

Growth and superconducting properties of $\text{Pb}_{1-y}\text{Bi}_y\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$ epitaxial films

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Abstract. $\text{Pb}_{1-y}\text{Bi}_y\text{Sr}_2\text{Y}_{1-x}\text{Ca}_x\text{Cu}_2\text{O}_{7+\delta}$ (PbBi1212) single-crystal thin films have been grown on SrTiO_3 (100) substrates by the ex-situ growth method in which an amorphous film is annealed at 970 °C in a closed ceramic container made of the same material as the film. It is found that PbBi1212 exhibits superconductivity when the Ca concentration x is greater than 0.3. It is also found that a quench into liquid nitrogen from 815 °C is required for the films to exhibit the superconductivity. The highest onset temperature of the superconducting transition attained in the present study is 65 K.

1. Introduction

It has been reported that PbBi1212 shows superconductivity at T_c higher than 90 K.[1, 2, 3, 4] PbBi1212 is of industrial importance because it mainly consists of low-cost elements such as Pb and Ca rather than Bi and Y, which are currently used for high- T_c superconducting wires. However, the superconductivity in PbBi1212 has been investigated only a little because no single-crystal sample has been obtained. As a matter of fact, since the previous reports on PbBi1212 is based on multi-phased bulk sample including Bi2212, some papers[6, 7] claim that PbBi1212 is even non-superconducting. Therefore, the central concern of this study is to grow single-crystal PbBi1212 epitaxial films and to verify its superconductivity and substitution effects. Thin film growth of cuprates including Pb and Bi is highly challenging because their vapor pressure is too high to keep the chemical composition of the film at the growth temperature ~ 700 °C. Although we had tried to grow PbBi1212 by a conventional in-situ sputtering technique, we had never obtained its single-phase films due to re-evaporation of Pb and Bi from the substrate.

In the present paper, we describe an ex-situ growth technique which allows to keep the chemical composition of the film. [8] In this technique, an amorphous film of PbBi1212 deposited by a low temperature sputtering method is annealed at a high temperature of 970 °C in a closed ceramic container made of the same material as the film. We have found that this technique leads to the epitaxial growth of single-phase PbBi1212 thin films. We have also found that the PbBi1212 system exhibits superconductivity with the maximum T_c^{onset} of 65 K with the composition of $x = 0.37$ and $y = 0.00$. The ex-situ growth technique may provide a method to fabricate new generation superconducting wires consisting of ubiquitous elements.



2. Methods

Crystal structures and the compositions of the prepared films were analyzed by using x-ray diffraction (XRD) and energy dispersive x-ray spectroscopy (EDS). Temperature dependence of the electrical resistivity was measured by a conventional DC four probe method. Temperature dependence of the Hall coefficient was measured by the AC four probe method with physical properties measurement system (PPMS), Quantum Design Co. Ltd. Hall coefficient was determined by the linear fitting to the transverse resistivity as a function of external magnetic field ($\parallel c$) between ± 5 T at various temperatures.

Ingredients of sputtering targets were synthesized by the solid state reaction method using high purity ($> 99.9\%$) powders of PbO, Bi₂O₃, SrCO₃, Y₂O₃, CaCO₃, and CuO. These powders were mixed into cationic compositions of (Pb_{0.75}Bi_{0.25})_{1.5}Sr₂Y_{1-x}Ca_xCu_{2.6}O_z ($x = 0.4 - 0.7$) and calcined twice, firstly at 860 °C for 10 h, and secondly at 880 °C for 10 h in air with pulverization in between. After the calcination, the powders were pressed into cylindrical pellets being 100 mm in diameter and 7 mm in height, and sintered at temperatures as a function of x as 1020 – 200 x °C for 24 h in air. The sputtering conditions used for depositing PbBi1212 amorphous films on the SrTiO₃ (STO) (100) substrates were as follows. The sputtering gas pressure was 100 mTorr (Ar 60 sccm O₂ 15 sccm), the anode voltage was 1.4 kV, and the substrate temperature was supposed to be around 200 °C because substrates were not heated in this case. A typical deposition time was set to 2 h which led to a film thickness of 3500 Å.

