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ABSTRACT

A coprecipitation method by a use of oxine was applied to a rapid synthesis of $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ superconducting films. The rapid syntheses means a method of crystallization through melt in a very short time. The film crystallized at 860°C for 1 hour considered to contain the superconducting phase with Tc 100 K, and a small amount of superconducting phase with Tc 70 K.

Key Words: Superconductor, Superconducting Film, Synthesis, Oxine, Precipitation method, Instantaneous Synthesis

Introduction

Since the discovery of high-Tc (transition temperature) superconductivity in La-Ba-Cu-O system by Bednorz and Muller,[1] intensive studies have been made on copper-based oxides to seek new types of high-Tc superconductors. Recently, Maeda et al.[2] have discovered two superconducting phases with Tc=105 K and 75 K in the new oxide with nominal composition $BiSrCaCu_2O_x$. They have also found that the volume fanction of the 105 K phase is very scarce in the sample, and is strongly dependent on the variation of nominal composition and on heat treatment.[2] Oota et al.[3] reported the occurence of almost single 105 k phase with nominal composition $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$.

On the other hand, superconducting behaviors are closely related to ceramics preparation processes such as the preparation method for powder materials and the sintering temperature and time. The coprecipitation method by a use of oxine is quite attractive in that this method is expected to give homogeneous and fine powder materials.[4,5] The difficulty in this method lies in a formation of precipitate from a solution. The difficulty increases especially in multicomponent systems. Oxide superconductors are usually prepared by a solid state reaction, it takes a very long time to obtain homogeneous samples by the calcination and sintering processes. Akamatsu et al.[6] recently developed a rapid procedure through melts to prepare Bi-Ca-Sr-Cu-O thick films on MgO single-crystal substrates with Tc of 93 K.

In this study we tried to prepare superconducting thick films with a nominal composition $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ by using the rapid procedure and coprecipitation method by a use of oxine.

Experimental

The process for the synthesis in this investigation is shown in **Fig. 1.** 0.155 g $Bi(NO_3)_2 \cdot 5H_2O$ was dissolved in 4.0 ml concentrated acetic acid. 0.045 g $Pb(NO_3)_2$, 0.098 $Sr(NO_3)_2$, 0.109 $Ca(NO_3)_2 \cdot 4H_2O$ and 0.240 g $Cu(NO_3)_2 \cdot 4H_2O$ were dissolved in 7 ml distilled water. These two solutions were mixed. The concentrations of these solutions were determined by atomic absorption spectroscopy (Pb^{2+}, Sr^{2+}, Ca^{2+}, Cu^{2+}) and colorimetry (Bi^{2+}). 12.0 g oxine was dissolved in 300 ml dilluted acetic acid solution (1:4). The solution was poured into the oxine solution.

Received April 10, 1991
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Then ammonium solution was dropped into the mixed solution with vigorous stirring untill the pH of the solution reached 9.4 at room temperature. The resulting yellow precipitate was filterd and washed with water and ethanol. To convert the precipitate into oxide powder the precipitate was fired at 700°C in air for 1 hour. The oxide powder was melted without any calcination or sinterring

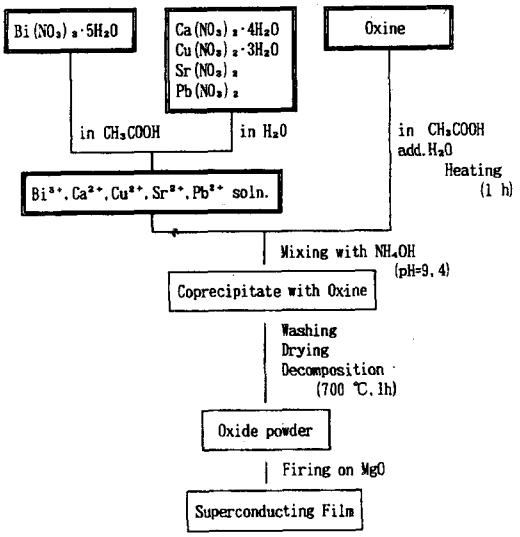

Fig. 1 Process for synthesis

on MgO single-crystal substrate (5 mm wide, 10 mm long, 1 mm thick) at 1200°C for 1 hour in air in an electric furnace. The melt was then cooled in the furnace (the cooling rate was about 40°C/min) down to a given temperature and held at that temperature for a given time for crystallization. After this annealing treatment, the sample was air-cooled to room temperature. X-ray diffraction measurements were carried out using CuKα radiation to determine the crystalline phase of these thick films. IR spectra measurements by KBr-disc techniqe were carried out to identify the coprecipitates containing oxine.

