Pb-substitution effect on the electronic properties of Bi2201, Bi2212 and Bi2223 superconductors

Yoshihito SHIMABUKURO¹,², Tetsuto WATANABE¹ and Shiro KAMBE¹

¹Department of Material Chemistry, Yamagata University

Although Pb²⁺ substitution for Bi³⁺ increases the hole concentration, p, in Pb-substituted Bi-based superconductors, the Pb substitution effect has yet to be studied in detail. Herein the Pb substitution effect on the electronic properties of Bi2201, 2212, and 2223 superconductors is investigated to elucidate the role of Pb on the correlation between p and formal valence, v. Consistent with Mott-Hubbard theory, p increases as v increases in the Pb-free Bi2201 and Pb-free Bi2212 phases. In contrast, p decreases with increasing v for the Pb-substituted Bi2201 phase, which contradicts Mott-Hubbard theory but can be explained by the increase in Pb⁴⁺. For the Pb-substituted Bi2212 phase, p increases with increasing v from 2.0 to 2.2, and then remains constant at p = 0.10–0.20 from v 2.2 to 2.63. When v increases from 2.0 to 2.2, the hole is doped at a Cu site, which is the same behavior as that of the Pb-free Bi2212 phase. As v increases from 2.2 to 2.63, the Pb is doped in a Pb site and not a Cu one. For the Pb-substituted Bi2223 phase, p decreases with increasing v, and a mixed-valence state between Pb⁵⁺ and Pb⁴⁺ may coexist. As the v increases, the Pb valence increases and the Cu valence decreases. These results indicate two factors influence p. One is correlated with the substitution of Sr²⁺ for La³⁺ or Y³⁺ for Ca²⁺, which obeys Mott-Hubbard theory. The other is correlated with the substitution of Pb²⁺/⁴⁺ for Bi³⁺, which does not obey Mott-Hubbard theory. The results strongly suggest that Pb substitution for Bi does not necessarily dope a hole but decreases the hole concentration.

Key-words : Pb-substitution effect, Bi2201, Bi2212, Bi2223

1. Introduction

In a homologous series of compounds, Bi(Pb)–Sr–Ca–Cu–O, Tl–Ba–Ca–Cu–O, and Hg–Ba–Ca–Cu–O, the superconducting transition temperature, Tc, increases as the number of CuO₂ planes, m, increases from m = 1 to 3. Thus, the maximum Tc is firstly determined by m. However, for two high-temperature superconductors with the same number of CuO₂ planes, Tc strongly depends on the hole concentration, p.¹

The (La,Sr)₂CuO₄ system has a single CuO₂ square network. As the hole concentration increases, the system changes from an antiferromagnetic insulator to a superconductor. However, further increasing the hole concentration causes the superconductivity to disappear and it becomes similar to a normal metal.² Moreover, YBa₂Cu₃O₇³ and Bi₂Sr₂Ca₁₋ₓYₓCu₂O₈ systems,⁴–⁶ which have a double layer of the CuO₂ square network, display a similar change in Tc but the superconductivity does not disappear in the high hole concentration region.

Fukushima et al.⁷ reported that Pb substitution for Bi in the Bi₂Sr₂CaCu₂O₈ and subsequent annealing in N₂, removes oxygen from the system, causing the Tc value to rise to the 90 K class. Similarly, the Bi2201 and Bi2212 phases display higher Tc values by Pb substitution and N₂ annealing.⁸,⁹ From the viewpoint of the crystallographic structure, the lattice mismatch relaxation mechanism differs between the Pb-free and Pb-substituted Bi2212 phases.¹⁰ For the Pb-free Bi2212 phase, insertion of oxygen into the BiO layer relaxes the lattice mismatch between the BiO and CuO₂ layer. In contrast, the relaxation of the lattice mismatch between the BiO and CuO₂ layers due to the change in the Pb valence induces relaxation of Pb-substituted Bi2212. From high-resolution analytical electron microscopy observation, it is indicated that the Pb atoms are located in the Bi–O layer.¹¹

