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Growth of the substrate crystals for $La_{2-x}Sr_xCuO_4$ thick films

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Abstract The distribution coefficients of Ni and Zn to the Cu site in La_2CuO_4 (LCO) were investigated to determine the suitable solvent composition for crystal growth of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) (LCMO), and were found to be 4.2 for Ni and 0.66 for Zn, respectively. Single crystals of LCO, and LCMO of high homogeneity were grown by traveling solvent floating zone technique using suitable solvents. No diamagnetic signals were observed for all substituted crystals. This fact suggests that crystals of LCO partially substituted by Ni or Zn are useful as substrate crystals.

1. Introduction

High quality single crystalline superconducting films on non-superconducting substrates are desired to realize the superconducting switching devices. The selection of the substrate is an important factor. The main features desired for the substrate are high lattice matching with superconducting films and non-superconductivity. In this paper, we tried to grow substrate crystals for $La_{2-x}Sr_xCuO_4$ (LSCO) films. La_2CuO_4 (LCO) was focused from the point of view of lattice matching. LCO has another advantage because it is an insulator in the stoichiometric composition [1]. However, excess oxygen easily dissolves into LCO. One percent of excess oxygen makes LCO a superconductor [2]. This is a demerit as a substrate. When small amount of an impurity such as Fe, Co, Ni, Zn, Ga, and Al is substituted to Cu site, superconductivity of LSCO is drastically suppressed [3]. To find a way out of the weak point of LCO as a substrate, impurity substitution was examined. In this study, Ni as a magnetic element and Zn as an non-magnetic element were selected as partially substituted impurities in LCO.

First, the distribution coefficients of Ni and Zn are estimated by zone melting technique. Using suitable solvent composition, estimated by the distribution coefficient values, single crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) or La_2CuO_4 were grown by the traveling floating zone (TSFZ) method. All grown crystals except LCO were found to be non-superconductors even after annealing in oxygen atmosphere. These results suggest that these crystals may be useful as substrates for LSCO films.

2. Experiment

La_2O_3 (> 99.99 %), CuO (> 99.9 %), ZnO (> 99.99 %), NiO (> 99.9 %) powders were used as raw materials. La_2CuO_4, $La_2Cu_{1-x}M_xO_4$ (M = Ni (x = 0.01, 0.02, 0.03, 0.04), Zn (x = 0.01, 0.02, 0.03)) powders were prepared by the conventional solid state reaction. These powders were pressed into a rod shape and sintered to prepare a feed rod. The powders for solvents (78~80 mol% ((1 - x)CuO + xMO (M = Ni, Zn))) were also prepared by the solid state reaction. First, the distribution coefficients of substituted elements were estimated using the zone melting method. For both substitution elements Ni and Zn, crystals were grown using feed rods (x = 0.03) and solvents (x = 0.03). The chemical compositions of grown crystals were analyzed along growth direction from seeding points. The distribution coefficients of Ni and Zn were estimated by their distribution as a function of growth length. Using the distribution coefficient values, suitable compositions of solvents were estimated and crystals were grown by the TSFZ technique. The compositions of grown crystals were analyzed by X-ray microanalyzer (XMA : JEOL Co., model JXA-8600M) to check the homogeneity of crystals. Magnetization of crystals was investigated by superconducting quantum interference device (SQUID : QUANTUM DESIGN Co., model MPMS-5S).

3. Result and discussions

Figure 1 indicates the results of the chemical analysis of crystals along growth direction which were

