Effect of the fluorine substitution for oxygen in the heavily Pb-doped Bi-2212 phase of (Bi,Pb)_{2}(Sr,Ba)_{2}CaCu_{2}O_{8}

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Abstract. Polycrystalline samples of the Bi-2212 phase of Bi_{2−x}Pb_{x}Sr_{2}CaCu_{2}O_{8−δ}F_{y} with x(Pb) = 0.6 and 1.0 have been prepared. All the samples are almost of the single phase with the Bi-2212 structure for x(Pb) = 0.6. The value of Tc ~ 82 K for z(F) = 0 increases up to 86–88 K for z(F) = 0.2–0.6. This may be due to the decrease in the amount of vacancy at the O-site by the introduction of F−. In addition, we have successfully synthesized the partially Ba-substituted Bi-2212 phase of Bi_{1−y}Pb_{0.2}Sr_{2−z}Ba_{y}CaCu_{2}O_{8−δ}F_{0.2} with 0 ≤ y(Ba) ≤ 0.5. Tc increases up to 98 K for y(Ba) = 0.5. The enhancement of Tc through the Ba-substitution may be due to the increase in the distance between Cu and the apical oxygen.

1. Introduction

Among many superconducting materials, Bi-based cuprates are promising candidates for the practical application of superconductivity especially as power transmission cables at the liquid nitrogen temperature. Much attention has been paid to the Bi-2223 phase of Bi_{2−x}Sr_{2}CaCu_{2}O_{8−δ} with the highest Tc = 110 K among the Bi-based cuprate superconductors. However, the production of the single phase of Bi-2223 requires long processing time and is very hard because the Bi-2223 phase is stable within a narrow temperature range of about 50°C only. On the other hand, the Bi-2212 phase is stable in a wider range of processing temperatures and its production of single phase is relatively easy. Furthermore, the Bi-2212 phase has an advantage that its critical current density Jc at low temperatures is higher than that of the Bi-2223 phase. However, Tc ~ 80 K of the Bi-2212 phase is too low for the practical application at the liquid nitrogen temperature, which points to a need for an enhancement of Tc.

The reason of the relatively low Tc of the Bi-2212 phase is that the hole-concentration is situated in the overdoped region because extra oxygen atoms easily introduced in the BiO plane supply the CuO2 plane with holes excessively. Therefore, its Tc increases to ~ 90–96 K by the decrease in the hole concentration through the substitution of RE3+ for Ca3+ or the reduction annealing [1–7]. Moreover, Tc increases up to ~ 98 K in Bi_{1.6}Pb_{0.4}Sr_{2}CaCu_{2}O_{8} by removing extra oxygen ions through the reduction annealing and the Pb-substitution for Bi [8]. Recently, we have observed the highest Tc of 102 K in Bi_{1.6}Pb_{0.3}Sr_{2}CaCu_{2}O_{8} with the optimized Pb-content [9]. However, its Tc is still lower than those of the Tl-2212 phase of Tl_{2}Ba_{2}CaCu_{2}O_{8} and the Hg-1212 phase of HgBa_{2}CaCu_{2}O_{8}. According to the empirical rule of high Tc in cuprate superconductors, Tc increases with increasing distance between Cu and the so-called apical oxygen Oap. The larger Ba-substitution for the smaller Sr is effective way to increase the Cu-Oap distance. However, it is widely recognized that Ba cannot be substituted for Sr in the Bi-based cuprate superconductors by the solid-state reaction method because BaBiO3 is produced as an impurity.
phase. Very recently, we have successfully synthesized the Ba-substituted Bi-2212 phase of BiPbBa$_2$NdCu$_2$O$_8$ [10]. It has been found that the Ba substitution for Sr requires the expansion of the Bi-O layers through the larger Pb$^{2+}$-substitution for the smaller Bi$^{3+}$. Unfortunately, holes cannot be doped at all and no superconductivity appears. This may be because the Nd$^{3+}$-substitution for Ca$^{2+}$, which is necessary to keep the charge neutrality against the Pb$^{2+}$-substitution for Bi$^{3+}$, increases the positive electrostatic potential around the CuO$_2$ plane and prevents the hole doping into the CuO$_2$ plane. However, in the heavily Pb-doped BiPbBa$_2$CaCu$_2$O$_{8-δ}$ without the Nd$^{3+}$-substitution for Ca$^{2+}$, the oxygen deficiency is expected to be caused. In fact, the oxygen deficiency occurs and $T_c$ decreases in Sr-based Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8-δ}$ with $x$(Pb) $>$ 0.4 [11, 12]. Therefore, an effective substitution instead of the Nd$^{3+}$-substitution for Ca$^{2+}$ is desired. The F$^-$-substitution for O$^{2-}$ is believed to be one of the effective substitutions. In this research, we have investigated whether the F$/\text{O}^{2-}$-substitution is possible in the heavily Pb-doped Bi-2212 phase of Sr-based (Bi,Pb)$_2$(Sr,Ba)$_2$CaCu$_2$O$_{8-δ}$ which is expected to be easier to be obtained than Ba-based (Bi,Pb)$_2$Ba$_2$CaCu$_2$O$_{8-δ}$, and then have attempted the synthesis of the Sr$^{2+}$/Ba$^{2+}$-substituted (Bi,Pb)$_2$(Sr,Ba)$_2$CaCu$_2$(O,F)$_8$.