To date, most studies have measured the hole concentration either using Hall coefficient measurements or isodometric measurements. Few works have reported using both. One exception is a study by Maeda et al.⁶ They measured both the Hall coefficient and the formal valence, which is the average Cu valence, assuming Bi³⁺ from iodometry of the Bi₂Sr₂Ca₁₋ₓCuₓO₈ system (m = 1, 2). They revealed that for Pb-free Bi2201 (m = 1) and Bi2212 (m = 2) phases, the Hall coefficient roughly scales with the inverse of v measured from the formal valence, v. We previously examined the correlation between p

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measured by the Hall coefficient and \( v \) measured by iodo-metry for Pb-free Bi2201 and Pb-free Bi2212 phases.\(^{12}\) In these phases, \( p \) scales with \( v \), revealing a Mott-Hubbard-like character, which agrees well with the data by Maeda et al.\(^{6}\)

Maeda et al. revealed that for the Pb-substituted Bi2201 phase, the Hall coefficient deviates from the inverse of \( (v+2) \) measured from the formal valence.\(^{6}\) Additionally, we found that \( p \) does not scale with \( v \) for Pb-substituted Bi2223.\(^{12}\) These results suggest that holes are not doped into the CuO2 plane for the Pb-substituted Bi2201 and Bi2212 phases. The deviation from Mott-Hubbard theory for the Pb-substituted Bi2201 and Bi2212 phases has not been explained clearly.

This study aims to elucidate the correlation between \( p \) and \( v \) of the Pb-substituted Bi-based superconductors (Bi2201, 2212 and 2223 phases) and clarify the role of Pb.

2. Experimental

A conventional solid-state reaction was used to prepare specimens of Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_{1.8}\)CuO\(_y\), Bi\(_{1.8}\)Sr\(_{1.9}\)La\(_{1.8}\)Cu\(_{2}\)O\(_{y}\) (X = 0–1.0), Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_{1.8}\)Ca\(_{1.8}\)CuO\(_y\) (X = 0–1.0), and Bi\(_{1.8}\)Sr\(_{1.8}\)Pb\(_{0.3}\)Sr\(_{1.9}\)Ca\(_{1.8}\)CuO\(_y\). Powders of Bi2O3, PbO, SrCO\(_3\), CaCO\(_3\), Y\(_2\)O\(_3\), and CuO were mixed with an agate mortar and calcined at 770 °C for 12 h in air and cooled in a furnace. These powders were mixed again and pressed into pellets. The pellets were sintered several times at 820–850 °C for 20 h and quenched. Annealing with Ar, N\(_2\), or O\(_2\) changed the oxygen content.

X-ray powder diffraction (XRD; RIGAKU Ultima IV) confirmed that the samples are a single phase. Figures 1 and 2 shows the XRD pattern of Bi\(_{1.8}\)Pb\(_{0.4}\)Sr\(_{1.8}\)CuO\(_y\) and Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_{1.9}\)Ca\(_{2.03}\)Cu\(_{3.06}\)O\(_y\), respectively. All peaks were indexed as Bi\(_{1.6}\)Pb\(_{0.4}\)Sr\(_{1.8}\)CuO\(_y\). The XRD patterns of Bi2212 phase is referred to the Ref. 10.

A coulometric method determined the oxygen content, \( y \), and \( u \).\(^{13}\) The formal valence represents the average Cu valence, assuming the valences of Bi and Pb are 3\(^+\) and 2\(^+\), respectively. The Hall coefficient measurement measured \( p \) at room temperature. A magnetic flux density, \( B \), of ±1 T and an electric current, \( I \), of 10 mA was applied to the sample. The Hall coefficient, \( R_{H} \), is described as

\[
R_{H} = \frac{dV_{H}}{IB},
\]

where \( d \), \( V_{H} \), \( I \), and \( B \) are the specimen thickness, Hall electromotive force, electric current, and magnetic field, respectively. \( n \) is expressed as

\[
n = \frac{1}{qR_{H}}.
\]

where \( q \) is the elementary electric charge. \( p \) is described as

\[
p = \frac{n}{v}.\]

where \( s \) and \( v \) are the number of Cu ions per unit cell and the unit cell volume, respectively.