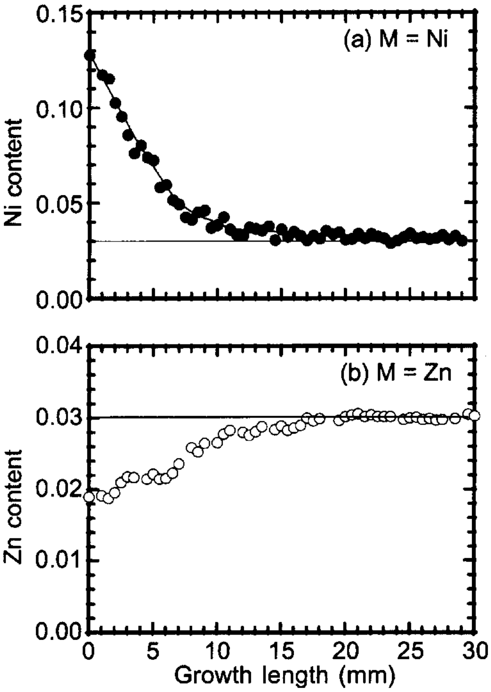

Fig. 1. The distribution of the substituted elements (M = Ni, Zn) in $La_2Cu_{1-x}M_xO_4$ grown crystals along the growth direction. Both chemical compositions of feed rods and solvents were x = 0.03.

grown using feed rods of x = 0.03 and solvents of x = 0.03. Figure 1 (a) corresponds to Ni substitution and Fig. 1 (b) to Zn substitution. In the Ni substitution, Ni concentration at the initial growth region is higher than that of the feed rod and the solvent and gradually reduced down to x = 0.03. On the other hand, Zn concentration in a grown crystal is 0.02 (< 0.03; Zn concentration of the feed rod and the solvent) and gradually increased up to 0.03. These results indicated that the distribution coefficient value of Ni is larger than unity and that of Zn is smaller. When the distribution coefficient is assumed to be independent of the concentration of the substituted elements, the concentrations of crystals grown by zone melting technique can be expressed as $c/c_0 = 1 - (1 - k)e^{-kx/L}$, where k is the distribution coefficient, c and c_0 are the concentration of the substituted element in the grown crystal and that in the feed rod, L is the zone length (4 mm) and x is the length from the seeding point [4]. This equation can be modified as $\ln|1 - c/c_0| = \ln|1 - k| - kx/L$. Therefore, when $\ln|1 - c/c_0|$ is plotted as a function x/L, the distribution coefficient can be decided by the slope of this plot. The plot shows the distribution coefficients of Ni and Zn are 4.2 and 0.66, respectively. Using these values, suitable compositions of solvents were determined, which were summarized in Table 1. Average values of the analyzed composition were also shown there. The photographs of crystals grown by TSFZ were shown in Fig. 2. Grown crystals were black and metallic luster is recognized on the surface. It was found that the grown crystals were single phase and have no subgrain by

Table 1
Chemical composition of feed rods, solvents and grown crystals

	Nominal composition		Analytical cmposition	
	Feeds (x)	Solvents (x)	Grown crystals (x)	
			Initial part	Final part
Ni	0.01	0.002	0.009 (1)	0.010 (1)
	0.02	0.005	0.020 (1)	0.020 (1)
	0.03	0.007	0.030 (1)	0.030 (1)
	0.04	0.010	0.041 (1)	0.040 (1)
Zn	0.01	0.015	0.010 (1)	0.010 (1)
	0.02	0.030	0.020 (1)	0.020 (1)
	0.03	0.045	0.030 (1)	0.030 (1)

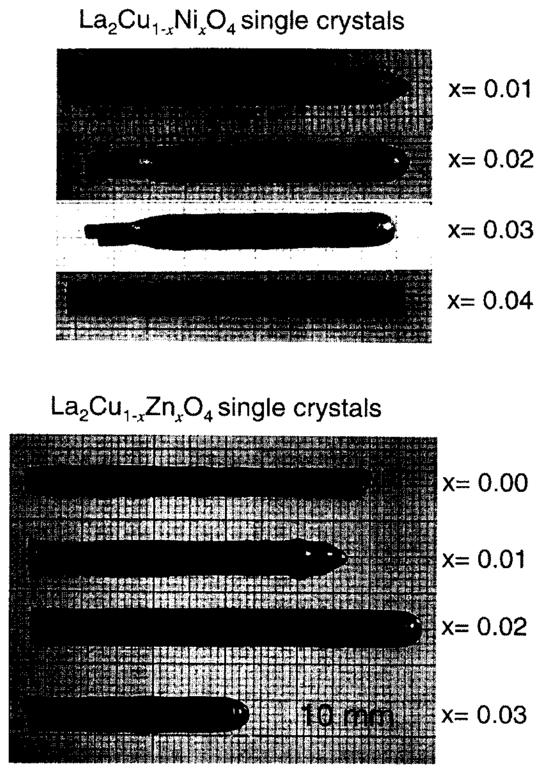

Fig. 2. The photographs of grown crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) and La_2CuO_4.

