Phase Relationships of the La-Ba-Cu-O System

H. Kojima, M. Kameda, H. Tanabe, and I. Tanaka
Institute of Inorganic Synthesis, Faculty of Engineering
Yamanashi University
7 Miyamae, Kofu, 400, Japan

ABSTRACT

The phase behavior of the ternary system La$_2$O$_3$-BaO-CuO (LBCO) has been studied. The liquidus temperature and the stable regions of primary phases have been determined over selected composition ranges by TG-DTA and a Slow Cooling Floating Zone Method (SCFZ). An EPMA has been employed to analyze the quenched sample by the SCFZ method. It has been shown that the distribution coefficients, $k$, of Ba ion into the solid LBCO crystals are approximately 0.12-0.20. However, when the concentration of Ba in the liquid is greater than $x = 1.0$ of mole fraction, other phases like 101 and 212 are easily formed.

INTRODUCTION

La$_{2-x}$Ba$_x$CuO$_4$ (LBCO) is a p-type superconducting material which is formed by substitute Ba for La ion in La$_2$CuO$_4$ (LCO). LBCO shows superconducting behavior in the range of Ba concentration $0.06 \leq x \leq 0.3$ and a local minimum near $x = 0.125$. Also, this material shows metallic behavior over $x > 0.3$. These data were found by using sintered materials. However, these materials have anisotropic properties, so it is desirable to measure the physical properties by using single crystals of LBCO. The phase relations of the La-Ba-Cu-O system, which will be necessary to grow the LBCO single crystals by using the Traveling Solvent Floating Zone Method (TSFZ), will be made clear in this study.

EXPERIMENTAL

Phase relationships were determined by using a Slow Cooling Floating Zone Method (SCFZ) and thermal differential analysis (TG-DTA). Stoichiometric amounts of La$_2$O$_3$BaO and CuO were mixed in ethanol, dried and calcined at 900-950°C for 24 hours in air. The preheated powder was formed into a cylindrical shape 6 mm in diameter by 70mm in length, sintered at 1280°C for 12-20 hrs in oxygen, and then used as the feed rod for the SCFZ method. The apparatus for the SCFZ method was an infrared heating furnace with a 1.5 kw halogen lamp as the heat source. The composition of the solid before melting was analyzed by an electron probe microanalyzer (EPMA).

The growth of LBCO single crystals was performed by using the TSFZ method in order to be sure of the phase relations. The apparatus for single crystal growth was a single ellipsoidal infrared heating furnace with a 1.5 kw halogen lamp as the heat source. The growth conditions were as follows: the solvent composition was 78-85 mol.% CuO, the oxygen gas pressure was 2 atmospherics and the growth rate was 1mm/hr.
RESULTS

The composition of the liquids in equilibrium with solid LCO is 75-89 mol.% CuO according to the phase diagram of the La$_2$O$_3$-CuO system (1). It was reported that the suitable solvent composition was 78-80 mol.% CuO for growing single crystals of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) (1). In this study, the same composition has been used.

The samples, whose Ba concentration was changing in the solvent, were analyzed by a TG-DTA method. These results are shown in Fig. 1. In the case where the Ba concentration was $x=0.075$ and 78 mol.% CuO, two endothermic peaks and a weight loss were observed at 1000°C while heating the sample to 1400°C. In the cooling stage, three exothermic peaks were observed at 1300°C, 1010°C and 1000°C and the weight increased at 1300°C and 1010°C. The weight decrease during heating may be due to the decomposition of CuO to Cu$_2$O or the vaporization of Cu$_2$O. The exothermic peak, which seemed to be a primary deposition, was observed to divide into two peaks in the Ba concentration range $x=0.1-0.3$. Variations in peak intensity and deposition temperature are also observed over the same concentration range. The maximum deposition temperature reached was 1310°C at a Ba concentration of $x=0.25$. However, the peaks corresponding to the primary deposition of LBCO did not appear at a Ba concentration $x\leq0.6$. The reason why the peaks for primary deposition became very weak seems to be that other phases besides LBCO such as La$_{2-x}$Ba$_x$Cu$_2$O$_5$ (101 phase) and La$_{2-x}$Ba$_{1+x}$Cu$_2$O$_5$ (212 phase) precipitate.

Fig. 2 shows the change in concentration of the Ba ion in the solid LBCO vs. that of the solvent, which was determined by EPMA analysis of the samples solidified by the SCFZ method. These results suggest that the effective distribution coefficient ($k$) of Ba into solid LBCO is less than unity and will be $0.12< k <0.2$ at the concentration of Ba $0\leq x \leq 1.0$.

Fig. 3 shows the effective distribution coefficient ($k$) of Ba ion vs. the concentration of Ba in the 214 phase. In this case, the composition of Ba in the solvent phase was $x=1.0$, and Ba concentration in the solid LBCO was 0.124. However, if the concentration of Ba in the solvent phase increased to more than $x=1.0$, other phases like the 101 and 212 phases will be easily precipitated.

In the crystal growth experiments, the Ba concentration in the feeding materials were from $x=0.1$ to 0.2. However, the Ba concentrations in the grown crystals were $x=0.06-0.1$ even if solvents of high Ba concentration were used. Table 1 shows the composition of grown single crystals and the solvents used. These results agree with the results from the phase relations mentioned above.

The sizes of the grown crystals were about 60mm in length and 5mm in diameter. Crystals were black colored and lusterless. Characterization was carried out by using a Laue back diffraction X-ray camera which revealed the single crystal structure. The superconductivity of the grown crystals measured by a SQUID shows that the $T_c$ onset is 24K.

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Fig. 1 DTA Curves of $\text{La}_{2-x}\text{Ba}_x\text{CuO}_4 (0.0 \leq x \leq 1.0)$
Fig. 2 Relation of Ba content $x$ between solvents (80mol\%CuO) and $\La_{2-x}$\Ba$_x$\CuO$_4$.

Fig. 3 Effective distribution coefficient $k$ of Ba into $\La_2$\CuO$_4$.

Table 1 Composition of $La_{2-x}$Ba$_x$CuO$_4$ grown crystals

| Feeds | Solvents | Crystals  |
|-------|----------|-----------|
| 0.100 | 0.300    | 0.060(2)  |
| 0.100 | 0.800    | 0.060(2)  |
| 0.160 | 0.700    | 0.079(4)  |
| 0.160 | 0.800    | 0.101(5)  |
| 0.200 | 0.800    | 0.105(3)  |