

# An XPS Study on Hg-Doping Effect on Electronic Structure of BaPb<sub>0.75</sub>Bi<sub>0.25</sub>O<sub>3</sub> Superconductor

Y. Zhang<sup>1</sup>, C.H. Cheng<sup>2</sup>, Y. L. Chen<sup>1</sup>, Y.J. Cui<sup>1</sup>, H.T. Lin<sup>3</sup> and Y. Zhao<sup>1,2,\*</sup>

<sup>1</sup>Key Laboratory of Magnetic Levitation Technologies and Maglev Trains (Ministry of Education of China), Superconductivity R&D Center (SRDC), Mail Stop 165#, Southwest Jiaotong University, Chengdu, Sichuan 610031, China; <sup>2</sup>Superconductivity Research Group, School of Materials Science and Engineering, University of New South Wales, Sydney, 2052 NSW, Australia and <sup>3</sup>Faculty of Information Technology, Cheng Shui University, Kaohsiung, Taiwan

**Abstract:** The electronic structure of BaPb<sub>0.75-x</sub>Hg<sub>x</sub>Bi<sub>0.25</sub>O<sub>3</sub> (BPHBO) system is studied with x-ray photoemission spectroscopy (XPS). It is found that the core levels of Pb4*f* and O1*s* states shift towards low energy with the mercury doping induced, and at the meantime, the core level of Bi4*f* state shifts towards high energy. The results and analyses reveal that the mercury doping induces a systematic change of the electronic structure of the system, which consequently affects the superconductivity. Accordingly, the suppression of superconductivity at low doping level ( $x < 0.2$ ) is attributed to suppressed charge-disproportionate state whereas the recovery of the superconductivity in the doping level region  $0.3 < x \leq 0.4$  is due to a new M-I transition which converts the system from an insulating state to metallic one with the dominant carriers of charge being holes.

**Key Words:** X-ray photoemission spectroscopy, superconductor, Hg-substituted BaPb<sub>0.75</sub>Bi<sub>0.25</sub>O<sub>3</sub>.

## 1. INTRODUCTION

BaPb<sub>1-y</sub>Bi<sub>y</sub>O<sub>3</sub> (BPBO) is a copper-free oxide with infinite three dimensions perovskite-type structure, which shows superconductivity between  $y = 0$  and  $0.35$  with the maximum  $T_c$  of 12 K around  $y = 0.25$  [1-3]. The origin of the superconductivity in BPBO has not been settled yet. Different from high- $T_c$  cuprates and Fe-based oxides, the BPBO is dominated by *sp* electrons other than magnetic *d* electrons, excluding the possibility of magnetic pairing mechanisms. Understanding the electronic structure of BPBO is a necessary step to elucidate the mechanism of its superconductivity. So far many experimental studies have been performed on BPBO including doping effect experiments and x-ray photoemission spectroscopy (XPS) analysis [4,5] to understand the correlation of the superconductivity mechanism with its electronic structure. Although many elements have been investigated as a chemical dopant for BPBO system, no research has been reported on the doping effect of Hg in BPBO. The chemical properties of Bi, Pb and Hg are similar since they are very close in the period table, thus suggesting Hg being a potential dopant for Bi or Pb in BPBO. Therefore, it is interesting to explore if doping Hg can lead to what kind change to superconductivity in BPBO.

It is reported recently that the crystal structure and superconductivity of BPBO change systematically with Hg doping level [6]. However, the mechanism beneath the physical phenomena is not clear. With Pb being really substituted

with Hg in BPBO, the chemical environment or bonding state of the component elements must be different from that of BPBO. XPS provides us with a useful tool to obtain information about the electronic states and chemical shifts of the electronic compounds, therefore, is suitable for studying the doping effect of Hg on the electronic structure of BPBO.

In this work, XPS was used to study the chemical environment changes of the elements in BaPb<sub>0.75-x</sub>Hg<sub>x</sub>Bi<sub>0.25</sub>O<sub>3</sub> (BPHBO) with the composition for a better understanding of the changes of the electronic structure and superconductivity. A systematic study covering a wider composition range has been performed, which reveals that the variation of the superconducting transition temperature is closely correlated with the systematical change of the Fermi level of the BPBO system induced by Hg doping.

## II. EXPERIMENT

BaPb<sub>0.75-x</sub>Hg<sub>x</sub>Bi<sub>0.25</sub>O<sub>3</sub> compound with  $x=0, 0.10, 0.25, 0.30, 0.35, 0.40,$  and  $0.75$  were synthesized by a two-step method [6]: firstly forming a precursor of BaPb<sub>0.75-x</sub>Bi<sub>0.25</sub>O<sub>3</sub>, then reacting HgO with the precursor inside an evacuated quartz tube. The precursor was prepared by the solid-state reaction in which high-purity powders of BaCO<sub>3</sub>, Pb<sub>3</sub>O<sub>4</sub> and Bi<sub>2</sub>O<sub>3</sub> were thoroughly mixed and then heated in an alumina crucible at 720°C for 12h in flowing O<sub>2</sub> atmosphere. The precursor was mixed with HgO powder at a ratio of 1:  $x$  and reground, and then palletized into disks and sintered at 800°C in an evacuated quartz tube for 48h before slowly cooled down to room temperature.