3. Results and discussion

Table 1 lists the composition, sintering conditions, \( v \), and \( p \) of (Bi\(_{1-x}\)Pb\(_x\))(Sr\(_{1-y}\)La\(_y\))CuO\(_y\), where \( v \) is controlled by varying \( y \) and the sintering conditions. In general, the increase in \( y \) or partial pressure of O\(_2\) decreases \( v \).

Figure 3 shows the correlation between \( v \) and \( p \) of the Bi2201 phase. The \( v \) values of the Pb-free and Pb-substituted Bi2212 phases are from Refs. 6 and 12. The open and closed circles represent the Pb-free and Pb-substituted Bi2201 phases, respectively. For the Pb-free Bi2201 phase, \( p \) increases as \( v \) increases. This tendency coincides with Mott-Hubbard theory. It seems that the slope of the curve in 2.2 < \( v \) < 2.25 is larger than that in 2.0 < \( v \) < 2.2, which may be due to the semiconducto to metal transition. On the other hand, for the Pb-substituted Bi2201 phase, the \( v \) value of the Pb-substituted Bi2201 spans a wide range from 2.1 to 2.8. While \( v \) of the Pb-free Bi2201 phase changes from 2.0 to 2.25, suggesting that Pb...
substitution for Bi increases \( v \). This can be explained by the substitution of \( \text{Pb}^{2+} \) for \( \text{Bi}^{3+} \). However, \( p \) clearly decreases as \( v \) increases, which contradicts Mott-Hubbard theory.

**Figure 4** shows the hole-doping scheme of the Pb-free and Pb-substituted Bi2201 phases. As \( v \) increases, \( p \) increases in the Pb-free Bi2201 phase due to the increase in the Cu valence [Fig. 4(a)], whereas \( p \) decreases in the Pb-substituted Bi2201 phase [Fig. 4(b)]. The behavior of the Pb-free Bi2201 phase is consistent with Mott-Hubbard theory, but that of the Pb-substituted Bi2201 phase is not. This difference may be due to Pb substitution. In oxides, Pb is usually stable in both the divalent and tetravalent states. Thus, a mixed valence state between \( \text{Pb}^{2+} \) and \( \text{Pb}^{4+} \) should exist. If the increase in the formal valence leads to a drastic increase in the Pb valence, then the Cu valence will decrease as shown in Fig. 4(b). It should be noted that the Pb valence has an assumed average formal valence of \( 3^{+} \).

### Table 1. Composition, sintering conditions, formal valence, \( v \) and the number of holes per a Cu, \( p \) of (Bi\(_{1-x}\)Pb\(_x\))(Sr\(_{1-y}\)La\(_y\))\(_2\)CuO\(_6\) \((x, y)\)

