Effects of the Ba-substitution for Sr in the Bi-2201 phase of BiPb(Sr,La)₂CuO₆₊δ

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Abstract. Polycrystalline samples of the Bi-2201 phase of BiPbSr₁.₅ₓBaₓLa₀.₈₅CuO₆₊δ have been prepared by the conventional solid-state reaction method. Through the Ba-substitution for Sr, the lattice becomes large while Tc decreases gradually. With increasing x(Ba), the hole concentration in the CuO₂ plane decreases despite the increase in the number of excess oxygen. The suppression of the superconductivity may be due to the decrease in the hole concentration in the CuO₂ plane and the increase in the local lattice-distortion caused by excess oxygen.

1. Introduction

Among a lot of superconductors, the Bi-2223 cuprate superconductor is most expected for the practical application of superconductivity at the liquid nitrogen temperature because of its relatively high value of the superconducting transition temperature Tc ~110 K. However, it is 15-25 K lower than those of poisonous Tl-2223 and Hg-1223 cuprate superconductors, the crystal structures of which are analogous to that of the Bi-2223 cuprate superconductor. Elucidating why its Tc is low and increasing Tc up to ~135 K will promote the practical application of the Bi-2223 cuprate superconductor. There have been many efforts since the discovery of the Bi-2223 cuprate superconductor, but the problem has not yet been solved. In order to solve this problem, it is meaningful to investigate the Bi-2201 phase among three kinds of Bi-based cuprate superconductors of Bi₂Sr₂Cun₋₁CuO₂n₊₄⁺δ (n = 1, 2, 3), because the crystal structure is simple and the synthesis can readily be done, though its Tc is low.

The value of Tc in the Bi-2201 phase of Bi₂Sr₂⁺ₓSr₂₋ₓCuO₆₊δ at the time of discovery is ~ 8 K [1]. It increases up to ~ 15 K in Bi₂Sr₂CuO₆₊δ in which Bi does not occupy the Sr site [2]. However, this value is much smaller than 90 - 95 K in the Tl-2201 phase of Tl₂Ba₂CuO₆₊δ and the Hg-1201 phase of HgBa₂CuO₄₊δ [3,4]. One of causes of the low Tc in Bi₂Sr₂CuO₆₊δ is a large amount of excess oxygen introduced into the Bi₂O₂ layer which supplies the conductive CuO₂ plane with holes excessively to cause the local distortion. Therefore, Tc increases up to ~30 K by decreasing the hole concentration through the partial substitution of La³⁺ for Sr²⁺ [5]. Moreover, Tc is improved to ~40 K in (Bi,Pb)₂(Sr,La)₂CuO₆ by removing excess oxygen through the partial substitution of Pb²⁺ for Bi³⁺ with keeping the hole concentration at the optimum [6,7].

According to the empirical rule of high Tc in cuprate superconductors, Tc increases with increasing distance between Cu and O. The Cu-O distance in Bi₂Sr₂CuO₆₊δ is shorter than that in HgBa₂CuO₄₊δ and Tl₂Ba₂CuO₆₊δ, because smaller Sr²⁺ ions in Bi₂Sr₂CuO₆₊δ are replaced by larger Ba²⁺ ions in HgBa₂CuO₄₊δ and Tl₂Ba₂CuO₆₊δ. In this research, we have attempted to increase Tc further in the Bi-
2201 phase by extending the Cu-O distance through the substitution of Ba for Sr in (Bi,Pb)₂(Sr,La)₂CuO₆₋ₓ.

2. Experimental
Polycrystalline samples of BiPbSr₁.₁₅₋ₓBaₓLa₀.₈₅CuO₆₋ₓ were prepared by the solid-state reaction method. Stoichiometric amounts of Bi₂O₃, PbO, SrCO₃, BaCO₃ and CuO powders were mixed, pressed into pellets and heated at 770°C for 24 h in flowing gas of Ar for 24 h. The products were then annealed at 500°C for 3 h in flowing gas of O₂. The structural analysis was carried out by the powder x-ray diffraction using CuKα 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 [8]. 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 Tc.

3. Results
Figure 1 shows the powder x-ray diffraction patterns of BiPbSr₁.₁₅₋ₓBaₓLa₀.₈₅CuO₆₋ₓ. All the samples are almost of the single phase with the Bi-2201 structure, although a small amount of Ba(Bi,Pb)O₃ is included for x ≥ 0.8. The crystal structure is orthorhombic for all the samples. As shown in Fig. 2, the lattice parameters increase linearly with increasing x(Ba) for x(Ba) ≤ 1.0, suggesting that the Cu-O distance increases through the Ba-substitution.

