Superconductivity above 100 K in the Bi-2212 phase of (Bi,Pb)$_2$Sr$_2$CaCu$_2$O$_8$

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Abstract. Polycrystalline samples of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ (0.32 $\leq$ x(Pb) $\leq$ 0.42) have been prepared by the conventional solid-state reaction method. It has been found that the maximum value of $T_c$, defined as the onset temperature of the shielding effect in the magnetic susceptibility measurements, is 102 K for x(Pb)=0.36. The present compound is the first superconductor with $T_c$ above 100 K in the Bi-2212 phase.

1. Introduction

Among many superconducting materials, the Bi-based cuprate superconductor is one of the promising candidates for practical application of superconductivity at the liquid nitrogen temperature 77 K because of its relatively high value of the superconducting transition temperature $T_c$. The Bi-2223 phase of Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+\delta}$, which is a member ($n=3$) of the homologous series of the Bi-based cuprate superconductors Bi$_2$Sr$_2$Ca$_{n-1}$Cu$_n$O$_{2n+4+\delta}$, has the highest $T_c$ = 110 K among the Bi-based cuprate superconductors. However, it is known as a material whose sample of the single phase is extremely hard to be synthesized. On the other hand, the synthesis of the Bi-2212 phase of Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ with $n=2$ is relatively easy. However, the value of $T_c$ of the Bi-2212 phase prepared in air is ~ 80 K, which is too low for the practical application at 77 K. Therefore, a further increase in $T_c$ is desired.

$T_c$ is well known to be sensitive to the hole concentration per Cu in the CuO$_2$ plane $p$. With the doping of hole carriers, superconductivity appears at $p$ ~ 0.05. With increasing $p$, $T_c$ increases in the underdoped region, takes the maximum at $p$ ~ 0.16 and then decreases in the overdoped region. The Bi-2212 phase prepared in air is situated in the overdoped region, because excess oxygen atoms are easily introduced in the BiO plane. Therefore, its $T_c$ increases up to about 95 K by the decrease in the hole concentration through the reduction annealing or the substitution of Y$^{3+}$ for Ca$^{2+}$ [1, 2]. In addition, the highest $T_c$ of 98.5 K is observed in Pb-substituted Bi$_{1.8}$Pb$_{0.2}$Sr$_2$CaCu$_2$O$_8$ annealed in flowing gas of N$_2$ [3]. This increase in $T_c$ is because excess oxygen atoms causing the local distortion are completely removed both through the Pb-substitution and through the annealing in flowing N$_2$ gas.

In this research, we have attempted to increase $T_c$ further in Pb-substituted Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ without excess oxygen by optimizing the Pb content, namely, the hole concentration in the CuO$_2$ plane.

2. Experimental

Polycrystalline samples of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ (0.32 $\leq$ x(Pb) $\leq$ 0.42) were prepared by the conventional solid-state reaction method as follows. Stoichiometric amounts of Bi$_2$O$_3$, PbO, SrCO$_3$, CaCO$_3$, CuO powders were mixed and calcined at 800°C for 24 h in air. The calcined mixture was
reground and pressed into pellets, and sintered at 830°C for 40 h in air. The sintered pellets were annealed in an Ar gas flow of 50 ml/min at 775°C for 8 h. The structural analysis was carried out by the powder x-ray diffraction using Cu Kα radiation. The iodometric titration was carried out to estimate the oxygen content. Measurements of the thermoelectric power at room temperature were carried out to estimate the hole-concentration in the CuO₂ plane [4]. Magnetic susceptibility measurements were performed for the powdered samples using a SQUID magnetometer in a magnetic field of 10 Oe on warming after zero-field cooling in order to determine \( T_c \). Electrical resistivity measurements were also performed by the standard dc four-probe method to determine \( T_c \).

3. Results

Figure 1 shows the powder x-ray diffraction patterns of Bi\(_{2-x}\)Pb\(_x\)Sr\(_2\)CaCu\(_2\)O\(_8\) with 0.32 ≤ \( x \)(Pb) ≤ 0.42. It is found that all samples are of the single Bi-2212 phase. The peaks are indexed on the basis of the orthorhombic symmetry. As reported in the literature [3], the crystal structure of Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_2\)CaCu\(_2\)O\(_8+\)\(\delta\) with \(\delta\) ~ 0 is monoclinic. For our samples, however, the peak splitting due to the monoclinic distortion cannot be observed clearly within our experimental accuracy, but the broadening of (113), (115) and (117) peaks due to its distortion is observed. Figure 2 shows the dependence of the lattice parameters on the Pb-content \( x \)(Pb). The \( a \)-axis length tends to decrease slightly with increasing \( x \)(Pb) and both \( b \)-axis and \( c \)-axis lengths are almost constant.