The crystal structure was studied by X-ray powder diffraction (XRD) using a Philips X'Pert MRD diffractometer with CuK $\alpha$  radiation. The data revealed that the main phase

\*Address correspondence to this author at the Key Laboratory of Magnetic Levitation Technologies and Maglev Trains (Ministry of Education of China), Superconductivity R&D Center (SRDC), Mail Stop 165#, Southwest Jiaotong University, Chengdu, Sichuan 610031, China; Tel: +86-28-87600786; Fax: +86-28-87601824; E-mail: yzhao@swjtu.edu.cn

**Table 1.** The Doping Level,  $x$ , and the Superconducting Transition Temperature,  $T_c$ , for the Samples Used in this Study. NS Means the Sample is Nonsuperconducting Down to 1.9K

$x$	0	0.1	0.25	0.3	0.35	0.4	0.75
$T_c$ (K)	12.2	10.1	NS	NS	10.5	8.8	NS

was  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  with trace amounts of  $\text{Bi}_2\text{O}_3$  at high doping levels ( $x > 0.4$ ). It should be pointed out that the real chemical stoichiometry of the samples may be affected by various factors and need to be precisely determined, thus the composition of the samples presented in this study is only the nominal one although, within the error of the XRD analyses, it is quite close to the real chemical stoichiometry, especially for the samples with low doping levels ( $x < 0.4$ ).

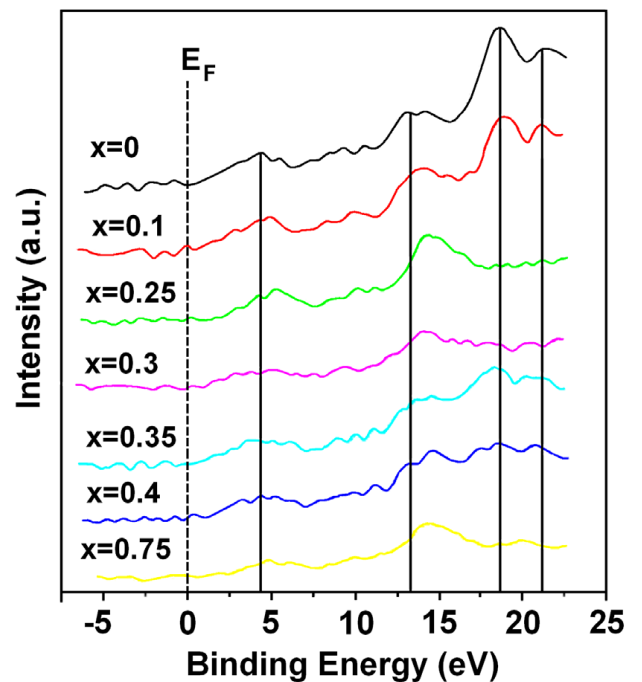
DC magnetization measurement was used to determine the superconducting transition temperature of the samples. The superconducting transition temperature of the samples used in this study is listed in Table 1. XPS measurements were performed using the Mg  $K\alpha$  line ( $h\nu = 1253.6$  eV) and photoelectrons were collected using a PHI DCMA. The shift of the binding energy due to surface charge effect was calibrated by assuming the binding energy of  $\text{C}1s$  to always be 284.6 eV. The base pressure in the spectrometer was  $3 \times 10^{-9}$  Torr. All the XPS measurements were performed at room temperature in order to avoid possible charge effect in the sample of low conductivity. The samples were ground into powder and then press into pellet for measurements.

### III. RESULTS AND DISCUSSION

Fig. (1) shows the XPS valence-band spectra for the BPHO samples with  $x = 0, 0.10, 0.25, 0.30, 0.35, 0.40$  and  $0.75$ . The spectra for  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$  consist of four main bands centered at around 4eV, 13eV, 18eV and 21eV, respectively, and it is clearly found that the main bands centered at around 4eV and 13eV shifted away the Fermi level,  $E_F$ , gradually by the substitution of mercury for lead. The shift between  $x=0$  and  $x=0.75$  is about 1eV for both main bands. It should be noted that, for  $x=0, 0.1, 0.35,$  and  $0.4$  samples which are superconducting, there are two peaks around 18eV and 21eV for these samples, and more interestingly, for  $x=0.25, 0.3$  and  $0.75$  samples which are nonsuperconducting, the two peaks disappear. As reported previously [6], superconductivity was observed for  $0.00 \leq x < 0.20$  and disappeared for  $0.2 < x \leq 0.3$ , and recovered for  $0.3 < x \leq 0.40$ . Therefore, it seems that there is a certain correlation between these two peaks and superconductivity. Furthermore, a clear Fermi edge is observed for  $x=0, 0.1, 0.35,$  and  $0.4$  samples, which indicates that these materials are highly metallic. On the other hand, for  $x=0.25, 0.3$  and  $0.75$ , the top of the valence bands does not reach to the Fermi level, which suggests a semiconductive feature of these materials. Such a situation is quite different from that in fluorine doped  $\text{SmFeAsO}$  system [7] where both superconducting and nonsuperconducting samples show highly metallic feature.

The shallow core-level spectra may be associated with the excitation of an electron from the ionic valence band with atoms of Ba, Pb, Bi and O since the energy levels of the states are approximately 1.0 eV for  $\text{Bi}6p^{1/2}$ , 1.0 eV for  $\text{Pb}6p$ , 3.0 eV for  $\text{Pb}6s$ , 3.2 eV for  $\text{Bi}6p^{3/2}$ , 7.0 eV for  $\text{O}2p$ , 10.0eV