PbBi1212 polycrystalline containers utilized for the ex-situ growth were prepared in the same way as the sputtering targets at cationic compositions of Pb_{1-y}Bi_ySr₂Y_{0.3}Ca_{0.7}Cu₂O_z ($y = 0 - 0.5$). The mixed powders were calcined three times in this case at 880 °C for 10 h in air, pressed into two cylindrical pellets being 26 mm in diameter and 5 mm in height, and sintered at 1007 °C for 3 h in air. After the sintering we dug a pit in the center of one pellet about $8 \times 8 \times 2$ mm³ in size, where an amorphous film on a STO substrate was placed for the growth. The other pellet was used as a lid of the growth container. These pellets are polished to be flat with sandpaper and flushed with acetone. If the surface of these pellets is not sufficiently smooth, samples are not heated equally during the growth. In the ex-situ growth, the container with the film was put on the zirconia substrate ($30 \times 30 \times 3$ mm³) and heated in a muffle furnace at 970 °C for 6 h under O₂ atmosphere and cooled down to room temperature at a rate of 200 °C/h. The EDS analyses on films before and after the growth reveal that the grown film concentrations depend strongly on the compositions of both the sputtering target and the growth container. Pb and Bi concentrations of the films drastically change during the growth and depend strongly on the compositions of the growth container. The concentrations of the other elements of the films depend strongly on those of the sputtering target.

3. Results and discussion

Figure 1 shows the out-of-plane θ - 2θ scan XRD results for the single-phase PbBi1212 thin film. Only the c -axis oriented (00 n) peaks of PbBi1212 are seen. It was found that both the Ca concentration $x < 0.36$ and the Bi concentration $y < 0.20$ are required to obtain single-phase PbBi1212 films. For a single-phase PbBi1212 thin film, the peaks from other phases were completely absent or less than 0.5% of the PbBi1212 (005) peak magnitude. Impurity phases such as Bi2212 were found in samples whose concentration of Ca or Bi exceeds these limits. In order to prevent the growth of the impurity phase, the Ca concentration of the sputtering target has to be less than 0.5 and the Bi concentration of the growth container has to be less than 0.25.

Figure 2 shows SEM images for the single-phase PbBi1212 film. It is evident that the surface morphologies of the films are very smooth except for some steps. None of cracks, grain boundaries, and impurity phase precipitations were observed on the entire surface of the film.

Figure 3 (a) shows the result of the in-plane $2\theta_{\chi}$ - ϕ scan for the single-phase PbBi1212 film. The peaks of STO (200) and PbBi1212 (200) are identified. This implies that the lattice

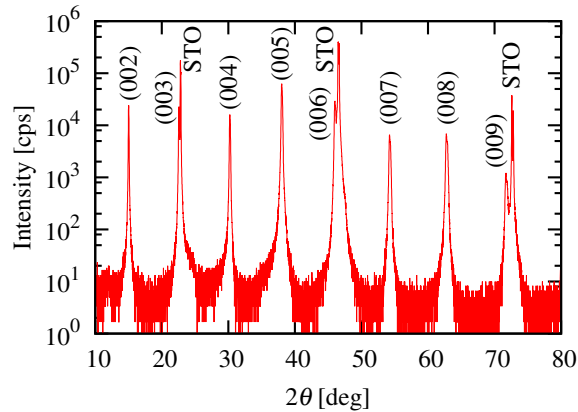


Figure 1. Out-of-plane XRD θ - 2θ scans of the single-phase PbBi1212 sample.