![Figure 1](image1.png)

**Figure 1.** Powder x-ray diffraction patterns of Bi\(_{2-x}\)Pb\(_x\)Sr\(_2\)CaCu\(_2\)O\(_8\) (0.32 ≤ \( x \)(Pb) ≤ 0.42).

![Figure 2](image2.png)

**Figure 2.** Variations of the lattice parameters \( a \), \( b \) and \( c \) with the Pb-content \( x \)(Pb) in Bi\(_{2-x}\)Pb\(_x\)Sr\(_2\)CaCu\(_2\)O\(_8\) (0.32 ≤ \( x \)(Pb) ≤ 0.42).

As shown in Fig. 3, values of the average oxygen-content \( 8+\delta \) are lower than the stoichiometric oxygen-content of 8 for all \( x \)(Pb), which may be due to the decomposition in the surface of crystalline grains through the reduction annealing at a temperature as high as 775°C rather than due to the oxygen deficiency in the Bi-2212 phase. Moreover, the average oxygen-content \( 8+\delta \) decreases with increasing \( x \)(Pb). This is because the melting point decreases with increasing \( x \)(Pb) so that the decomposition is more likely to occur.
Figure 4(a) shows the temperature dependence of the magnetic susceptibility $\chi$ for Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8+\delta}$. A single-step diamagnetic signal due to the shielding effect is observed for all samples. The superconducting volume fraction estimated from the shielding signal at 10 K is about 20-25%, indicating the appearance of bulk superconductivity. The value of $T_c$, defined as the onset temperature of the shielding effect, is about 100 K for all samples, as shown in Fig. 4(b). In particular, the maximum $T_c$ of 102 K is observed for $x$(Pb)=0.36 and is larger than the maximum value of 98.5 K observed so far for $x$(Pb)=0.40 [3]. The present compound is the first superconductor with $T_c$ above 100 K in the Bi-2212 phase.

![Oxygen Content vs Pb Content](image)

**Figure 3.** Dependence of the oxygen content $8+\delta$ on the Pb content $x$(Pb) in Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$.

![Magnetic Susceptibility vs Temperature](image)

**Figure 4.** (a) Temperature dependence of the magnetic susceptibility $\chi$ for Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8+\delta}$, and (b) that around $T_c$. 

![Graph](image)
Figure 5 shows the temperature dependence of the electrical resistivity $\rho$ for Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ with $x$(Pb)=0.36. With decreasing temperature, $\rho$ starts to deviate from the extrapolated line in the normal state below ~110 K owing to the superconducting fluctuation and decreases sharply below ~102 K which is in good agreement with the value of $T_{c \text{ onset}}$ determined from the magnetic susceptibility measurement. The value of $T_c$, defined at the midpoint of the transition curve, is 90.5 K. Then, a somewhat broad tail in the $\rho$-$T$ curve is observed below ~85 K and then the zero-resistivity is realized at low temperatures below 72 K. The hole concentration in the CuO$_2$ plane is estimated to be about 0.17 from the value of the thermoelectric power at room temperature, indicating that holes are doped almost optimally. Therefore, the broad tail and semiconductive behaviour in the normal state may be due to the weak link between crystalline grains, the surface of which is decomposed through the reduction annealing at a high temperature as mentioned above.

4. Conclusions
We have successfully synthesized the Bi-2212 phase with $T_c$ above 100 K in Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_8$ for the first time. It has been found that the maximum value of $T_{c \text{ onset}}$ is 102 K for $x$(Pb)=0.36. Unfortunately, the zero resistivity is exhibited only below $T_{c \text{ zero}} = 72$ K due to the weak link between crystalline grains, the surface of which is decomposed by the reduction annealing at a high temperature. Nevertheless, the improvement of the annealing condition will allow for the increase in $T_{c \text{ zero}}$.

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