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PREPARATION AND SUPERCONDUCTING PROPERTIES OF THICK FILMS IN THE Bi-Sr-Ca-Cu-O SYSTEM WITH ADDITION OF Pb

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Abstract Thick films in the Bi-Pb-Sr-Ca-Cu-O system have been synthesized using a fine particle size powder milled with 2mmφ zirconia balls. Films prepared on the single crystal (100) MgO substrates show strongly textured orientation with c-axis of the predominant low Tc $Bi_2Sr_2CaCu_2O_x$ phase normal to the film plane. Partial substitution of Pb for Bi in the Bi-Sr-Ca-Cu-O system has been found to increase the volum fraction of the high Tc phase which is responsible for the superconductivity of Tc~110K. $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ film sintered at 835°C for 20h in a P_{O_2} of 1/11atm showed Tc(R=0)=107.1K, and Jc(77K, zero magnetic field)=33A/cm^2.

INTRODUCTION

Recently, cuprate superconductors have been prepared[1,2] which contain Bi but no rare earths or yttrium. Maeda et al[3] report that the composition $BiSrCaCu_2O_x$ (abbreviated to 1112) has a resistance Tc of about 105K and that the oxide must contain both Sr and Ca if it should have a high Tc. Furthermore, it has been clarified that there are two kinds of superconducting phases with transition temperatures of 105K (a high Tc phase) and 80K (a low Tc phase)[4]. Their former phase has a longer c-axis than the latter phase.

As mentioned in many reports, it is difficult to prepare the high Tc phase as a single phase. However, Takano et al[5] have found that Pb-substitution in Bi-Sr-Ca-Cu-O superconductors results in the stabilization of the high Tc phase.

In this report, we will describe the structural and superconducting properties of oxide thick films in the Bi-Sr-Ca-Cu-O system. It is also reported that extremely good

results are obtained by partially substituting Pb for Bi in reduced oxygen atmosphere.

EXPERIMENTAL

Thick films were fabricated by the following procedure shown in the flow chart of Figure 1. High purity bismuth, lead and copper oxides and strontium and calcium carbonates were used as starting materials. Powder mixtures with metal atom ratio Bi:Pb:Sr:Ca:Cu=1.95:0.6:2:2.2:3.5 were milled with 2mmϕ zirconia balls for 120 hours in ethyl-alcohol. These powders were then dried and calcined at 800°C for 6 hours. Calcining was repeated 2 times and reground with 2mmϕ zirconia balls for 120 hours in ethyl-alcohol. This mixture (slurry) was pasted with the solvent of $CH_3(CH_2)_6OH$. The pastes were coated on the single crystal (100) MgO substrates. They were fired at 835°C-855°C for 10-100 hours in the capped alumina crucible to avoid vaporization of Pb. Preparing conditions of the samples are summarized in Table 1. Judging from cross sectional SEM view, the values of thickness in these films were 40-60μm.

The reaction process and the products were examined by X-ray diffraction analysis using CuKα radiation. Chemical compositions, except for oxygen, in the films were analyzed by ICPS (inductively coupled plasma emission spectrometry). Critical current density (Jc) and electrical resistivity measurement were performed for all the films using the standard four-probe method. Jc measurements were done at 77K and zero field with a voltage criterion of 1.0μV/cm. For resistivity measurement, the current density used was 1.0A/cm^2.

RESULTS AND DISCUSSION

Figures 2 and 3 show the X-ray diffraction patterns of samples (a), (b), (c) and sample (d), respectively. The peaks denoted by ● are corresponding to low Tc phase, and indexed peaks are corresponding to high Tc phase. It exhibits the existence of the high-Tc phase and the low-

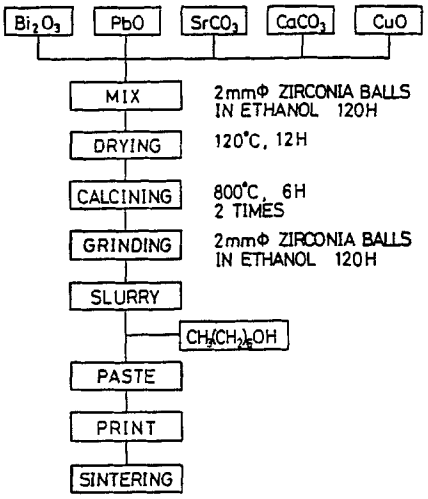

FIGURE 1
Flowchart for preparation of Bi-Pb-Sr-Ca-Cu-O thick films.

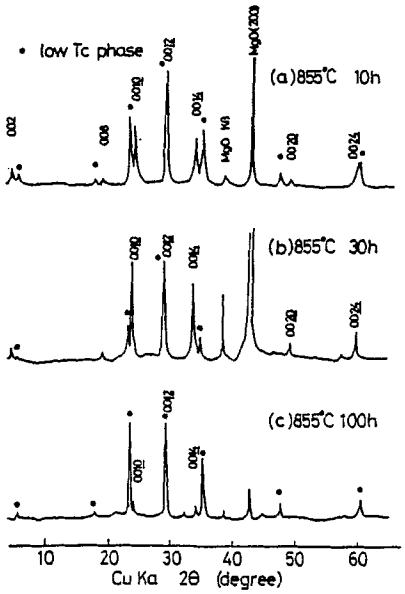

FIGURE 2
X-ray diffraction patterns of the surface of $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ films fired at 855°C for (a)10h, (b)30h and (c)100h.