| \( x \) | \( y \) | Temperature [°C] | Sintering time [h] | Atmosphere | Partial pressure of O\(_2\) [%] | \( v \) | \( p \) |
|---|---|---|---|---|---|---|---|
| 0 | 0.2 | 850 | 15 | air | 20 | 2.15 | 1.11 |
| 0 | 0.3 | 850 | 15 | air | 20 | 2.14 | 1.15 |
| 0 | 0.4 | 850 | 15 | air | 20 | 2.13 | 1.106 |
| 0 | 0.5 | 850 | 15 | air | 20 | 2.12 | 0.851 |
| 0 | 0.6 | 850 | 15 | air | 20 | 2.11 | 0.614 |
| 0 | 0.7 | 850 | 15 | air | 20 | 2.10 | 0.520 |
| 0 | 0.8 | 850 | 15 | air | 20 | 2.09 | 0.228 |
| 0 | 0.9 | 850 | 15 | air | 20 | 2.08 | 0.138 |
| 0 | 1 | 850 | 15 | air | 20 | 2.07 | 0.122 |
| 0.05 | 0 | 850 | 15 | air | 20 | 2.24 | 2.68 |
| 0.1 | 0 | 850 | 15 | air | 20 | 2.25 | 1.831 |
| 0.15 | 0 | 850 | 15 | air | 20 | 2.26 | 1.228 |
| 0.2 | 0 | 850 | 15 | air | 20 | 2.27 | 0.928 |
| 0 | 0.3 | 860 | 100 | air | 20 | 2.24 | 0.893 |
| 0 | 0.4 | 860 | 100 | air | 20 | 2.21 | 0.714 |
| 0 | 0.5 | 860 | 100 | air | 20 | 2.19 | 0.486 |
| 0 | 0.6 | 860 | 100 | air | 20 | 2.16 | 0.479 |
| 0 | 0.7 | 860 | 100 | air | 20 | 2.16 | 0.393 |
| 0 | 0.8 | 860 | 100 | air | 20 | 2.10 | 0.227 |
| 0 | 0.9 | 860 | 100 | air | 20 | 2.09 | 0.141 |
| 0 | 1 | 860 | 100 | air | 20 | 2.03 | 0.052 |
| 0 | 0.3 | 700 | 20 | Ar | 0 | 2.17 | 0.191 |
| 0 | 0.4 | 700 | 29 | Ar | 0 | 2.14 | 0.216 |
| 0 | 0.5 | 700 | 20 | Ar | 0 | 2.11 | 0.132 |
| 0 | 0.6 | 700 | 20 | Ar | 0 | 2.09 | 0.089 |
| 0 | 0.7 | 700 | 20 | Ar | 0 | 2.07 | 0.1 |
| 0 | 0.8 | 700 | 20 | Ar | 0 | 2.04 | 0.046 |
| 0 | 0.9 | 700 | 20 | Ar | 0 | 2.03 | 0.036 |
| 0 | 1 | 700 | 20 | Ar | 0 | 2 | 0.023 |
| 0.2 | 0 | 600 | 48 | N\(_2\) | 0 | 2.43 | 0.587 |
| 0.2 | 0 | 600 | 72 | N\(_2\) | 0 | 2.41 | 0.782 |
| 0.2 | 0 | 600 | 96 | N\(_2\) | 0 | 2.43 | 0.584 |
| 0.2 | 0 | 600 | 144 | N\(_2\) | 0 | 2.32 | 0.54 |
| 0.2 | 0 | 600 | 48 | Ar, O\(_2\) | 50 | 2.37 | 0.673 |
| 0.2 | 0 | 600 | 48 | Ar, O\(_2\) | 10 | 2.35 | 0.808 |
| 0.2 | 0 | 600 | 48 | Ar | 0 | 2.24 | 0.563 |
| 0.2 | 0 | 600 | 72 | Ar, O\(_2\) | 50 | 2.31 | 0.8 |
| 0.2 | 0 | 600 | 72 | Ar, O\(_2\) | 10 | 2.53 | 0.61 |
| 0.2 | 0 | 600 | 72 | Ar, O\(_2\) | 1 | 2.26 | 0.85 |
| 0.2 | 0 | 600 | 72 | Ar | 0 | 2.36 | 0.549 |
| 0.2 | 0 | 600 | 96 | Ar | 0 | 2.12 | 0.562 |
| 0.2 | 0 | 700 | 96 | Ar | 0 | 2.34 | 0.793 |
| 0.2 | 0 | 700 | 96 | Ar | 0 | 2.35 | 0.511 |
| 0.2 | 0 | 650 | 20 | O\(_2\) | 100 | 2.702 | 0.335 |
| 0.2 | 0 | 650 | 48 | O\(_2\) | 100 | 2.464 | 0.415 |
| 0.2 | 0 | 650 | 48 | O\(_2\) | 100 | 2.564 | 0.443 |
| 0.2 | 0 | 650 | 48 | O\(_2\) | 100 | 2.754 | 0.205 |
| 0.2 | 0 | 500 | 72 | O\(_2\) | 100 | 2.508 | 0.237 |
| 0.2 | 0 | 650 | 72 | O\(_2\) | 100 | 2.774 | 0.210 |
| 0.2 | 0 | 500 | 48 | O\(_2\), Ar | 50 | 2.392 | 0.500 |
| 0.2 | 0 | 650 | 48 | O\(_2\), Ar | 50 | 2.578 | 0.260 |
| 0.2 | 0 | 650 | 48 | O\(_2\), Ar | 50 | 2.722 | 0.311 |
because the real value of the Pb valence is unclear. Since the holes detected by the Hall effect originate from the CuO$_2$ layer, the holes in the Pb layer are trapped and do not move freely. As the change in the Pb valence should be observable by XPS, we are planning to conduct an XPS experiment.