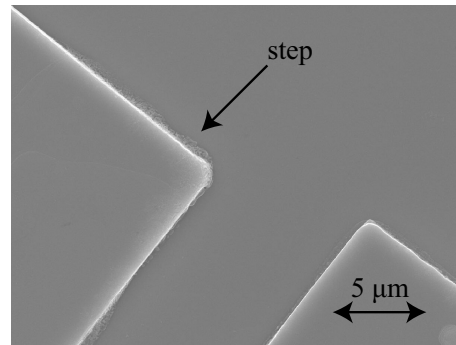


Figure 2. SEM images for the single-phase PbBi1212 epitaxial film.

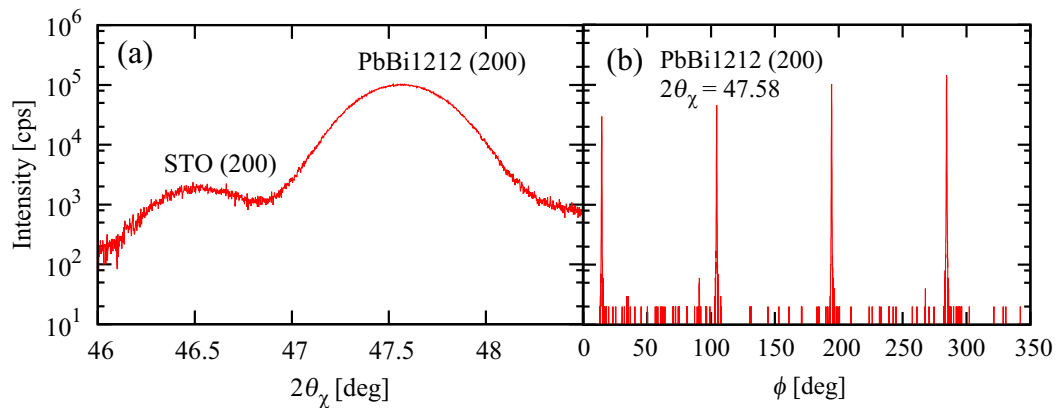


Figure 3. (a) In-plane XRD $2\theta_\chi$ - ϕ scan pattern around the (200) peaks of PbBi1212 and STO, and (b) ϕ scan pattern at PbBi1212 (200) ($2\theta_\chi = 47.58^\circ$).

relaxation occurs from the 2% in-plane lattice mismatch between STO and PbBi1212. Figure 3 (b) shows the in-plane ϕ scan result at PbBi1212 (200) ($2\theta_\chi = 47.58^\circ$). Four peaks appearing at every 90° suggest that PbBi1212 has a fourfold in-plane rotational symmetry and tetragonal crystal structure. The difference in peak angle between STO and PbBi1212 was at most 0.7° . This indicates that the PbBi1212 thin films were epitaxially grown on STO (100) substrates.

The resistivity measurements show that as-grown PbBi1212 epitaxial films exhibit semiconductor-like temperature dependence and no trace of superconductivity. However, the films change to show superconductivity after the quenching treatment. In this treatment, the sample is put into the quartz tube, and annealed at 815°C in air in a muffle furnace. After 1 h annealing, the quartz tube is taken out from the furnace and quenched into liquid nitrogen within 2 seconds. Figures 4 (a) and (b) show temperature dependence of the resistivity $\rho(T)$ and the Hall coefficients $R_H(T)$ for samples with different Ca concentrations. It is suggested that substitution of a Ca^{2+} for a Y^{3+} has an effect to dope a hole. Figure 5 represents the distribution of the Ca and Bi concentrations of the superconducting (non-superconducting) single-phase PbBi1212 films. It was found that the Ca concentration $x > 0.3$ is essential, and lower Bi concentration is preferable for emergence of the superconductivity in PbBi1212.