Table 1 Preparing conditions of the samples

Sample	nominal composition	firing temperature	firing times	firing atmosphere
a	$Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$	855°C	10h	air
b		855°C	30h	air
c		855°C	100h	air
d		835°C	20h	O_2:Ar = 1:10

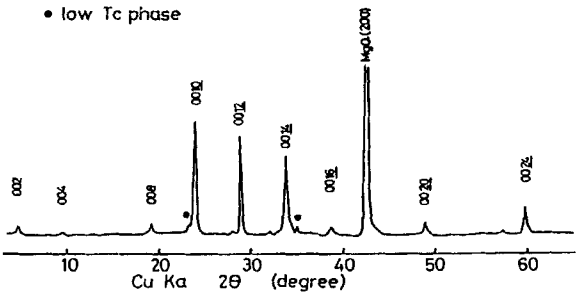

FIGURE 3 X-ray diffraction pattern of the surface of $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ film fired at 835°C for 20h in 1/11 atm O_2.

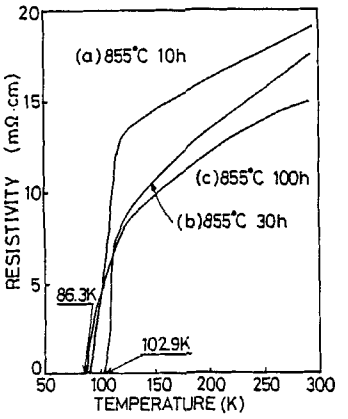

FIGURE 4 Resistivity versus temperature of $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ films fired at 855°C for (a)10h, (b)30h and (c)100h.

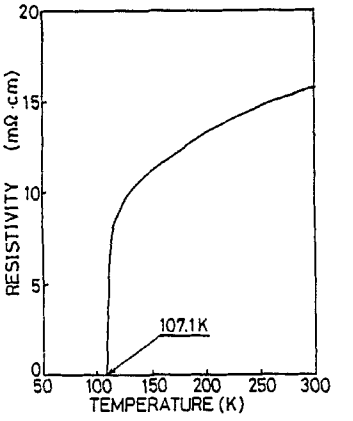

FIGURE 5 Resistivity versus temperature of $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ film fired at 835°C for 20h in 1/11 atm O_2.

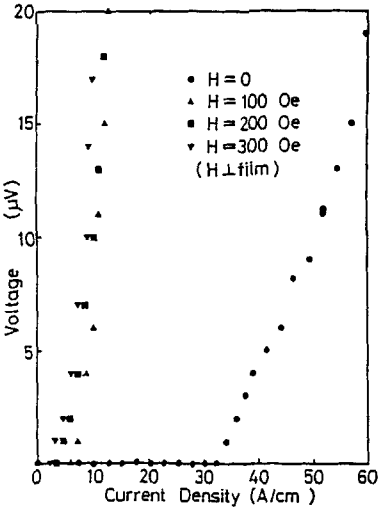

Table 2 Compositions analyzed by ICP

Sample	Compositions				
	Bi	Pb	Sr	Ca	Cu
nominal	1.95	0.60	2	2.2	3.5
PASTE	1.95	0.59	2.12	2.51	3.57
(a)855°C 10h	1.95	0.42	2.03	2.48	3.55
(b)855°C 30h	1.95	0.14	1.93	2.20	3.19
(c)855°C100h	1.95	0.03	2.00	2.31	3.36
(d)835°C 20h 1/11O_2	1.95	0.21	2.02	2.39	3.45

FIGURE 6 Current-voltage characteristic curves at 77K for $Bi_{1.95}Pb_{0.6}Sr_2Ca_{2.2}Cu_{3.5}O_z$ film fired at 835°C for 20h in 1/11 atm O_2.

Tc phase in these patterns as seen from the (002) peak at $2\theta=4.7$ for the high Tc phase and $2\theta=5.7°$ for the low-Tc phase, respectively. It is found in Fig.3 that the sample sintered at 835°C for 20h in 1/11atmO_2 shows almost single phase of high-Tc phase.

Figures 4 and 5 show resistivity versus temperature of various kinds of sample and sample (d), respectively. It is found in samples (a), (b) and (c) that the resistivities are slightly decreasing around 115K and has tailed curves. The lower zero resistance may be due to the existence of the low Tc phase. Sample (d) shows a sharp resistive transition at Tc=107.1 K.

The current-voltage characteristic curves at 77K in the zero field and H=300 Oe for sample (d) are shown in Figure 6. The value of Jc (77K) in the zero field has been estimated to be $33A/cm^2$. This film has anisotropic Jc value for field direction. The results of ICP analyses for paste and film compositions are shown in Table 2. These values are normalized by 2 of Sr. The remarkable decrease of Pb is noticed in this table. This may be due to evaporation of Pb during sintering.

CONCLUSION

1. It was difficult to prepare thick films with the high Tc phase as a single phase. There are structure and electrical evidence indicating the high Tc phase is stabilized by the presence of Pb in the reduced oxygen atmosphere.
2. The X-ray diffraction of the thick films showed that these films had the c-axis orientation.

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REFERENCES

1. C.Michel,M.Hervieu,M.M.Borel,A.Grandin,F.Deslandes, J.Provost and B.Raveau, Z.Physik, B68, 421 (1987).
2. J.Akimitsu,A.Yamazaki,H.Sawa and H.Fujiki,Jpn.J.Appl. Phys., 26, L208 (1987).
3. H.Maeda,Y.Tanaka,M.Fukutomi and T.Asano, Jpn.J.Appl. Phys., 27, L209 (1988).
4. M.A.Subramanian,C.C.Torardi,J.C.Calabrese,J.Gopolakrishnan,K.J.Morrissey,T.R.Askew,R.B.Flippen, U.Chowdahri and A.W.Sleight, Science, 239, 1015 (1988).
5. M.Takano,J.Takada,K.Oda,H.Kitaguchi,Y.Miura,Y.Ikeda Y.Tomii and H.Mazaki, Jpn.J.Appl.Phys., 27, L1041 (1988).