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PREPARATION OF THE HIGH-Tc PHASE IN THE Bi-Pb-Sr-Ca-Cu-O SYSTEM

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Abstract The high-Tc phase in the Bi-Pb-Sr-Ca-Cu-O system has been prepared by the conventional ceramic method with the usage of co-precipitated oxalates with the nominal composition of $Bi_{0.726}Pb_{0.374}Sr_{1.0}Ca_{1.0}Cu_{1.65}O_x$ as starting materials. The formation process of the high-Tc phase and the optimized condition of the heat treatment have been studied. The electric resistivity of the sample heat treated at 848°C for 120h dropped to zero at 110K within the experimental limit of 10^{-6}ohm.

INTRODUCTION

Since the high-Tc superconductors in the Bi-Sr-Ca-Cu-O system was found by Maeda et al.[1], much effort has been made to prepare the single phase and thereby clarify various properties of the high-Tc phase. It has been widely recognized that a partial substitution of lead for bismuth drastically increases the volume fraction of the high-Tc phase. In our earliest paper[2], we reported two optimum starting compositions of Bi:Pb:Sr:Ca:Cu=0.7:0.3:1.0:1.0:1.8 and 0.96:0.24:1.0:1.0:1.6 which were found after many trials. Moreover, it has become clear that the high-Tc phases with Pb/Bi=0 and Pb/Bi=1/5 have different modulation modes as evidenced by means of transmission electron microscopy[3,4]. This paper reports our further study on the lead-rich samples with a nominal composition of Bi:Pb:Sr:Ca:Cu=0.726:0.374:1.0:1.0:1.65.

EXPERIMENTAL

Co-precipitated oxalates containing the relevant cations at the ratios of (a)Bi:Pb:Sr:Ca:Cu=0.96:0.24:1.0:1.1:1.6 and (b)0.726:0.374:1.0:1.0:1.65 were used as the starting materials. After the drying and the thermal decomposition, the samples were ground and mixed adequately, then calcined at 800°C for 12h in air. The products again ground and mixed were pressed into disks (20mm in diameter and 1mm in thickness) at 150MPa and the pellets were heat treated at 848°C for various periods in air. The samples thus obtained were examined using XRD (Cu-Ka). The DTA experiments were also carried out at a heating rate of 10°C/min. The electric resistivity was measured by means of the dc four probe method.

RESULTS AND DISCUSSION

Figure 1(a) and (b) show the XRD patterns of the samples with the nominal compositions (a) and (b), respectively, calcined at 800°C for 12h. Both samples consist of at least four crystal phases such as the low-Tc phase ($Bi_2Sr_2Ca_1Cu_2O_x$), Ca_2PbO_4, Ca_2CuO_3, and CuO. It is notable that

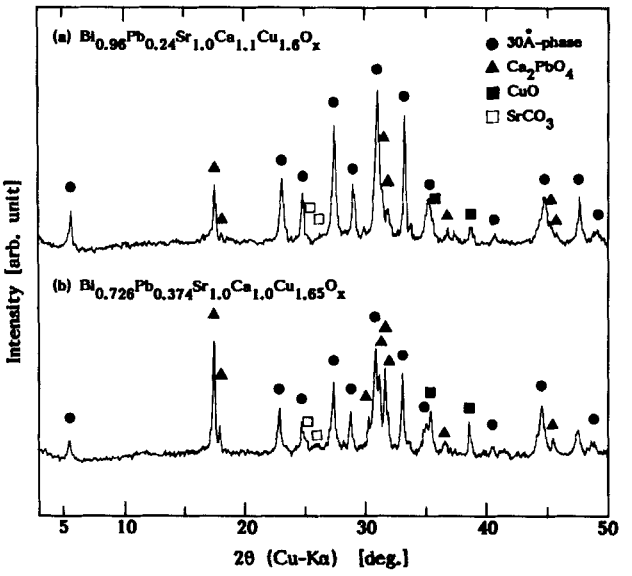

FIGURE 1 XRD patterns of the samples with the nominal compositions (a)Bi:Pb:Sr:Ca:Cu=0.96:0.24:1.0:1.1:1.6 and (b)Bi:Pb:Sr:Ca:Cu=0.726:0.374:1.0:1.0:1.65 calcined at 800°C for 12h in air.

the larger amount of Ca_2PbO_4 forms in the sample (b) than in the sample (a).

Figure 2 indicates the DTA curves of the samples as shown in figure 1. Each curve has two endothermic peaks. The one is observed at 855°C and 850°C for samples with compositions of (a) and (b), respectively. These peaks are due to the partial melting that plays an important role in the formation of the high-Tc phase. The other observed at 875°C and 870°C for samples (a) and (b), respectively, is ascribed to the decomposition of the low-Tc phase. The decrease in temperature of each peak is assumed to be derived from the increase in lead content in the samples.

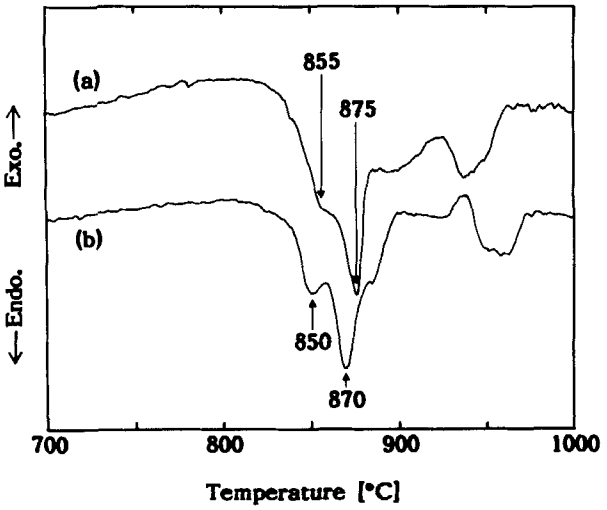

FIGURE 2 DTA curves for the samples as shown in Figure 1 with the nominal compositions (a) and (b) calcined at 800°C for 12h in air.