for  $\text{Ba}5p$ , 19.0eV for  $\text{Pb}5d^{5/2}$ , 21.0eV for  $\text{Pb}5d^{3/2}$ , 23.1 eV for  $\text{O}2s$ , 24.0eV for  $\text{Bi}5d^{5/2}$ , and 26.0eV for  $\text{Bi}5d^{3/2}$ , respectively. Relatively, the ionic valence band with atom Hg is far away from the Fermi level, the contribution of the electrons from the Hg to the electronic states around Fermi level can be negligible. The peak at 4 eV below the Fermi level may be reasonably assigned to the hybridization of  $\text{Bi}6p^{1/2}$  (1.0eV),  $\text{Bi}6p^{3/2}$  (3.2eV),  $\text{Pb}6p$  (1.0eV) and  $\text{Pb}6s$  (3.0eV) with  $\text{O}2p$  (7.0eV), the 13eV band structure can be due to the hybridization of  $\text{Ba}5p$  (10.0eV) with  $\text{O}2s$  (23.1eV), the 18eV band structure can be due to the orbital of  $\text{Pb}5d^{5/2}$  (19.0eV), and the 21eV band structure due to the orbital of  $\text{Pb}5d^{3/2}$  (21.0eV). It can be seen from the structure of the valence-band spectra that both  $\text{Bi}6p$  and  $\text{Pb}6p$  dominate the electronic properties since the bands associated with the hybridization of  $\text{Bi}6p$ ,  $\text{Pb}6p$  and  $\text{Pb}6s$  with  $\text{O}2p$  are the nearest to the Fermi level of the system. As mercury is doped into the system, a clear energy shift away from  $E_F$  is observed for the four main bands in the valence-band spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$ . The energy shift away from  $E_F$  may be understood by considering the valence electrons of Hg being lower than those of Pb and Bi, which results in the decrease of the charge carriers (itinerant electrons) in this system. The presence of peaks at 18eV and 21eV in those superconducting samples indicates that the superconductivity correlates to the  $\text{Pb}5d$  electrons, which further indicates that Pb takes an important role to the superconductivity in BPBO system.



**Fig. (1).** Valence-band spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  measured by Mg $K\alpha$  line ( $h\nu = 1253.6$  eV) XPS for  $x = 0, 0.10, 0.25, 0.30, 0.35, 0.40,$  and  $0.75$ .

Fig. (2) shows the O1s core-level spectra of BPHBO samples with  $x = 0, 0.10, 0.25, 0.30, 0.35, 0.40$  and  $0.75$ . It was noted that the XPS spectra of O1s are cleaved. They can be decomposed into two peaks located at around 528 eV and 531 eV. The chemical shift associated with the photoelectron transitions is intimately linked with the effective atomic charge on the atoms probed. Let us consider the ratio,  $Z/r$ , of the ions bonded to the oxygen as a approximate measure of their ability to remove charge from the oxygen and, thus, increase the O1s binding energy (here  $Z$  being the nominal charge on the ion and  $r$  being the ion radius in nm). The  $Z/r$  values are 51.6 ( $\text{Pb}^{4+}$ ), 16.8 ( $\text{Pb}^{2+}$ ), 19.6 ( $\text{Hg}^{2+}$ ), 8.4 ( $\text{Hg}^+$ ), 29.1 ( $\text{Bi}^{3+}$ ), 65.8 ( $\text{Bi}^{5+}$ ) and 14.8 ( $\text{Ba}^{2+}$ ), respectively. On this simple basis we would expect that, the O1s binding energy is increase as this order:  $\text{Hg}_2\text{O} < \text{BaO} \approx \text{PbO} < \text{HgO} < \text{Bi}_2\text{O}_3 < \text{PbO}_2 < \text{Bi}_2\text{O}_5$ . According to the polarity of Ba-O, Pb-O and Bi-O bonds, it is easy for us to assign the peak with lowest binding energy to the oxygen associated with the Ba-O and Pb-O bond and to attribute the peak with higher binding energy to the oxygen affiliated with the Bi-O bond. It can be seen from Fig. (2) that the both peaks move to lower binding energy after Hg doping. This suggests that Hg doping at Pb site has influence on the chemical environment of both Pb and Bi atoms.

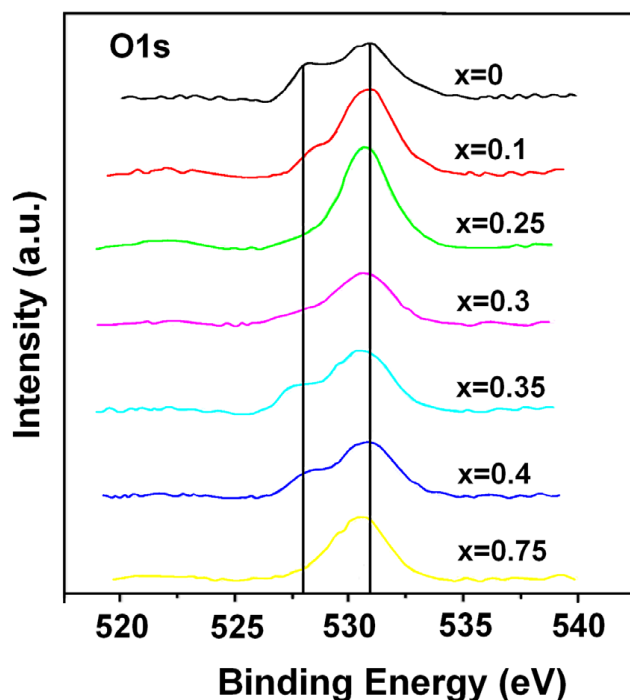


Fig. (2). O1s core-level spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  measured by  $\text{MgK}\alpha$  line ( $h\nu = 1253.6$  eV) XPS for  $x = 0, 0.10, 0.25, 0.30, 0.35, 0.40$ , and  $0.75$ .

