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Preparation and Characterization of the 110 K Phase in the (Bi,Pb)–Ca–Sr–Cu–O Superconducting System

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Nearly monophasic 110 K ($n = 3$ phase) superconductor in the Bi–Pb–Ca–Sr–Cu–O system has been prepared starting from compositions of $Bi_{0.7}Pb_{0.3}CaSrCu_2O_x$, $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$, and $Bi_{1.84}Pb_{0.34}Ca_{2.03}Sr_{1.91}Cu_{3.06}O_x$. Attempts have been made to prepare the $Bi_{1.5}Pb_{0.5}Ca_{2.6}Sr_{2.4}Cu_{4.09}O_x$ ($n = 4$ phase) and the $n = 3$ phase by hot pressing and the results will be discussed.

Recently, tremendous effort has been put forth to prepare a single-phase 110 K ($n = 3$) superconductor in the $Bi_2(Ca,Sr)_{n+1}Cu_nO_{2n+4+\partial}$ system (*1, 2*). Successful attempts have been made to increase the volume fraction of the 110 K phase by partially substituting Pb (*3–5*) for Bi. It has been proposed that substitution of Pb reduces the distortion of the fragile bismuth layer in these superconducting oxides accompanied by a shortening of the unit cell parameters. We have investigated this system in view of the fact that most of the results reported so far are on multiphasic oxides and have been investigated by resistivity measurements rather than by susceptibility data. We have used two starting compositions for preparing this phase: $Bi_{0.7}Pb_{0.3}CaSrCu_2O_x$ and $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$. We have also prepared the composition $Bi_{1.84}Pb_{0.34}Ca_{2.03}Sr_{1.91}Cu_{3.06}O_x$ after Koyama *et al.* (*6*). In this letter we also report our attempts to prepare $Bi_{1.84}Pb_{0.34}Ca_{2.6}Sr_{2.4}Cu_{4.09}O_x$ ($n = 4$) (*7*) and $Bi_{1.84}Pb_{0.34}Ca_{2.03}Sr_{1.91}Cu_{3.09}O_x$ by hot pressing.

All the compositions of the Bi–Pb–Ca–Sr–Cu–O system were prepared by the usual solid-state ceramic method. Stoichiometric amounts of Bi_2O_3, PbO, CaO, SrO, and CuO were mixed, ground thoroughly, and heated at 1115 K for 2–15 days. Repeated grinding and pelletizing were carried out to ensure the completion of the reaction and the formation of monophasic compounds. All the samples were air quenched after sintering at 1115 K. X-ray diffraction patterns were taken on a Seifert–Scintag PAD-II diffractometer using Cu$K\alpha$ radiation. Superconducting properties of these samples were detected in nearly zero magnetic field (50 μT) by using magnetic induction technique. Four-probe resistivity measurements were also carried out to characterize the superconducting properties of these samples.

The starting compositions of both $Bi_{0.7}$

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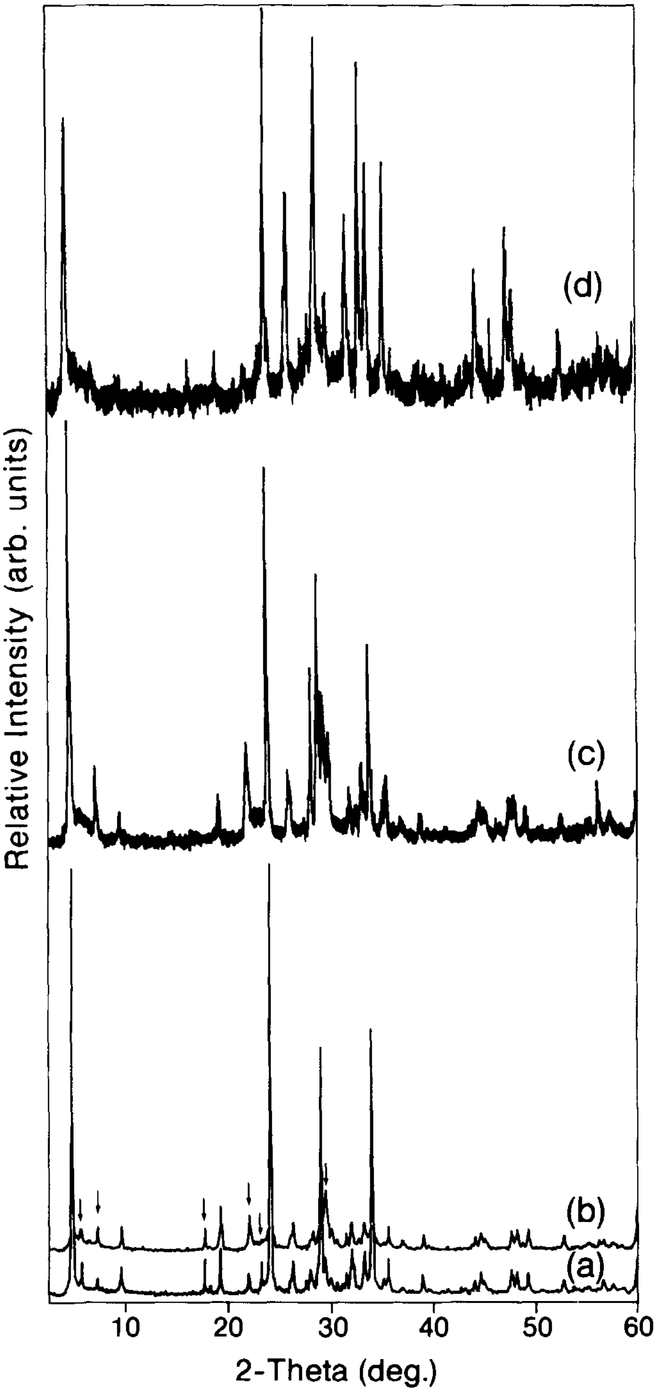