It is well known that Ba cannot be substituted for Sr at all in Bi₂Sr₂CuO₆. In contrast, Ba-substituted samples are successfully synthesized in the present system. This may be explained as follows. In Bi₂Sr₂CuO₆, the Ba-substitution is impossible owing to the enhancement of the size mismatch between the smaller Bi-O layer and the larger Sr-O layer. On the other hand, the size mismatch is reduced in (Bi,Pb)₂(Sr,La)₂CuO₆, because larger Pb is substituted for smaller Bi and smaller La is substituted for larger Sr, which allows for the Ba-substitution for Sr in the present system.

Figure 1. Powder x-ray diffraction patterns for BiPbSr₁.₁₅₋ₓBaₓLa₀.₈₅CuO₆₋ₓ. Peaks marked by ▼ are due to Ba(Bi,Pb)O₃.

Figure 2. Dependence of lattice parameters on the Ba content x(Ba) for BiPbSr₁.₁₅₋ₓBaₓLa₀.₈₅CuO₆₋ₓ.
Figure 3 shows the temperature dependence of the magnetic susceptibility $\chi$ for BiPbSr$_{1.15-x}$Ba$_x$La$_{0.85}$CuO$_{6+\delta}$. A diamagnetic signal due to the shielding effect is observed for all the samples. It is found that $T_c$ tends to decrease and the superconducting volume fraction decreases with increasing $x$(Ba).

Figure 3. Temperature dependence of the magnetic susceptibility $\chi$ for BiPbSr$_{1.15-x}$Ba$_x$La$_{0.85}$CuO$_{6+\delta}$.

Figure 4 displays the $x$(Ba)-dependences of $T_c$ and the superconducting volume fraction at 5 K $V_{sc}$, the oxygen content 6+$\delta$, the hole concentration in the CuO$_2$ plane $p$ on the Ba content $x$(Ba) in BiPbSr$_{1.15-x}$Ba$_x$La$_{0.85}$CuO$_{6+\delta}$.

Figure 4. Dependences of $T_c$ and the superconducting volume fraction at 5 K $V_{sc}$, the oxygen content 6+$\delta$, the hole concentration in the CuO$_2$ plane $p$ on the Ba content $x$(Ba) in BiPbSr$_{1.15-x}$Ba$_x$La$_{0.85}$CuO$_{6+\delta}$.

Figure 4 displays the $x$(Ba)-dependences of $T_c$, defined at the temperature where $\chi$ changes by 0.1% of the value indicating the perfect-diamagnetism from the normal-state value, and the superconducting volume fraction $V_{sc}$ estimated from the value of $\chi$ at 5 K. The $x$(Ba)-dependences of the hole concentration in the CuO$_2$ plane $p$ and the oxygen content 6+$\delta$ are also shown. Although the lattice becomes large monotonically through the Ba-substitution for Sr as shown in Fig. 2, both $T_c$ and $V_{sc}$ decreases gradually contrary to the empirical rule of high $T_c$ in cuprate superconductors. The $x$(Ba)-dependence of $T_c$ is quite similar to that of $p$. The $p$ is as low as ~0.12 and tends to decrease slightly with increasing $x$(Ba), though the excess oxygen content increases with increasing $x$(Ba). This suggests that holes generated by excess oxygen are supplied to the (Bi, Pb)$_2$O$_2$ layer rather than to the CuO$_2$ plane. Form these results, it is concluded that the suppression of the superconductivity through the Ba-substitution is due to the decrease in $p$ and the increase in the local lattice-distortion caused by excess oxygen. Similarly, the reason why the maximum value of $T_c$ ~ 30 K in the present system is lower than the highest $T_c$ ~40 K in the Bi-2201 phase reported [6,7] is concluded to be the low hole-concentration ~0.12 and the local lattice-distortion caused by excess oxygen.
4. Conclusions
Polycrystalline samples of the Bi-2201 phase of BiPbSr_{1.15-x}Ba_xLa_{0.85}CuO_{6+δ} have been prepared by the conventional solid-state reaction method. With increasing x(Ba), the lattice becomes large, while T_c decreases from ~30 K gradually. The unexpected suppression of the superconductivity may be due to the local lattice-distortion caused by excess oxygen, the number of which increases with increasing x(Ba). Despite the increase in excess oxygen, the hole concentration in the CuO_2 plane decreases slightly, indicating that holes generated by excess oxygen are supplied to the (Bi,Pb)_2O_2 layer rather than to the CuO_2 plane. This decrease in the hole concentration in the CuO_2 plane also suppresses the superconductivity. Therefore, the removal of excess oxygen through the reduction annealing and the increase in the hole concentration in the CuO_2 plane through the decrease in the La-content will allow for the investigation of effects of the enlargement of the Cu-O distance on the superconductivity in the present system.

Acknowledgments
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