2. Experimental
Polycrystalline samples of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8-δ}$-F$_2$ (x(Pb) = 0.6, 1.0) and Bi$_{1.4}$Pb$_{0.6}$Sr$_2$.Ba$_x$CaCu$_2$O$_{7.5}$F$_{0.2}$ (0 ≤ $x$(Ba) ≤ 0.5) were prepared by the solid-state reaction method. Starting materials were powders of Bi$_2$O$_3$, PbO, SrCO$_3$, BaCO$_3$, CaCO$_3$, CuO, SrF$_2$. The powders weighted stoichiometrically were mixed and calcined at 750°C for 24 h in air. The calcined mixture was reground, pressed into pellets and sintered for 48 h at 740°C for Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8-δ}$-F$_2$ and at 730°C for Bi$_{2-x}$Pb$_x$Sr$_2$.Ba$_x$CaCu$_2$O$_{7.5}$F$_{0.2}$. This sintering process was carried out in flowing gas of Ar to suppress the formation of impurity phases with Pb$^{4+}$. The structural analysis was carried out by the powder x-ray diffraction using Cu Kα radiation. Measurements of the thermoelectric power at room temperature were carried out to estimate the hole-concentration in the CuO$_2$ plane [13]. Magnetic susceptibility measurements were performed using a SQUID magnetometer to determine $T_c$.

3. Results
Figure 1 shows the powder x-ray diffraction patterns of the obtained samples of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8-δ}$-F$_2$ with x(Pb) = 0.6. All the samples are almost of the single phase with the Bi-2212 structure, although the tiny amounts of an impurity phase of SrF$_2$ is included. The broadening of 11l peaks are due to the monoclinic distortion observed for the samples of Bi-2212 phase of (Bi,Pb)$_2$Sr$_2$CaCu$_2$O$_8$ without extra oxygen ions as reported in the literature [8]. The z(F)-dependence of lattice parameters is shown in Fig. 2. With increasing z(F), a-axis, b-axis and c-axis lengths increase and then tend to saturate for z(F) $>$ 0.2, indicating that the solution limit of F is z(F) $>$ 0.2. Figure 3 shows the powder x-ray diffraction patterns of the obtained samples of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{8-δ}$-F$_2$ with x(Pb) = 1.0. All the F-substituted samples contain the significant amounts of the impurity phase of SrF$_2$, unlike x(Pb) = 0.6. However, the Bi-2212 phase becomes dominant through the F/O-substitution. These results indicate that the F-substitution is effective for the formation of the heavily Pb-doped Bi-2212 phase. The determination of the F-content in the samples by the electron-probe microanalysis is underway.
Figure 1. Powder x-ray diffraction patterns of $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_{8-z}\text{F}_z$ ($0 \leq z(F) \leq 0.6$). The peaks are indexed on the basis of the orthorhombic symmetry.