FIG. 1. X-ray diffraction patterns of (a) $Bi_{0.7}Pb_{0.3}CaSrCu_2O_x$, (b) $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$, (c) $Bi_{1.84}Pb_{0.34}Ca_{2.03}Sr_{1.91}Cu_{3.06}O_x$ (hot pressed), and (d) $Bi_{1.5}Pb_{0.5}Ca_{2.6}Sr_{2.4}Cu_{4.09}O_x$. (Arrows indicate reflections due to low-T_c phases).

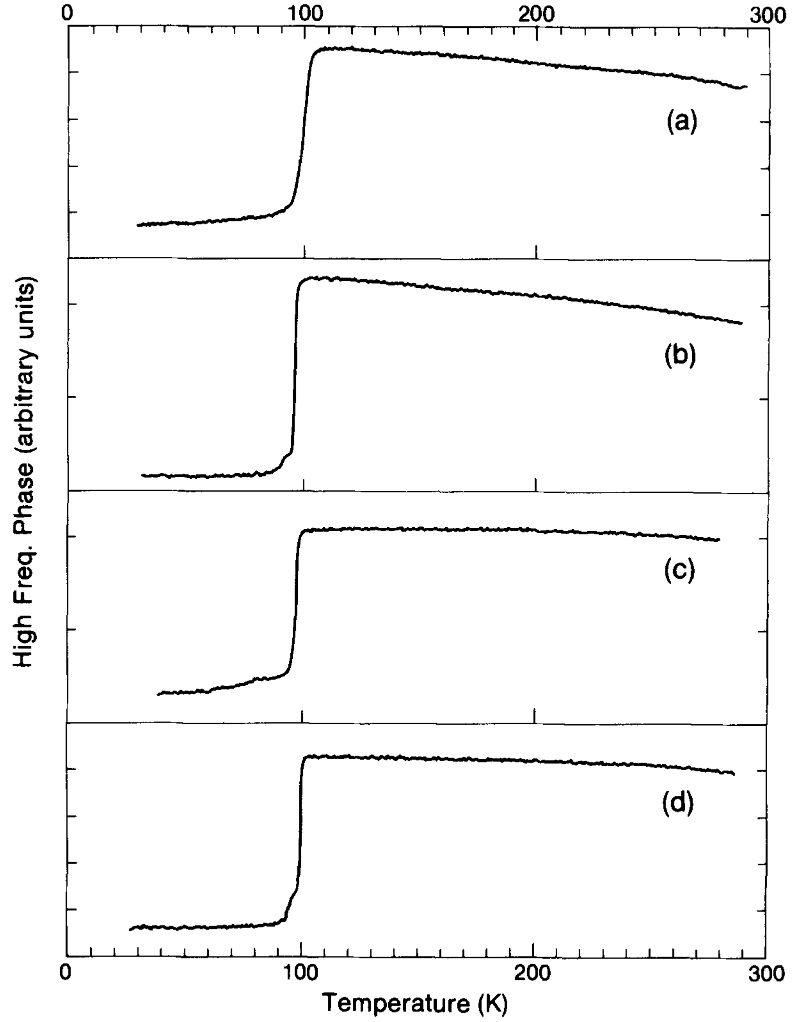

FIG. 2. High-frequency impedance vs temperature plots of (a) $Bi_{0.7}Pb_{0.3}CaSrCu_2O_x$, (b) $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$, (c) $Bi_{1.84}Pb_{0.34}Ca_{2.03}Sr_{1.91}Cu_{3.06}O_x$ after 15 days of annealing, and (d) $Bi_{1.5}Pb_{0.5}Ca_{2.6}Sr_{2.4}Cu_{4.09}O_x$ after 10 days of heating.