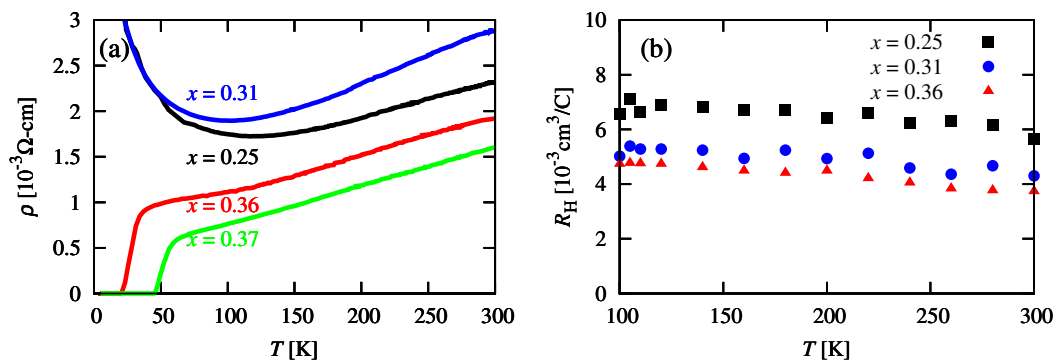


Figure 4. (a) $\rho(T)$ and (b) $R_H(T)$ in the samples with different Ca concentrations x . The black line and squares show data in $x = 0.25$, $y = 0.15$. The blue line and circles show data in $x = 0.31$, $y = 0.13$. The red line and triangles show data in $x = 0.36$, $y = 0.17$. The green line represents data in sample showing the highest T_c^{onset} of 65 K and $T_c^{\rho=0}$ of 48 K with the composition of $x = 0.37$, $y = 0.00$.

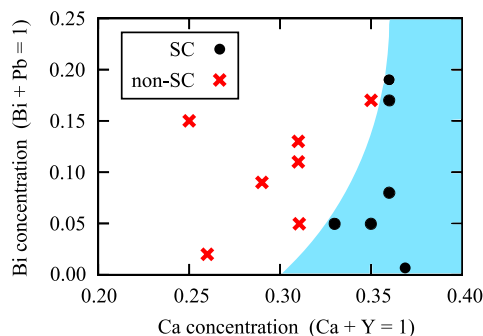


Figure 5. Distribution of Ca and Bi concentrations of the single-phase samples and their superconductivity. The black circles show the superconducting (SC) samples and the red crosses show the non-superconducting (non-SC) samples. The shaded area shows the concentrations where the superconducting films considered to be obtained.

4. Summary

In summary, we confirmed the superconductivity in PbBi₁₂12 by measuring transport properties of epitaxial films prepared by the ex-situ growth method. The single-phase PbBi₁₂12 films were obtained with a Ca concentration of less than 0.36 and Bi concentration of less than 0.20. Ca concentration of greater than 0.3 and the quench treatment are essential to make the epitaxial film superconducting. The increase in Ca and the decrease in Bi concentration lead to the increase in the hole density. The highest T_c^{onset} attained in the present study is 65 K.

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References

- [1] Bauer A, Zoller P, Glaser J, Ehmann A, Wischert W and Kemmler S 1996 *Physica C* **256** 177
- [2] Frank H, Stollmann R, Lethen J, Müller R, Gasparov L V, Zakharov N D, Hesse D and Güntherodt G 1996 *Physica C* **268** 100
- [3] Zoller P, Ehmann A, Glaser J, Wischert W and Kemmler-Sack S 1998 *Physica C* **306** 119
- [4] Schneider D, Köbel S and Gauckler L J 2000 *Supercond. Sci. Technol.* **13** 1476
- [5] Hughes R A, Lu Y, Timusk T and Prestön J S 1991 *Appl. Phys. Lett.* **59** 2597
- [6] Kaesche S, Majewski P and Aldinger F 1999 *J. Am. Ceram. Soc.* **82** 197
- [7] Wang J, Takano S, Wakata M, Usami R, Hamada K, Fukuoka A and Yamauchi H 1994 *Physica C* **219** 33
- [8] Yan S L, Cao H L, Yang X M and Zhou X D 1991 *J. Appl. Phys.* **70** 526