Table 2 lists the composition, sintering conditions, $v$, and $p$, of (Bi$_{1-x}$Pb$_x$)$_2$Sr$_2$Ca$_{1-x}$Y$_x$Cu$_2$O$_y$, where $v$ is controlled by changing $y$ and the sintering conditions.

**Figure 5** shows the correlation between $v$ and $p$ of the Bi2212 phase. The open and closed circles represent the Pb-free and Pb-substituted Bi2212 phase, respectively. Consistent with previous data and Mott-Hubbard theory, $p$ increases with increasing $v$ for the Pb-free Bi2212 phase. These results suggest that the holes are doped in the CuO$_2$ layer.

On the other hand, the Pb-substituted Bi2212 phase shows a different trend. From $2.0 < v < 2.2$, $p$ increases,
Table 2. Composition, sintering conditions, formal valence, \( v \), and the number of holes per a Cu, \( p \), of (Bi\(_{1-x}\)Pb\(_x\))\(_2\)Sr\(_2\)Ca\(_{1-y}\)Y\(_y\)Cu\(_2\)O\(_{8+\delta}\))

| \( x \) | \( y \) | Temperature [°C] | Sintering time [h] | Atmosphere | Partial pressure of O\(_2\) [%] | \( v \) | \( p \) |
|---|---|---|---|---|---|---|---|
| 0  | 0  | 820  | 20  | air  | 20  | 2.23 | 0.225 |
| 0  | 0  | 820  | 20  | air  | 20  | 2.28 | 0.202 |
| 0  | 0.1 | 820  | 20  | air  | 20  | 2.19 | 0.226 |
| 0  | 0.2 | 820  | 20  | air  | 20  | 2.22 | 0.220 |
| 0  | 0.25 | 820  | 20  | air  | 20  | 2.17 | 0.109 |
| 0  | 0.3 | 820  | 20  | air  | 20  | 2.10 | 0.146 |
| 0  | 0.4 | 820  | 20  | air  | 20  | 2.05 | 0.117 |
| 0  | 0.5 | 820  | 20  | air  | 20  | 2.04 | 0.032 |
| 0  | 0.5 | 820  | 20  | air  | 20  | 2.17 | 0.001 |
| 0  | 0.6 | 820  | 20  | air  | 20  | 2.00 | 0.014 |
| 0  | 0.6 | 820  | 20  | air  | 20  | 1.96 | 0.000 |
| 0  | 0.65 | 820  | 20  | air  | 20  | 2.07 | 0.015 |
| 0  | 0.7 | 820  | 20  | air  | 20  | 1.98 | 0.000 |
| 0  | 0.7 | 820  | 20  | air  | 20  | 1.98 | 0.000 |
| 0  | 0.7 | 820  | 20  | air  | 20  | 2.06 | 0.000 |
| 0  | 0.7 | 820  | 20  | air  | 20  | 2.03 | 0.000 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.16 | 0.439 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.13 | 0.409 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.10 | 0.314 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.08 | 0.240 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.04 | 0.143 |
| 0  | 0.75 | 820  | 100 | air  | 100 | 2.03 | 0.076 |
| 0  | 0  | 700  | 20  | O\(_2\) | 100 | 2.21 | 0.589 |
| 0  | 0.1 | 700  | 20  | O\(_2\) | 100 | 2.15 | 0.479 |
| 0  | 0.1 | 700  | 20  | O\(_2\) | 100 | 2.12 | 0.477 |
| 0  | 0.2 | 700  | 20  | O\(_2\) | 100 | 2.12 | 0.241 |
| 0  | 0.3 | 700  | 20  | O\(_2\) | 100 | 2.12 | 0.143 |
| 0  | 0.3 | 700  | 20  | O\(_2\) | 100 | 2.07 | 0.071 |
| 0  | 0.4 | 700  | 20  | Ar  | 0  | 2.09 | 0.211 |
| 0  | 0.4 | 700  | 20  | Ar  | 0  | 2.10 | 0.125 |
| 0  | 0.5 | 700  | 20  | Ar  | 0  | 2.06 | 0.112 |
| 0  | 0.5 | 700  | 20  | Ar  | 0  | 2.06 | 0.074 |
| 0  | 0.5 | 700  | 20  | Ar  | 0  | 2.03 | 0.078 |
