA measurement. On the base of these results, $Nd_{2-x}Ce_xCuO_4$ single crystals were grown by the TSFZ method using an infrared heating furnace. The as-grown crystals of $Nd_{1.86}Ce_{0.14}CuO_4$, which were 5 mm in diameter and 50 mm in length with a lusterless black, were obtained. However, the grown crystals contained some inclusions of CuO, and had a few subgrains. In the results of magnetization measurement, the as-grown crystals were not superconductive, but the annealed crystals were superconductive below Tc_{onset}=19 K. The transition temperature lower than that of the sintered $Nd_{2-x}Ce_xCuO_4$ may be caused from precipitation of CuO in the grown crystals. The more good quality single crystals of $Nd_{2-x}Ce_xCuO_4$ will be grown by the TSFZ method with using the optimum solvent.

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