Fig. (3) shows the Pb4f core-level spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$ . Because there is no Pb in the sample with  $x=0.75$ , the spectra are only for the samples with  $x = 0, 0.10, 0.25, 0.30, 0.35$  and  $0.40$ . The Pb4f photoemission is in fact split between two peaks, one at around 137.5eV binding energy attributed to  $\text{Pb}4f_{7/2}$  and the other at around 142.4 eV binding energy attributed to  $\text{Pb}4f_{5/2}$ , with an intensity ratio generally about 4:3. This arises from spin-orbit coupling effects in the final state. The inner core electronic configura-

tion of the initial state of the Pb is:  $[\text{Xe}](4f)^{14} (5d)^{10} (6s)2 (6p)^2$  with all sub-shells completely full. The removal of an electron from the 4f sub-shell by photo-ionization leads to a  $(4f)^{13}$  configuration for the final state. Since the f-orbital have non-zero orbital angular momentum, there will be coupling between the unpaired spin and orbital angular momentum. This spin-orbit splitting is of course not evident with s-levels, but is seen with p, d and f core-levels which all show characteristic spin-orbit doublets. From Fig. (3), it can be seen the dependence of the binding energy of  $\text{Pb}4f_{7/2}$  and  $\text{Pb}4f_{5/2}$  on the concentration of Hg in the samples. The binding energy of  $\text{Pb}4f_{7/2}$  and  $\text{Pb}4f_{5/2}$  monotonously decrease with the increase of Hg content. Usually, an increase of covalence of the compound may result in a smaller binding energy. This kind of effect is usually ascribed to a less efficient screening of the nuclear charge by electrons in other levels. In the present case, the decrease in efficient screening of  $\text{Pb}4f_{7/2}$  and  $\text{Pb}4f_{5/2}$  states indicates the decrease in the average electron density surrounding Pb atoms. This implies that the chemical characteristic of Pb-O bond is modified with the increase of Hg content in the samples, from more ionic bond at low Hg content transfers to more covalent bond at high Hg concentration. Accordingly, the decrease of the binding energy of  $\text{Pb}4f_{7/2}$  and  $\text{Pb}4f_{5/2}$  with the increase of Hg content is understandable. Due to the decomposition of HgO metal Hg which plays the role of reducer, the covalent degree of Pb-O bond (which is the result of polarization) in this oxide system will increase with Hg content. With increasing Hg doping level from  $x = 0$  to  $0.40$ , each  $\text{Pb}4f_{7/2}$  and  $\text{Pb}4f_{5/2}$  core level gradually moves to lower binding energy by 0.2-1.2 eV. More specifically,  $\text{Pb}4f_{7/2}$  line shifts towards  $E_F$  by 1.2eV from 137.5eV to 136.3eV and  $\text{Pb}4f_{5/2}$  line shift to  $E_F$  by 1.2eV from 142.4eV to 141.2eV as Hg doping level,  $x$ , increases from 0 to 0.4.

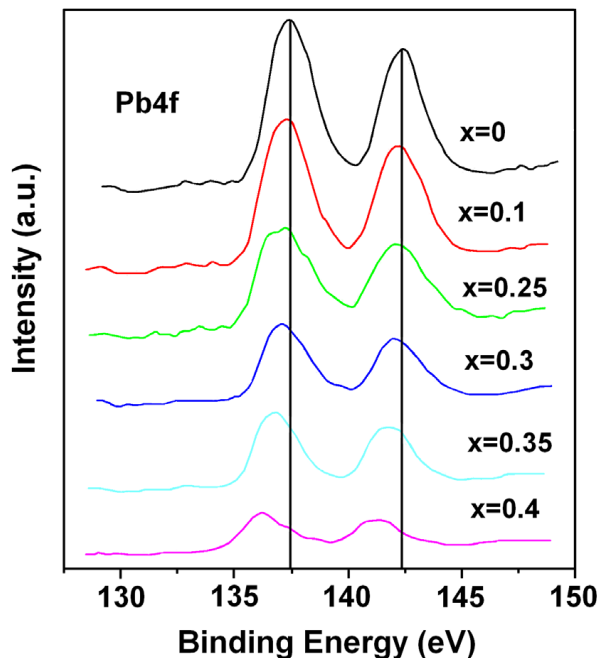


Fig. (3). Pb4f core-level spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  measured by  $\text{MgK}\alpha$  line ( $h\nu = 1253.6$  eV) XPS for  $x = 0, 0.10, 0.25, 0.30, 0.35$  and  $0.40$ .

The gradual decreasing in binding energies as increasing Hg content clearly indicate the smooth transition of the Pb-O bond from ionic to covalent states. The Pb4f spectrum have a slight asymmetry towards higher binding energy, which can be taken as an indication of a coupling of the core levels to excited states in the lower valence state of the PbO blocking [8].

Fig. (4) shows the Bi4f core-level spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  as a function of Hg content. The Bi4f spectrum consists of two multiple-split peaks, which also have a slight asymmetry towards higher binding energy in the Hg doped samples in the samples with a higher Hg doping level ( $x > 0.3$ ), which indicates that there is a tendency of the increase for the average valence of bismuth ions towards higher value. The average binding energy shift of Bi4f<sub>7/2</sub> lines around 158eV and Bi4f<sub>5/2</sub> lines around 163 eV is around 0.5 eV as  $x$  increases from 0 to 0.75.

The core levels for other elements such as Hg and Ba are also investigated (the results are not shown here), which show no detectable changes with increase doping level, thus indicates that the valence state and chemical environment are relatively insensitive to the doping level.