Figure 2. Variations of the lattice parameters $a$, $b$ and $c$ with the $F$-content $z(F)$ in $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_{8-z}\text{F}_z$ ($0 \leq z(F) \leq 0.6$).

Figure 3. Powder x-ray diffraction patterns of $\text{Bi}_1\text{Pb}_1\text{Sr}_2\text{CaCu}_2\text{O}_{8-z}\text{F}_z$ ($0 \leq z(F) \leq 1.0$). The peaks are indexed on the basis of the orthorhombic symmetry.
Figure 4 (a) shows the temperature dependence of the magnetic susceptibility $\chi$ in a magnetic field of 10 Oe on warming after zero-field cooling for the almost single-phase samples of $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_8-z\text{F}_z$. 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 20–40%, indicating the appearance of bulk superconductivity. The value of $T_c$ is defined as the onset temperature of the shielding effect, as shown in figure 4(b). The $z(F)$-dependence of $T_c$ is shown together with the hole concentration in the $\text{Cu}(2)\text{O}_2$ plane $p$ estimated from the thermoelectric power at room temperature in figure 5. The value of $T_c \sim 82$ K for $z(F)=0$ increases up to 86–88 K for $z(F)=0.2$–0.6, which is similar to the $z(F)$-dependence of the lattice parameters. On the other hand, the hole concentration in the $\text{Cu}(2)\text{O}_2$ plane $p \sim 0.19$ (Cu) is almost constant through the F/O-substitution. Therefore, the increase in $T_c$ may be due to the decrease in the amount of vacancy at the O-site by the introduction of F, because one $\text{O}^{2-}$ ion is substituted by two $\text{F}^-$ ions to keep the charge neutrality. These results indicate the F-introduction is effective for the compensation of the oxygen vacancy in the heavily Pb-doped Bi-2212 phase. However, the highest $T_c=86$ K is much lower than $\sim 100$ K for $\text{Bi}_{1.6}\text{Pb}_{0.4}\text{Sr}_2\text{CaCu}_2\text{O}_8$. This may be because the disorder caused by the F/O-substitution and/or the cation non-stoichiometry due to the formation of the impurity phase of SrF$_2$. Further investigation is required to clarify the reason for lower $T_c$.

**Figure 4.** (a) Temperature dependence of the magnetic susceptibility $\chi$ for $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_8-z\text{F}_z$ ($0 \leq z(F) \leq 0.6$), and (b) that around $T_c$.

Next, we show the results of the Ba-substitution for Sr in $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2\text{CaCu}_2\text{O}_8-z\text{F}_z$, the hole concentration of which is expected to be optimal from the nominal composition. Shown in figure 6, the powder x-ray diffraction patterns of the Ba-substituted samples of $\text{Bi}_{1.4}\text{Pb}_{0.6}\text{Sr}_2-\text{Ba}_x\text{CaCu}_2\text{O}_8-z\text{F}_z$ with
0 ≤ y(Ba) ≤ 0.5 obtained by sintering at 730°C, which is lower than that for Bi$_{1.4}$Pb$_{0.6}$Sr$_2$CaCu$_2$O$_{8-x}$-F$_{0.2}$ because the melting point is lowered through the Ba-substitution. The nominal hole-concentration of Bi$_{1.4}$Pb$_{0.6}$Sr$_2$-Ba$_y$CaCu$_2$O$_{7.8}$-F$_{0.2}$ is same as that for Bi$_{1.4}$Pb$_{0.6}$Sr$_2$CaCu$_2$O$_8$ with $T_c$ ~ 100 K. The samples are almost of the single phase with the Bi-2212 structure for y(Ba) ≤ 0.5, while Bi-2212 phase is dominant but the peaks due to the impurity phases are observed for y(Ba) = 0.5. The y(Ba)-dependence of lattice parameters is shown in figure 7. With increasing y(Ba), a-axis, b-axis and c-axis lengths tend to increase for y(Ba) ≤ 0.4. These results indicate the successful synthesis of the partially Ba-substituted samples. Considering that Ba is not substituted in Bi$_2$Sr$_2$CaCu$_2$O$_8$, the expansion of (Bi,Pb)-O plane is effective for the Ba-substitution for Sr, as reported in our previous work [10]. The 111 peaks become sharp with increasing y(Ba), indicating that the lattice expansion through the Ba-substitution for Sr may alleviate the monoclinic distortion. This behavior is also observed in BiPb(Sr,Ba)$_2$NdCu$_2$O$_8$ [10].