Results and Disscution

Preparation of Oxide Powder by a Use of Oxine

The nominal composition of coprecipitate was $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$, which was estimated by chemical analysis of the filtrate, when the solution pH was 9.4. It was found that all metals in the solution were almost completly precipitated.

Figure 2 shows IR spectra of oxine and coprecipitated sample. Structural formulas of oxine and oxine complex of metals in Fig 3. The

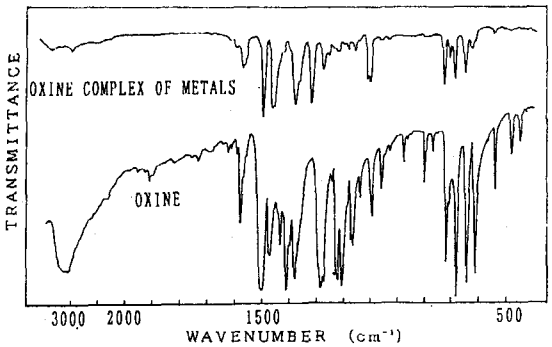

Fig. 2. IR spectra of oxine and coprecipitated sample

IR spectrum of the coprecipitated sample was quite similar to that of oxine. The clear difference was a absorption band at about 3000 cm^{-1}. The coprecipitated sample had no strong absorption band at about 3000 cm^{-1}. This band is assinged to OH stretching[7]. Disappear of OH stretching band can be explained by metal substitution of hydrogen ion of OH group in oxine. From the comparison of the two spectra, coprecipiteted sample was thought to be oxine complex of metals. The coprecipitated sample was converted into oxide powder by firing.

Preparation of superconducting Films

Superconducting films were formed by a rapid procedure[6] using of the oxide powder made by a use of oxine. The film thickness was estimated to be about 100 μm.

Figure 4 shows the X-ray diffraction pattern of the samples held at various temperatures (850, 855, 860, and 870°C) for crystallization. The time for crystallization was kept constant at 2 hours. In

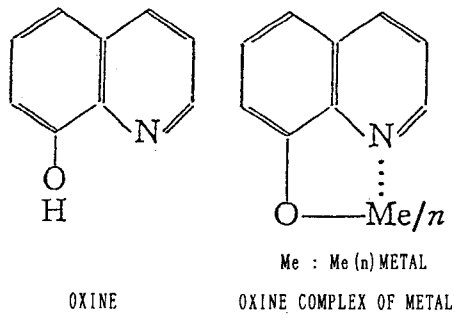

Fig. 3. Structural formulas of oxine and oxine complex of metals

Fig. 4, the peaks denoted by closed circles are at $2\theta = 28.9°$ and 31.7°.

These peaks were in fair agreement with those of superconducting phase with Tc ≈ 100 K[3]. The peaks denoted by open circles are at $2\theta = 23.0°$, 27.9° and 34.9°. These peaks almost coincide with those of superconducting phase with Tc ≈ 70 K[3]. The strong peak at $2\theta = 42.8$ are due to MgO substrate[8]. The films were considered to have two phases, which were the phase with Tc ≈ 100 K and the phase with Tc ≈ 70 K. When the temperature for crystallization was held at 870°C, the content of the phase with Tc ≈ 100 K was estimated to be 35 %. When the temperatures were 860°C and 855°C, the contents of the phase with Tc ≈ 100 K were 46 % and 30 % respectively. No phase with Tc ≈ 100 K was formed at 860°C. These contents were determined by measurement of the peak areas of the two phases. These results show that the best condition for crystallization temperature seem to be 860°C.