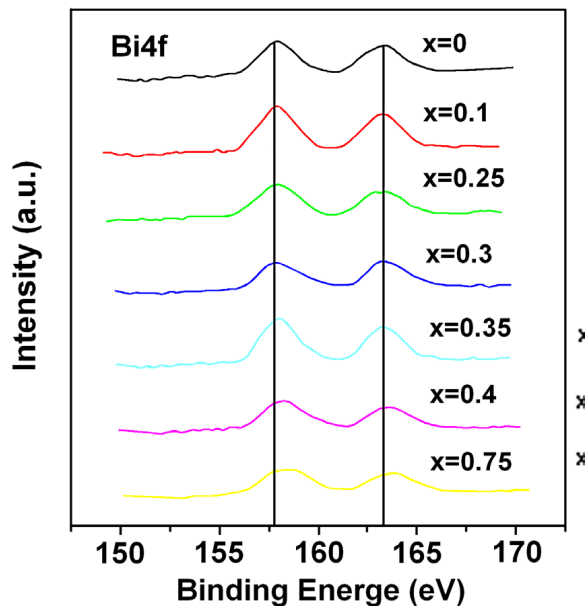


Fig. (4). Bi4f core-level spectra of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  measured by MgK $\alpha$  line ( $h\nu = 1253.6$  eV) XPS for  $x = 0, 0.10, 0.25, 0.30, 0.35, 0.40,$  and  $0.75$ .

In order to understand the mechanism of the binding energy shift in this system, Fig. (5) shows the doping level dependence of the binding energy shift,  $\Delta E_B$ , for O1s, Pb4f and Bi4f core levels. It is evident that, as the doping level  $x \leq 0.4$ , the binding energy shift for Pb4f,  $\Delta E_{B|\text{Pb}}$ , and the binding energy shift for O1s,  $\Delta E_{B|\text{O}}$  show a steady decrease with doping level, whereas the binding energy shift for Bi4f,  $\Delta E_{B|\text{Bi}}$ , displays a significant increase. At  $x > 0.4$ , the changes of the binding energy shifts for both  $\Delta E_{B|\text{O}}$  and  $\Delta E_{B|\text{Bi}}$  are getting slow. Usually, the binding energy shift  $\Delta E_B$  can be described by the formula below [9-11]:

$$\Delta E_B = \Delta\mu + K\Delta Q + \Delta V_M - \Delta E_R, \quad (1)$$

where  $\Delta\mu$  is the change in the chemical potential (or the shift of Fermi level,  $\Delta E_F$ ),  $K$  is the coupling constant of the Coulomb interaction between the valence and the core electrons,  $\Delta Q$  is the change in the number of valence electrons on the atom considered,  $\Delta V_M$  is the change in the Madelung potential, and  $\Delta E_R$  is the change in the extra-atomic relaxation energy. Here,  $K\Delta Q$  gives the so-called ‘‘chemical shift’’,  $\Delta E_R$  is due to changes in the screening of the core-hole potential by metallic-conduction electrons and polarizable surrounding ions. With the present  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  system, the substitution of Hg for Pb reduces the population of electrons to the system since the Hg has a valence of 2+ whereas Pb has both 2+ and 4+ valences in BPBO system [12-15]. This may induce the shift of the Fermi level to low energy direction. However, a part of Bi<sup>3+</sup> ions may transit to Bi<sup>5+</sup> to balance the decrease of the electrons in the system. It was pointed out that the charge-disproportionate state  $\text{Ba}_2(\text{Bi}^{3+}\text{Bi}^{5+})\text{O}_6$  in BPBO plays an important role for the electronic structure and the superconductivity in the system [12-15]. The binding energy shift for the core levels shown in Figs. (2-4) do reflect the modification of the electronic structure by Hg doping, which further affects the superconductivity of the system. Therefore, the influence of the Hg doping level on the Fermi level shift and the charge-disproportionate state of the system will be the most interesting and important information in this study. According to the analyses of the core levels for all of the elements of this system shown above and using Eq.(1), we can deduce the values for  $\Delta\mu$  and  $K\Delta Q_{|\text{Bi}}$ , except as here in after provided, the subscript behind the straight line ‘‘|’’ represents that the physical quantity is related to the specified atom. It is evident that  $K\Delta Q_{|\text{Bi}}$  is closely related to the change of the charge-disproportionate state of the BPBO system. Different from the layered compounds like SmFeAsO [7] in which only FeAs layers are conductive for electrons, BPBO is an isotropic system where charge carriers distribution in the system is relatively uniform. In this case, the screening effect of the conduction electrons on the core-level will be relatively weak. For simplicity,  $\Delta E_R$  in Eq.(1) is approximately taken as zero. In addition, the charge-disproportionate state is only related with the variation of the valence of Bi ions, instead of other