Figure 6. Powder x-ray diffraction patterns of Bi$_{1.4}$Pb$_{0.6}$Sr$_2$-Ba$_y$CaCu$_2$O$_{7.8}$-F$_{0.2}$ (0 ≤ y(Ba) ≤ 0.5). The peaks are indexed on the basis of the orthorhombic symmetry.

Figure 7. Variations of the lattice parameters $a$, $b$ and $c$ with the Ba-content y(Ba) in Bi$_{1.4}$Pb$_{0.6}$Sr$_2$-Ba$_y$CaCu$_2$O$_{7.8}$-F$_{0.2}$ (0 ≤ y(Ba) ≤ 0.5).

Figure 8(a) shows the temperature dependence of the magnetic susceptibility $\chi$ in a magnetic field of 10 Oe on warming after zero-field cooling for Bi$_{1.4}$Pb$_{0.6}$Sr$_2$-Ba$_y$CaCu$_2$O$_{7.8}$-F$_{0.2}$. Figure 9 displays the y(Ba) dependence of $T_c$ defined as the onset temperature of the shielding effect as shown in Fig. 8(b). With increasing y(Ba), $T_c$ increases from 86 K for y(Ba) = 0 up to 98 K for y(Ba) = 0.5. The hole concentration in the Cu(2)O$_2$ plane $p$ ~ 0.17–0.2 (Cu) is almost independent of y(Ba). Therefore, the enhancement of $T_c$ may be due to the increase in the the Cu-O$_{ap}$ distance through the Ba-substitution.
4. Conclusions

The partially F-substituted Bi-2212 phase of Bi$_{2-x}$Pb$_x$Sr$_2$CaCu$_2$O$_{7-z}$F$_z$ with $x$(Pb) = 0.6 and 1.0 have been prepared. As for $x$(Pb) = 0.6, almost single-phase samples can be obtained for $0 \leq y$(Ba) $\leq 0.5$. The value of $T_c$ ~ 82 K for $z$(F) = 0 increases up to 88 K for $z$(F) = 0.6, which may be due to the decrease in the
amount of vacancy at the O-site by the introduction of F. It has been found that the F\textsuperscript{-}-substitution for O\textsuperscript{2−} is effective to keep the charge neutrality instead of the oxygen deficiency in the heavily Pb-doped Bi-2212 phase. However, the highest $T_c = 88$ K is lower than $\sim 100$ K for Bi\textsubscript{1.6}Pb\textsubscript{0.4}Sr\textsubscript{2}CaCu\textsubscript{2}O\textsubscript{8}. Moreover, we have successfully synthesized the partially Ba-substituted Bi-2212 phase of Bi\textsubscript{1.4}Pb\textsubscript{0.6}Sr\textsubscript{2−$y$}Ba\textsubscript{$y$}CaCu\textsubscript{2}O\textsubscript{7.8}F\textsubscript{0.2} with $0 \leq y(\text{Ba}) \leq 0.5$. $T_c$ increases up to 98 K for $y(\text{Ba}) = 0.5$. The enhancement of $T_c$ through the Ba-substitution may be due to the increase in the Cu-O\textsubscript{ap} distance. The further increase in Pb- and Ba-contents will allow for the further increase in $T_c$.

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