| 0.2 | 0  | 820  | 20  | Ar  | 0  | 2.01 | 0.011 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.35 | 0.147 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.63 | 0.130 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.35 | 0.000 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.63 | 0.200 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.25 | 0.185 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.47 | 0.180 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.20 | 0.168 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.29 | 0.145 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.14 | 0.167 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.21 | 0.120 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.10 | 0.082 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.10 | 0.076 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.12 | 0.015 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.04 | 0.010 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.13 | 0.016 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.08 | 0.002 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.12 | 0.002 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.07 | 0.000 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.03 | 0.001 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.00 | 0.000 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 1.99 | 0.020 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 1.98 | 0.000 |
| 0.2 | 0 | 820  | 20  | Ar  | 0  | 2.04 | 0.000 |
| 0.2 | 0 | 500  | 20  | Ar  | 0 | 2 | 2.38 | 0.190 |
| 0.2 | 0 | 600  | 20  | Ar  | 0 | 2 | 2.33 | 0.250 |
| 0.2 | 0 | 700  | 20  | Ar  | 0 | 2 | 2.33 | 0.350 |
| 0.2 | 0 | 700  | 20  | Ar, O\(_2\) | 25 | 2.51 | 0.180 |
| 0.2 | 0 | 700  | 20  | Ar, O\(_2\) | 50 | 2.46 | 0.190 |
| 0.2 | 0 | 700  | 100 | O\(_2\) | 100 | 2.54 | 0.190 |
| 0.2 | 0 | 700  | 20  | Ar  | 0  | 2.46 | 0.123 |
| 0.2 | 0 | 700  | 20  | Ar  | 5  | 2.35 | 0.181 |
but remains constant from 2.2 < v < 2.63. The trend between 2.0 < v < 2.2 coincides with Mott-Hubbard theory. However, the trend between 2.2 < v < 2.63 does not.

Figure 6 shows the hole-doping scheme of the Pb-free and Pb-substituted Bi2212 phase. For the Pb-free Bi2212 phase, p increases as v increases because the holes are doped in the Cu layer. On the other hand, for the Pb-substituted Bi2212 phase, from 2.0 < v < 2.2, the Fermi energy of Cu decreases and the holes are doped in the CuO2 layer while the holes in the Pb layer remain constant. Note that the average Pb valence is assumed to be 3+ but is not measured in this study. However, p remains relatively constant at p = 0.10–0.20 between 2.2 < v < 2.63, which can be explained by a decrease in the Fermi energy of Pb instead of Cu. In other words, when v increases from 2.2 to 2.63, the holes are doped in Pb and not Cu. Similar to the Bi2201 phase, as the change in the Pb valence should be observable by XPS, we are planning to conduct an XPS experiment.

Table 3 lists the composition, sintering conditions, v and p of Bi1−xPbxCuxCa2ySr2−yCu3.06Oy, where v is controlled by varying the composition and the sintering conditions. It should be noted that the composition and sintering conditions when single-phase Bi2223 is formed is limited. In particular, Pb must be substituted for Bi.