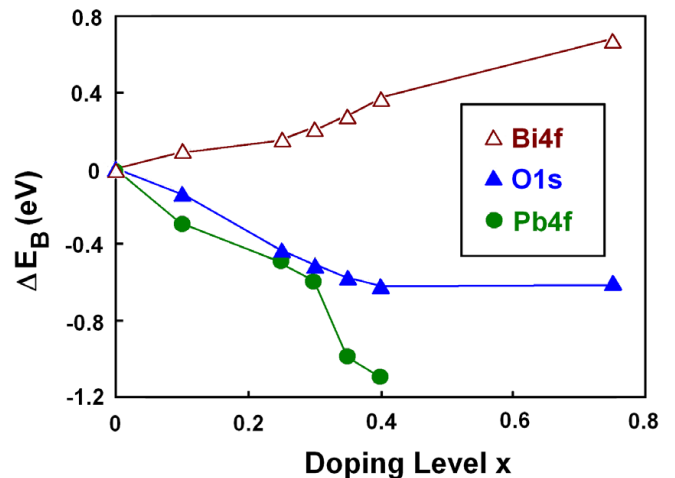
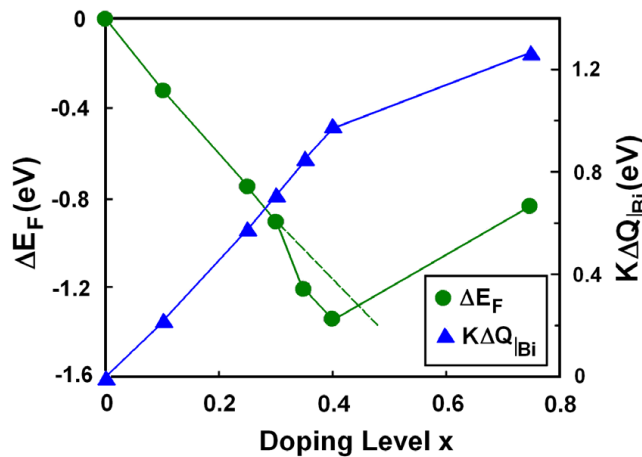


Fig. (5). Doping level dependence of the binding energy shift,  $\Delta E_B$ , for O1s, Pb4f and Bi4f core levels in  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  system.

elements. This means the change in the number of valence electrons in other elements in the system can be taken as zero. In such a circumstance, it can be deduced that  $\Delta\mu \approx (\Delta E_{B|Pb} + 2\Delta E_{B|O} - \Delta E_{B|Bi})/2$  and  $K\Delta Q_{|Bi} \approx \Delta E_{B|Bi} - \Delta E_{B|O}$ . For the sample of  $x=0.75$  which contains no Pb at all,  $\Delta\mu$  and  $K\Delta Q_{|Bi}$  is determined by the binding energy shift of the core levels of Bi, O, and Ba. Based on these two formula and the binding energy of the core-levels shown in Figs. (2-4), the variation of  $\Delta\mu$  (or  $\Delta E_F$ ) and  $K\Delta Q_{|Bi}$  with doping level can be obtained.

Fig. (6) shows the doping level dependence of Fermi level shift,  $\Delta E_F$ , and the change of charge-state of Bi ions in BPHBO system. The Fermi level shows a steady decrease with Hg doping level before  $x \leq 0.4$ . This may be due to the substitution of Hg for Pb which reduces the population of electrons to the system since the Hg has a valence of 2+ whereas Pb has both 2+ and 4+ valences in BPBO system [12-15]. It is interesting to note that at  $x=0.35$ , the Fermi level displays a deviation from the linear decrease and begins to drop more rapidly, contrasted to the relatively slow reduce in the low doping level region ( $0 < x < 0.3$ ). In addition, at  $x=0.75$ , the Fermi level begins to move up to higher energy. All these indicate that there may be some unusual change of the electronic structure of the system at these points. Different from the Fermi level shift, the change of the charge state of Bi ions,  $K\Delta Q_{|Bi}$ , show a nearly linear increase with doping level at  $x \leq 0.4$ . This indicates that a part of  $Bi^{3+}$  ions have transited to  $Bi^{5+}$  state to balance the decrease of the electrons in the system. In BPBO system, a special situation is that there exists always equal amount of  $Bi^{3+}$  and  $Bi^{5+}$  ions [16], which keeps the charge-disproportionate state  $Ba_2(Bi^{3+}Bi^{5+})O_6$  to sustain the superconductivity of the system. A significant change of the charge state of Bi ions,  $K\Delta Q_{|Bi}$ , indicates that the balance of  $Bi^{3+}$  and  $Bi^{5+}$  has been broken, which induces the steady suppression of superconductivity. However, such an explanation cannot explain the recovery of superconductivity at  $0.3 < x \leq 0.4$ , more detailed changes of the electronic structure of the system should be taken into account.



**Fig. (6).** Doping level dependence of the Fermi level shift,  $\Delta E_F$ , and the change of the change state of Bi,  $K\Delta Q_{|Bi}$ , for  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  system. The dashed line is the extrapolation of the linear decrease of  $\Delta E_F$  at low doping level.

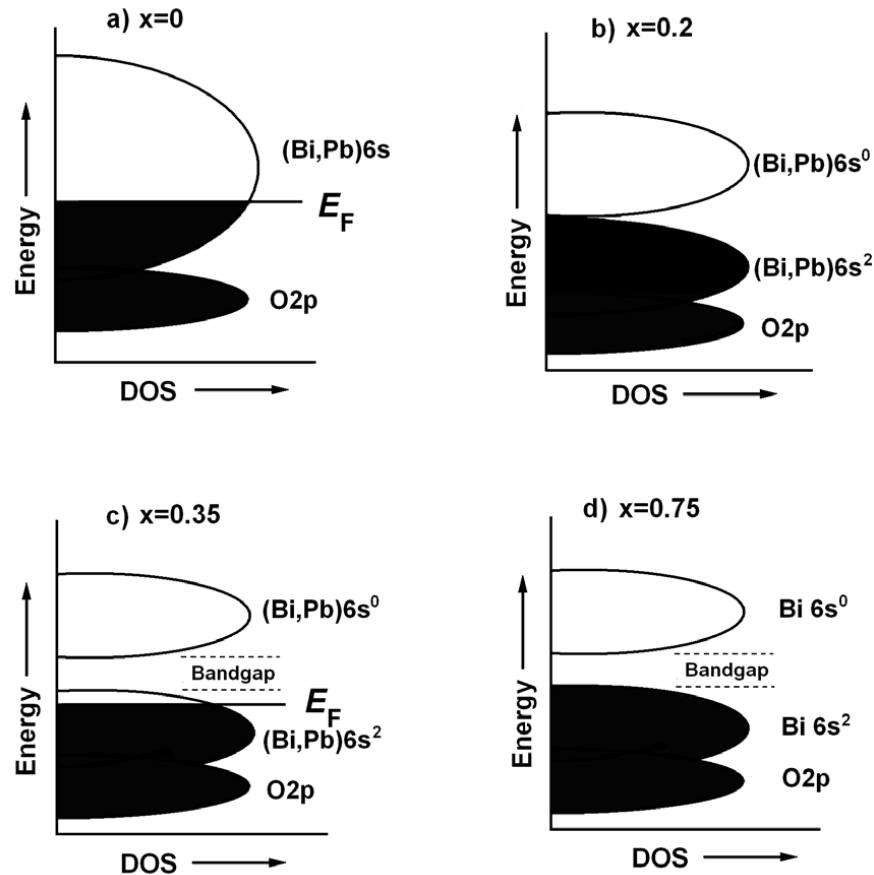
In order to understand the unusual change of superconductivity with the doping level in  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$ , the