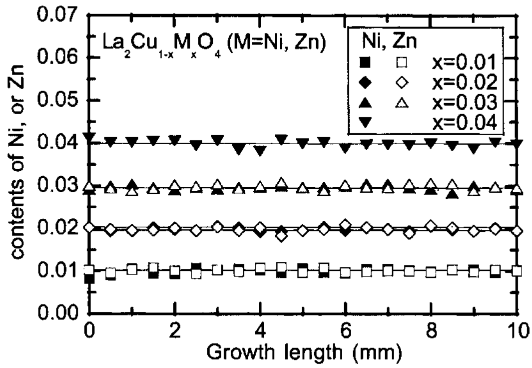

Fig. 3. The chemical composition of Ni and Zn in the grown crystals along the growth direction.

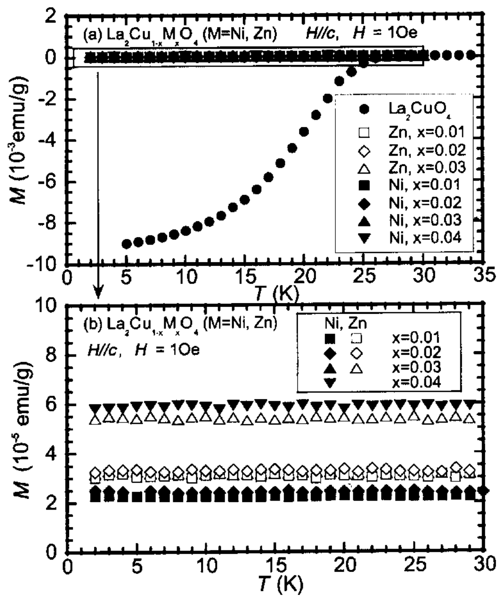

Fig. 4. The temperature dependence of the magnetization for as-grown crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni, Zn) and La_2CuO_4.

the polarized optical microscope observation.

The chemical composition of grown crystals was analyzed along the growth direction from seeding point and within the sections of both the initial and the final part. All these analyses show the uniform distribution of substituted elements in crystals. The distribution along growth direction was shown in Fig. 3 as a representative data, which show concentration of substituted elements in crystals was consistent with that of feed rods. This means uniform crystals. However, slight inhomogeneity was recognized in the section of the final part of the crystals substituted by Ni. In the crystals of x = 0.03 and 0.04, Ni content in the center regions of the section are slightly lower and that in the fringe regions was higher ($\Delta x = 0.002$).

Magnetic property of grown crystals was shown in Fig. 4. No diamagnetic signals accompanied by superconducting transition were observed for all crystals substituted by Ni and Zn. These behaviors did not changed even after the annealing under the oxygen flow atmosphere. Non-superconductivity of the substituted crystals is useful as substrate crystals.

4. Conclusions

The distribution coefficients of Ni and Zn for La_2CuO_4 (LCO) were examined by zone melting technique and found to be 4.2 and 0.66, respectively. Using distribution coefficient values, suitable solvent composition were determined to grow single crystals of $La_2Cu_{1-x}M_xO_4$ (M = Ni and Zn). Single crystals were grown by TSFZ method. Chemical compositions of grown crystals were found to be uniform all over the grown crystals. No diamagnetic signals, which represent superconductivity, were observed for all grown crystals except LCO. Same results were obtained for crystals annealed in oxygen atmosphere. This result means that Ni or Zn substitution is useful to make LCO non-superconductor and that the single crystals of LCO substituted by Ni and Zn may be useful as substrate crystals.

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