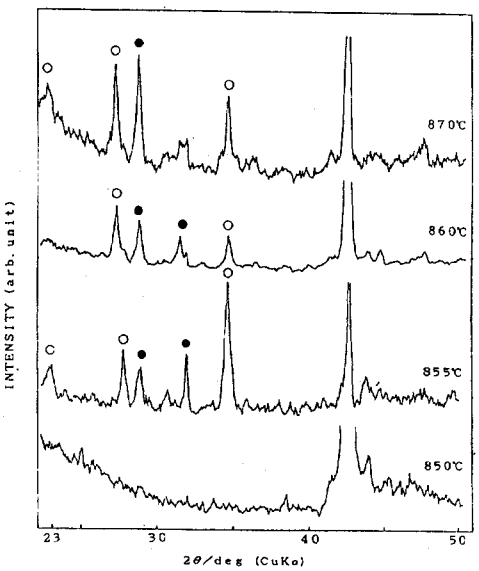

Fig. 4. X-ray diffraction pattern of the samples held at various temperatures (850, 855, 860, and 870°C) for crystallization. The time for crystallization was kept constant at 2 hours.

Figure 5 shows the X-ray diffraction pattern of the films given at various time (0.5, 1 and 2 hours) for crystallization. The constant temperature was 860°C. In Fig. 5 the peaks denoted by closed circles were considered to be characteristic of superconducting phase with Tc ≈ 100 K. The peaks denoted by open circles were characteristic of superconducting phase with Tc ≈ 70 K. The strong peak at $2\theta = 42.8°$ is due to MgO substrate[8]. The contents of the phase with Tc ≈ 100 K were estimated to be 58 %, 67 % and 46 %, when the times for crystallization were 0.5, 1 and 2 hours

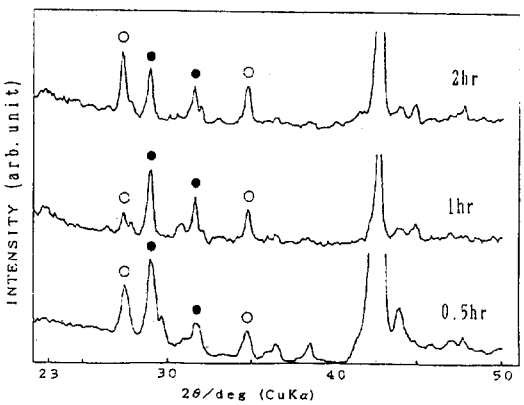

Fig. 5. X-ray diffraction pattern of the films given at various time (0.5, 1 and 2 hours) for crystallization. The constant temperature was 860°C.
superconducting phase with Tc ≈ 100 K (●)
superconducting phase with Tc ≈ 70 K (○)

respectively. At one hour of the time for crystallization, the content of the phase with Tc ≈ 100 K was the most abundant. Increase of the time for crystallization may not bring about increasing of the content of the phase with Tc ≈ 100 K.

Conclusion

The superconducting films were rapidly synthesised by the crystallization through melts in a very short time and by a use of the oxide powder. The oxide powder with nominal composition $Bi_{0.7}Pb_{0.3}SrCaCu_{1.8}O_x$ were synthesised by the coprecipitation method by a use of oxine. These films considered to have the superconducting phase with Tc ≈ 100 K, however these films was not single phase, in which a small amount of superconducting phase with Tc ≈ 70 K might coexist.

Acknowledgments

We thank professor Y.Higashimura and associate professor M.Suzaki in our college for permitting us the use of the X-ray diffraction meter. We are also gratefull to Miss. A. Nomachi for the assistance with the experiments.

References

1) J.G. Bednorz and K.A. Muller, Z. Phys. **B64** (1986) 189.
2) H. Maeda, Y. Tanaka, M. Fukutomi and T.Asano, Jpn. J. Appl. Phys. **27** (1988) L209
3) A. Oota, Y.Sasaki and A.Kirihigashi, Jpn.J.Appl.Phys. **27** (1988) L1445.
4) K. Kakegawa, T. Mohri, S. Shirasaki and K. Takahashi, J. Amer. Ceram. Soc. **67** (1984) C-2
5) K. Kakegawa, T. Wakabayashi and Y. Sasaki, ibid. **69** (1986) C-82.
6) Y. Akamatsu, M. Tatsumisago, N. Tohge, S. Tsuboi and T. Minami, Jpn. J. Appl. Phys. **27** (1988) L1696.
7) H. Horiguchi, "Sekigai kyuko-zusetsu-soran". Sankyo(1972) p112.
8) X-ray Data Card 4-829 (JCPDS).