electronic structure around the Fermi level should be examined. As revealed by the valence band shown in Fig. (1),  $Pb6s$ ,  $Pb6p$ ,  $Bi6s$ ,  $Bi6p$ , and  $O2p$  orbitals should have contribution to the band structure around the Fermi level. According to the band structure proposed for the  $BaPb_{1-y}Bi_yO_3$  at  $y < 0.3$  [17], the hybridization of the  $O2p$  with  $Bi6s$  and  $Pb6s$  electron constructs an electron-type conduction band (see Fig. 7a). With increasing Hg content, the Fermi level decreases, and at the meantime, the unit cell of the  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  is expanded [6], which reduces the inter-atomic overlap and consequently makes the band narrowed. Therefore, with increasing the Hg doping level, both the Fermi level and the band widths continuously decrease, and split into two sub-bands at  $x \approx 0.2$  with the upper band empty and the lower band full. The upper band is denoted as  $6s0$  band and the lower band denoted as  $6s2$  band (see Fig. 7b). The metal-insulator (M-I) transition in the  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  system is very similar to the M-I transition in the  $BaPb_{1-y}Bi_yO_3$  at  $y \approx 0.35$  [17]. Further increasing Hg content in the doping region of  $0.2 < x < 0.3$  keeps the insulator-like band structure with an expanded band gap. However, different from the situation in  $BaPb_{1-y}Bi_yO_3$  which keeps an insulator-like band structure at the whole range of  $y > 0.35$ , the  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  occurs a new M-I transition at  $x > 0.3$  by entering a hole-type conduction band (see Fig. 7c). This explains the recovery of the superconductivity at  $x > 0.3$  and suggests that the charge carriers of the system becomes hole dominant at  $x > 0.3$ . At  $x=0.75$ , the Fermi level is increased compared to the value at  $x=0.4$ , indicating that the hole-type conduction band is filled again (see Fig. 7d).

The above results and analyses for the  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  system show that at low doping level with  $x < 0.2$ , Hg doping decreases the Fermi level and breaks the balance of the  $Bi^{3+}$  and  $Bi^{5+}$  which is believed to be the base of the charge-disproportionate state  $Ba_2(Bi^{3+}Bi^{5+})O_6$ , and consequently suppresses the superconductivity. At the meantime, the band width decreases and splits into two sub-bands at  $x \approx 0.2$  with the upper band empty and the lower band full, resulting a M-I transition at  $x \approx 0.2$  which converts the system from a metal to an insulator. The recovery of superconductivity at  $x > 0.3$  is due to another M-I transition which converts the system from an insulator to a metal. These two metallic states are different with the former being electron-dominant and the later hole-dominant. The formation of the hole-dominant metallic state may be the consequence of the competition between the band filling effect and the modification of the charge-disproportionate state, both are induced by Hg doping. The former has a tendency to reduce the Fermi level whereas the later has an opposite effect. Due to an unchanged total amount of Bi atoms in all of the samples, the system can sustain a sufficiently wide band even when a large amount of Pb is replaced by Hg. This provides a possibility for the occurrence of a hole-dominant conduction band, as shown above. Further study is necessary to investigate the effect of the charge-disproportionate state  $Ba_2(Bi^{3+}Bi^{5+})O_6$  on the superconductivity in the hole-dominant region and understand the mechanism underpinning.

#### IV. CONCLUSION

XPS has been used to investigate the band structure features of  $BaPb_{0.75-x}Hg_xBi_{0.25}O_3$  superconductor and the changes of the band structure by various amounts of mercury



**Fig. (7).** Schematic representation of energy levels of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  for  $x=0$  (a),  $x=0.2$  (b),  $x=0.35$  (c), and  $x=0.75$  (d).

substituting for lead. The valence band of  $\text{BaPb}_{0.75-x}\text{Hg}_x\text{Bi}_{0.25}\text{O}_3$  show four peaks below the Fermi level at 4eV, 13eV, 18eV and 21eV, respectively, which corresponds to the  $\text{Bi}6p$ - $\text{O}2p$ ,  $\text{Pb}6p$ - $\text{O}2p$ ,  $\text{Pb}6s$ - $\text{O}2p$ ,  $\text{Ba}5p$ - $\text{O}2s$ ,  $\text{Pb}5d_{5/2}$  and  $\text{Pb}5d_{3/2}$  electrons, respectively. The core levels of  $\text{Pb}4f$  and  $\text{O}1s$  states shifting towards low energy can be attributed to the mercury doping induced Fermi level shift, but the core level of  $\text{Bi}4f$  state shifting towards high energy may be due to the broken balance between the  $\text{Bi}^{3+}$  and  $\text{Bi}^{5+}$  states. The core levels for other elements such as Hg and Ba are found no significant movement. The results and analyses show that the suppression of superconductivity at low doping level ( $x < 0.2$ ) is attributed to suppressed charge-disproportionate state whereas the recovery of the superconductivity in the doping level region  $0.3 < x \leq 0.4$  may be due to a new M-I transition which converts the system from an insulating state to metallic one with the dominant carriers of charge being holes.