Figure 3 shows the XRD patterns of the sample with the lead-rich composition (b) heat treated for various periods at 848°C. Figure 3(0), (1), (2), and (3) corresponds to the duration of 0h(as calcined at 800°C for 12h), 32h, 56h, and 120h, respectively. At the duration of 32h, $SrCO_3$ and CuO disappear, while the high-Tc phase and $(Ca,Sr)_{14}Cu_{24}O_{41}$ [5] form. The amount of the high-Tc phase increases with the extension of the duration in contrast to the decrease of Ca_2PbO_4 and the low-Tc phase. At the duration of 120h, the sample contains more than 50% in amount of the high-Tc phase while the extra phases such as the low-Tc phase and Ca_2PbO_4 still remain.

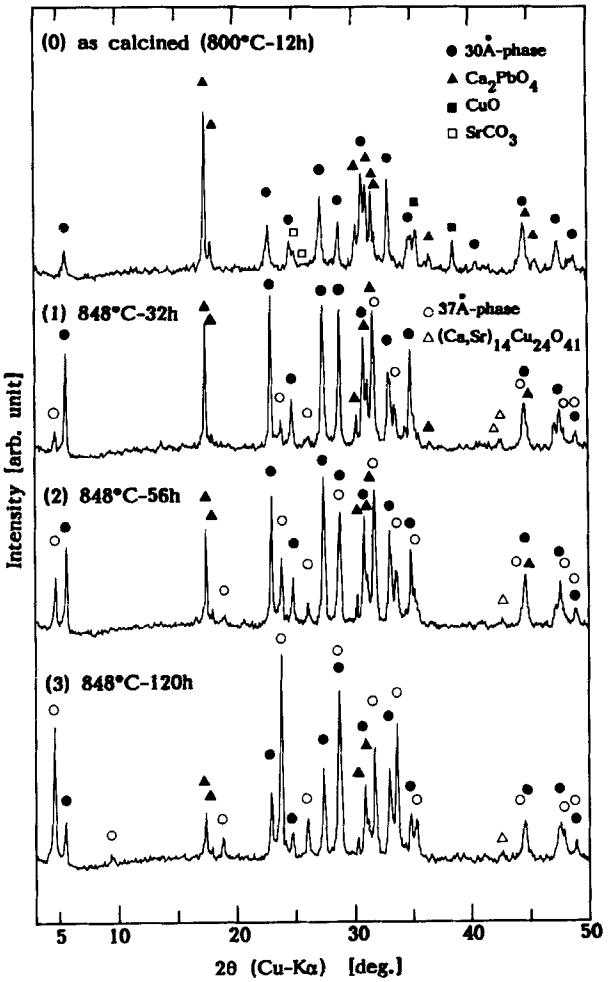

FIGURE 3 XRD patterns of the lead-rich sample with the composition (b) heat treated at 848°C for (0)0h(as calcined), (1)32h, (2)56h, and (3)120h.

The temperature dependences of the electric resistivity normalized at 300K for the lead-rich samples with the nominal composition of (b)$Bi_{0.726}Pb_{0.374}Sr_{1.0}Ca_{1.0}Cu_{1.65}O_x$ heat treated at 848°C for (1)32h, (2)56h, and (3)120h are shown in Figure 4. The resistivities decrease almost linearly with decreasing temperature in the range between 300K and 125K. The resistivity for (1) begins to deviate from the normal conducting behavior at 120K, drops between 120K and 110K, and below 110K decreases gradually to zero at 87K within the experimental limit of 10^{-6}ohm. For the samples (2) and (3), the resistivity steeply drop to zero at 108K and

110K, respectively. It is remarkable that the sample (3) shows a sharp superconducting transition and have a high Tc(zero) despite the existence of a fairly large amount of the extra phases. In our studies on the samples with the lead-poor composition (a), such a sharp transition as described above can not be attained under the existence of such a large amount of the extra phases.

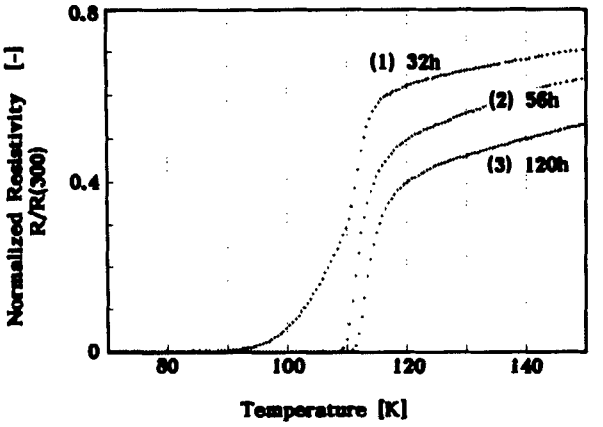

Figure 4 The normalized resistivity for the lead-rich sample (b) heat treated at 848°C for (1)32h, (2)56h, and (3)120h.

SUMMARY AND REMARK

The lead-rich sample with the nominal composition of Bi:Pb:Sr:Ca:Cu=0.726:0.374:1.0:1.0:1.65 heat treated at 848°C for 120h showed a sharp superconducting transition and had a high Tc(zero) despite the existence of a fairly large amount of the extra phases. For the lead-rich samples, more detailed studies on the microstructure and the behavior of the electric resistivity are in progress, and will be reported elsewhere.

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