

## Role of Pb in High- $T_c$ Bi-based Superconductors

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An investigation of the variation of hole concentration within the  $\text{CuO}_2$  planes using X-ray absorption near-edge structure (XANES) spectroscopy with synchrotron radiation in the  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  [(Bi,Pb)-2212] series of high- $T_c$  superconductors synthesized by solid state reaction in air is presented. Pb is found to have the valence of 2+ in the samples of this series. Moreover, the hole concentration increases with increasing Pb content. The results lead us to conclude that the substitution of  $\text{Pb}^{2+}$  in the  $\text{Bi}^{3+}$  sites of the (Bi,Pb)-2212 system causes the compounds to be in the over-doped state. This effect results in the compounds having a high critical current density.

PACS numbers: 74.60.Jg, 74.60.Mj, 74.70.-b

### I. INTRODUCTION

The Bi-based superconductors  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2(n+2)}$  have been widely studied in recent years [1, 2]. Among these compounds, the  $n = 2$  member (i.e.,  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ ; Bi-2212) is particularly attractive for practical applications in terms of its high  $T_c$  value, stability and relative ease of synthesis. Aside from  $T_c$ , another important for industrial applications is the transport critical current density  $J_c$ . Several methods have been used to enhance  $J_c$ , such as elemental substitution, changing processing conditions, etc.

Among these methods, Pb inclusion was thought to be a useful way to enhance  $J_c$ . Manivannan *et al.* [3] have shown that substitution of a large amount of Pb leads to modulation-free Bi-based superconductors. Chong *et al.* [4] have reported that the substitution of Pb at the Bi-site enhances  $J_c$  by the introduction of platelike domains having a modulation-free structure. However the Pb doping could also cause the hole concentration to increase, and the hole concentration was known responsible for the change of  $J_c$  value [5]. For a better understanding of the reason for the enhancement of  $J_c$  with Pb substitution, we have studied the variation of the hole concentration in the system  $(\text{Bi,Pb})_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  [(Bi,Pb)-2212] using the X-ray absorption near edge structure (XANES) spectroscopy. Furthermore, Crossley *et al.* [6] have reported that syntheses for Pb-containing Bi-2212 compounds in low oxygen content environment can enhance Pb solubility in the Bi-2212 phase. Also, T. Motohashi *et al.* [7] have reported the Pb inclusion in low oxygen pressure can improve the  $T_c$  value of Bi-2212 phase. In order to study the Pb inclusion property under different atmosphere, samples of (Bi,Pb)-2212 series sintered under nitrogen atmosphere have also been synthesized to study the effect of atmosphere. Crossley *et al.* [6] used only X-ray diffraction (XRD) to monitor the change. In this study, a systematic study of the atmosphere effect in (Bi,Pb)-2212 on hole variation has been performed.

## II. EXPERIMENTAL DETAILS

### II-1. (Bi,Pb)-2212 sintered in air

Samples of the  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  series with  $0.0 \leq x \leq 0.5$  were synthesized by the conventional solid state reaction method. All the samples were sintered at  $815^\circ\text{C}$  for 192 h in air with an intermediate grinding after every 24 h. The samples were analyzed by powder X-ray diffraction. For  $x = 0.0 \sim 0.2$ , the samples are confirmed as a single phase. The variation of  $T_{c,\text{onset}}$  was measured by a Quantum Design SQUID magnetometer. Bulk-sensitive fluorescence-yield XANES measurements at the O K-edge and Pb-LI edge were performed at the NSRRC, Taiwan [8].

### II-2. (Bi,Pb)-2212 sintered under nitrogen

Samples of the  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  series with  $0.2 \leq x \leq 0.6$  were also synthesized by the same method, but sintered at  $750^\circ\text{C}$  for 60 h in nitrogen and then annealed at  $650^\circ\text{C}$  for 2 h in air. The samples were also analyzed by powder X-ray diffraction, susceptibility measurement and measurement and XANES spectroscopy.