#### ACKNOWLEDGEMENTS

The authors are grateful for the financial support of the National Natural Science Foundation of China under Grant No's. 50588201 and 50872116, the National Basic Research Program of China (Program 973 under Grant No. 2007CB616906), the PCSIRT of the Ministry of Education of China (IRT0751), and Australian Research Council under Grant No's. DP0559872 and DP0881739. Y. Zhang and Y.L. Chen are also grateful for the financial support of the Inno-

vation Fund for Ph.D. Students of Southwest Jiaotong University.

#### REFERENCES

- [1] Tajima S, Uchida S, Masaki A, *et al.* Optical study of the metal-semiconductor transition in  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ . *Phys Rev B* 1985; 32: 6302-11.
- [2] Tajima S, Uchida S, Masaki A, *et al.* Electronic states of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$  in the semiconducting phase investigated by optical measurements. *Phys Rev B* 1987; 35: 696-703.
- [3] Chaillout C, Santoro A, Remeika J P, Cooper A S, Espinosa G P, Marezio M. Bismuth valence order-disorder study in  $\text{BaBiO}_3$  by powder neutron-diffraction. *Solid State Commun* 1988; 65: 1363-9.
- [4] Nagoshi M, Fukuda Y, Suzuki T, *et al.* Photoemission-study on  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_{3-\delta}$  and  $\text{BaPb}_x\text{Bi}_{1-x}\text{O}_{3-\delta}$ . *Phys C* 1991; 185: 1051-2.
- [5] Kobayashi K, Mizokawa T, Ino A, *et al.* Doping dependence of the electronic structure of  $\text{Ba}_{1-x}\text{K}_x\text{BiO}_3$  studied by x-ray-absorption spectroscopy. *Phys Rev B* 1999; 59: 15100-6.
- [6] Chen Y L, Cui Y J, Cheng C H, Zhang Y, Lin H.T, Zhao Y. Superconductivity in Hg-substituted  $\text{BaPb}_{0.75}\text{Bi}_{0.25}\text{O}_3$ . *Phys Lett A* 2008; (in press).
- [7] Zhang Y, Chen Y L, Cui Y J, Cheng C H, Zhang H, Zhao Y. A study on Fe-based superconductor  $\text{SmFeAsO}_{1-x}\text{F}_x$  by x-ray photoelectron spectroscopy. *Supercond Sci Technol* 2009; 22: 015007.
- [8] G. Rietveld, S. J. Collocott, D. van der Marel, Driver R, van der Marel D. Doping dependence of the chemical-potential in cuprate high- $T_c$  superconductors 2.  $(\text{Bi,Pb})_2\text{Sr}_2\text{Ca}_2\text{O}_{10-\delta}$ . *Phys C* 1995; 241: 273-8.
- [9] Hüfner S. *Photoelectron Spectroscopy*. Springer-Verlag: Berlin, 2003.
- [10] Fujimori A, Ino A, Matsuno J, Yoshida T, Tanaka K, Mizokawa T. Core-level photoemission measurements of the chemical potential shift as a probe of correlated electron systems. *J Electron Spectrosc Relat Phenom* 2002; 124: 127-38.

- [11] Ebata K, Wadati H, Takizawa M, *et al.* Chemical potential shift and spectral-weight transfer in  $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$  revealed by photoemission spectroscopy. *Phys Rev B* 2006; 74: 064419-1-6.
- [12] Rice T M, Sneddon L. Real-space and k-space electron pairing in  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ . *Phys Rev Lett* 1981; 47: 689-92.
- [13] Yoshioka D, Fukuyama H. A simple-model for superconductor-semiconductor transition. *J Phys Soc Jpn* 1985; 54: 2996-3003.
- [14] Mattheiss L F, Hamann D R. Electronic-structure of  $\text{BaPb}_{1-x}\text{Bi}_x\text{O}_3$ . *Phys Rev B* 1983; 28: 4227-31.
- [15] Noack R M, Scalapino D J, Scalettar R T. Charge-density-wave and pairing susceptibilities in a 2-dimensional electron-phonon model. *Phys Rev Lett* 1991; 66: 778-81.
- [16] Fu W F, Drost R J. Superconductivity in the  $\text{BaPb}_{1-x}\text{Bi}_{x/2}\text{Sb}_{x/2}\text{O}_3$  system. *Phys C* 1998; 304: 51-4.
- [17] Fu W T. Crystal chemistry of bismuthate-based superconductors: the origin of (local) charge disproportionation. *Phys C* 1995; 250:67-74.

---

Received: November 26, 2008

Revised: December 29, 2008

Accepted: February 5, 2009

© Zhang *et al.*; Licensee Bentham Open.

This is an open access article licensed under the terms of the Creative Commons Attribution Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0/>) which permits unrestricted, non-commercial use, distribution and reproduction in any medium, provided the work is properly cited.