$Pb_{0.3}CaSrCu_2O_x$ and $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$ showed a majority of the 80 K ($n = 2$) phase after 2 days of heating at 842°C. The peak corresponding to the d value of ~18.3 Å was a minority phase (20%). However, these samples were heated further and their superconducting properties and formation of the $n = 3$ phase were studied as a function of the duration of annealing at 842°C. The peak corresponding to ~18.3 Å ($n = 3$ phase) was found to grow in intensity with increased annealing. After 15 days of heating we had obtained a nearly monophasic oxide with unit cell parameters of a and b = 5.41 Å and c = 36.98 Å (Fig. 1). However, reflections due to $n = 2$ (30 Å) and $n = 1$ (24 Å) phases were also seen as impurities (~10%). Most of the researchers have characterized the superconductivity behavior by resistivity measurement, where high T_c (>100 K) can be readily observed due to connectivity, even though the $n = 3$ phase is not a major phase. Resistivity measurements of our samples also showed a T_c of

~105 K. In Fig. 2 we show the impedance measurements on these samples as a function of temperature showing a T_c of 103 and 101 K. The steps observed at lower temperatures in the impedance curve of the samples annealed for 2–3 days, due to $n = 1$ and $n = 2$ phases, were found to diminish with the increasing annealing period. It can be noted that these nearly monophasic superconducting oxides were made by us starting from stoichiometric compositions of 1112 and 2223, rather than from nonstoichiometric compositions such as $Bi_{0.7}Pb_{0.3}CaSrCu_{1.4}O_x$, $Bi_{0.7}Pb_{0.3}CaSrCu_{1.8}O_x$, and $Bi_{1.84}Pb_{0.34}Ca_{2.04}Sr_{1.91}Cu_{3.09}O_x$ (*3, 5, 6*) and the deficiency in copper sites or the excess of cations in the latter compositions has not been accounted for. We believe that long annealing periods are essential for these samples so that the CuO, PbO, Bi_2O_3 and (Ca,Sr)O layers can rearrange themselves to give long periodicity in the *c*-direction. We believe from our data that nearly monophasic 110 K phase ($n = 3$) can be obtained starting from the stoichiometric composition of $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$. However, other phases do form due to the similarity in the interfaces of these materials; this can be minimized by long annealing, thus giving enough time for the various layers to rearrange and to give long periodicity and high transition temperatures.

We also prepared a composition $Bi_{1.84}Pb_{0.34}Ca_{2.04}Sr_{1.96}Cu_{3.06}O_x$ after Koyama *et al.* (*6*). However, we could not obtain a monophasic oxide starting from this composition. We prepared this oxide by hot-pressing the initially fired material at 500°C for 4 hr at 4.5 tons of pressure. The X-ray diffraction pattern of this sample after 3 days of heating is shown in Fig. 1c. This shows a transition temperature of 100 K and a small tail at lower temperatures (95 K). We also attempted to prepare $Bi_{1.84}Pb_{0.34}Ca_{2.6}Sr_{2.4}Cu_{4.09}O_x$ ($n = 4$ phase). This resulted in a majority of the $n = 3$ phase and diffraction lines due to $n = 4$ phase were not observed. Almost 75% of the $n = 3$ phase formed with a heating time of only 2 days. The X-ray diffraction pattern and the impedance measurement on this oxide after 10 days of heating are shown in Figs. 1d and 2d. This impedance curve shows a T_c of 102 K and a little tail at 97 K. The presence of excess CuO in this oxide is likely to increase the formation of the $n = 3$ phase. The lower transition temperature of ~100 K, rather than 107 K as reported, and the small tail observed at lower temperatures can probably be due to oxygen vacancies rather than to the $n = 2$ phase, as the tail vanishes at ~94 K rather than at 80 K. Electron microscopic investigation of these oxides is underway.

Note added in proof. The phasic purity of the 110 K ($n = 3$) phase can be improved further by continued annealing (21 days) of the $Bi_{1.5}Pb_{0.5}Ca_2Sr_2Cu_3O_x$ composition.

Acknowledgment

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