Figure 7 shows the correlation between v and p of Bi1−xPbxCuxCa2ySr2−yCu3.06Oy. For the Bi2223 phase, p decreases with increasing v, which contradicts Mott-Hubbard theory. Figure 8 shows the hole-doping scheme of the Bi2223 phase. In contrast to Mott-Hubbard theory, p decreases with increasing v. This anomalous behavior can be explained by Pb-substitution, which is essential to prepare the Bi2223 phase. Similar to the Pb-substituted Bi2201 phase, the mixed valence state between Pb2+ and Pb4+ is assumed to coexist. As v increases, the Pb valence drastically increases. Consequently, the Cu valence decreases. The holes detected by the Hall effect originate in the CuO2 layer,1 suggesting that the holes are doped and trapped in

### Table 3. Composition, sintering conditions, formal valence, v and the number of holes per Cu, p of Bi1−xPbxCuxCa2ySr2−yCu3.06Oy

| Bi1−xPbxCuxCa2ySr2−yCu3.06Oy | Sintering condition |
|-------------------------------|---------------------|
| x y z w | Temperature [°C] | Time [h] | Atmosphere | v | p |
| 1.84 | 0.34 | 1.91 | 2.03 | 865 | 100 | air | 2.034 | 0.287 |
| 1.84 | 0.34 | 1.91 | 2.03 | 865 | 100 | air | 2.056 | 0.24 |
| 1.84 | 0.34 | 1.91 | 2.03 | 545 | 20 | O2 | 2.074 | 0.171 |
| 1.84 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.144 | 0.181 |
| 1.84 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.151 | 0.225 |
| 1.93 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.132 | 0.202 |
| 2.02 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.175 | 0.124 |
| 1.84 | 0.306 | 1.91 | 2.03 | 850 | 100 | air | 2.13 | 0.214 |
| 1.84 | 0.323 | 1.91 | 2.03 | 850 | 100 | air | 2.13 | 0.185 |
| 1.84 | 0.357 | 1.91 | 2.03 | 850 | 100 | air | 2.16 | 0.165 |
| 1.84 | 0.374 | 1.91 | 2.03 | 850 | 100 | air | 2.15 | 0.174 |
| 1.84 | 0.391 | 1.91 | 2.03 | 850 | 100 | air | 2.14 | 0.145 |
| 1.84 | 0.3408 | 1.91 | 2.03 | 850 | 100 | air | 2.15 | 0.171 |
| 1.84 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.177 | 0.073 |
| 1.84 | 0.34 | 1.95 | 2.03 | 850 | 100 | air | 2.213 | 0.080 |
| 1.84 | 0.34 | 2 | 2.03 | 850 | 100 | air | 2.207 | 0.116 |
| 1.84 | 0.34 | 1.91 | 1.93 | 850 | 100 | air | 2.165 | 0.150 |
| 1.84 | 0.34 | 1.91 | 1.98 | 850 | 100 | air | 2.159 | 0.184 |
| 1.84 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.103 | 0.100 |
| 1.84 | 0.34 | 1.91 | 2.03 | 850 | 100 | air | 2.177 | 0.073 |
| 1.84 | 0.34 | 1.95 | 1.99 | 850 | 100 | air | 2.213 | 0.080 |
| 1.84 | 0.34 | 2 | 1.94 | 850 | 100 | air | 2.207 | 0.116 |
| 1.86 | 0.34 | 2 | 2.03 | 850 | 100 | air | 2.124 | 0.170 |
| 1.843 | 0.357 | 2 | 2.03 | 850 | 100 | air | 2.120 | 0.177 |
| 1.826 | 0.374 | 2 | 2.03 | 850 | 100 | air | 2.134 | 0.180 |
| 1.809 | 0.391 | 2 | 2.03 | 850 | 100 | air | 2.135 | 0.175 |
| 1.792 | 0.408 | 2 | 2.03 | 850 | 100 | air | 2.132 | 0.151 |
| 1.84 | 0.391 | 2 | 2.03 | 660 | 60 | Ar, O2 | 2.280 | 0.069 |

Continued.
The Pb layer and have difficulty moving freely. As the change in the Pb valence should be observable by XPS, we are planning an XPS experiment.

From these results, two factors influence $p$. One is correlated with the substitution of Sr$^{2+}$ for La$^{3+}$ or Y$^{3+}$ for Ca$^{2+}$. The substitution changes the $p$ value and obeys the equation, $p = av$, ($a > 0$). That is, this factor is consistent with Mott-Hubbard theory. The other is correlated with the substitution of Pb$^{2+}/4+$ for Bi$^{3+}$, which changes the $p$ according to $p/v = -1$ or $p/v \geq 0$. For the Pb-substituted Bi2201 and Bi2223 phases, the trend, $b/v$ has a negative value around $-1$. On the other hand, for the Pb-substituted Bi2212 phase, the trend, $b/v$ has a positive value around 1 ($2.0 < v < 2.2$) or 0 ($2.2 < v < 2.63$). The difference may be explained by the substitution site. For the Pb-substituted Bi2201 and Bi2223 phases, substituted Sr$^{2+}$ or the excess oxygen is located in the block layer, whereas for Pb-substituted Bi2212, Ca$^{2+}$ is located between the CuO$_2$ layer, which may affect the trend of $p$ vs. $v$. By studying the trend for other cuprate superconductors, and calculating the Madelung potential around Cu and Pb, the reason for the difference should be elucidated.

4. Conclusion

Herein we investigated the Pb substitution effect on the electronic properties of the Bi2201, 2212, and 2223 phases. For the Pb-free Bi2201 phase, $p$ increases with increasing $v$. This tendency is consistent with Mott-Hubbard theory. The slope of the curve in $2.2 < v < 2.25$ is larger than that in $2.0 < v < 2.2$, which may be due to the change from a semiconductor to a metal. On the other hand, for the Pb-substituted Bi2201 phase, $v$ of Pb-substituted Bi2201 varies wildly from 2.1 to 2.8, while $v$ of the Pb-free Bi2201 phase changes from 2.0 to 2.25, suggesting that Pb substitution for Bi increases $v$. This increase can be explained by the substitution of Pb$^{2+}$ for Bi$^{3+}$. However, $p$ decreases with increasing $v$, which is inconsistent with Mott-Hubbard theory, but can be explained by the increase in Pb valence.

For the Pb-free Bi2212 phase, $p$ increases with increasing $v$, which is consistent with the previous data and agrees with Mott-Hubbard theory. On the other hand, for the Pb-substituted Bi2212 phase, $p$ increases with $2.0 < v < 2.2$ but remains constant for $2.2 < v < 2.63$. Although the trend coincides with Mott-Hubbard theory for $2.0 < v < 2.2$ of Pb-substituted Bi2212 phase, it is inconsistent for $2.2 < v < 2.63$. The anomalous trend may be explained by the following hole doping model. Similar to that of the Pb-free Bi2212 phase, when $v$ increases from 2.0 to 2.2, holes are doped in Cu. However, as when $v$ increases from 2.2 to 2.63, holes are doped in Pb and not Cu.

For the Pb-substituted Bi2223 phase, $p$ decreases as $v$ increases, which conflicts with Mott-Hubbard theory. It may be explained by Pb-substitution, which is essential to prepare the Bi2223 phase. As $v$ increases, the Pb valence also increases. Consequently, Cu valence decreases. The holes detected by the Hall effect originate from the CuO$_2$ layer, suggesting that the holes are trapped in the Pb layer and have difficulty moving freely. Similar to the Bi2201 and Bi2122 phases, as the change in the Pb valence should be observable by XPS, we are planning XPS experiments.

Two factors influence $p$. One is correlated with the substitution of Sr$^{2+}$ for La$^{3+}$ or Y$^{3+}$ for Ca$^{2+}$ and obeys Mott-Hubbard theory. The other is correlated with the substitution of Pb$^{2+}/4+$ for Bi$^{3+}$, which does not obey Mott-Hubbard theory. This difference may be explained by the substitution site. For the Pb-substituted Bi2201 and Bi2223 phases, the substituted Sr$^{2+}$ or Pb$^{2+}/4+$ is located in the block layer, whereas for Pb-substituted Bi2212, the substituted Ca$^{2+}$ is located between the CuO$_2$ layer. These influence the dominate trend of $p$ vs. $v$. The results strongly suggest that Pb substitution for Bi does not necessarily dope a hole but decreases the hole concentration.

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