## III. RESULTS AND DISCUSSION

### III-1. (Bi,Pb)-2212 sintered in air

For the present conditions of synthesis, the compositions with  $0 \leq x \leq 0.2$  were found to be of single phase. For  $x > 0.2$ , the  $\text{Ca}_2\text{PbO}_4$  phase appears, which shows that the solubility of Pb in  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  is about  $x = 0.2$ . Hence, we focus on the analysis of the samples in the range  $0 \leq x \leq 0.2$ . The intensity of the superlattice peak decreases with increasing Pb, showing that the addition of Pb reduces the superlattice behavior.

The  $T_{c,\text{onset}}$  decreases slightly from 79 K for  $x = 0.0$  to 76 K for  $x = 0.2$ . This trend is consistent with the observation of Chong *et al.* [4]. Fig. 1 shows the Pb L-edge XANES spectra of the series  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$ , together with the spectra of the standards PbO (where Pb has the valence of +2) and  $\text{PbO}_2$  (Pb in the 4+ valence state). It can be seen that spectra of  $x = 0.1$  and  $0.2$  are close to that of PbO, rather than that of  $\text{PbO}_2$ . This suggests that the valence of Pb in the compositions under study is +2.

Fig. 2 shows the O K-edge XANES spectra for  $0 \leq x \leq 0.2$ . The spectra mainly consist of a pre-edge peak around 528 eV and a broad peak above 530 eV. The pre-edge peak arises from a transition from the  $3d^9\bar{L}$  to  $O1s3d^9$  states ( $\bar{L}$  represents a hole in an  $O2p_{x,y}$  orbital). From polarization experiments, it was seen that the major contribution to this transition is from the  $\text{CuO}_2$  planes rather than apical CuO chains. Furthermore, the transition is directly related to the hole concentration within  $\text{CuO}_2$  planes. Thus the integrated area of the pre-edge peak is the indicator for change in the hole concentration. The pre-edge peak of each spectrum was fitted using a Gaussian function. The rest of the spectrum arises from antibonding  $\text{Bi}6p_{x,y,z}$ -O and other  $O2p$  bands [9], which can be resolved into

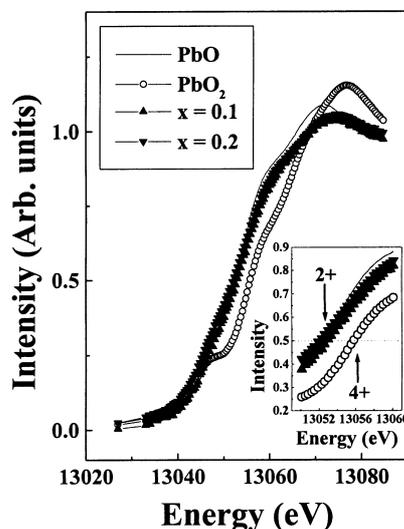


FIG. 1: Pb  $L_1$ -edge XANES spectra of the series  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$ ,  $x = 0.1$  and  $0.2$ , together with the spectra of the standards  $\text{PbO}$  and  $\text{PbO}_2$ .

seven peaks. The relative intensities of the last four peaks remain unchanged throughout the series and were hence chosen for normalization of the area of the pre-edge peak. The normalized relative intensity of pre-edge peak for each composition is shown in the embedded figure of Fig. 2. From this figure, it can be seen that the hole concentration, which is proportional to the intensity of the pre-edge peak, increases with Pb content. Combining this result with the trend of decrease in  $T_c$ , we can conclude that Pb doped Bi-2212 is in the overdoped region. According to the [4], the high  $J_c$  is caused by Pb columnar defects, and the hole concentration is a minor factor for the increase of  $J_c$ . But for similar compounds  $\text{Bi}_2\text{Sr}_2(\text{Ca}_{1-x}\text{Y}_x)\text{Cu}_2\text{O}_y$  [8] and the superconductor  $(\text{Y}_{1-x}\text{Ca}_x)\text{Ba}_2\text{Cu}_3\text{O}_y$  [10], it was seen that an increase in hole concentration is responsible for the high  $J_c$  and no columnar defects were observed in those compounds. We thus conclude that the  $J_c$  enhancement by Pb doping in Bi-2212 is mainly caused by an increase in hole concentration.

### III-2. (Bi,Pb)-2212 sintered under nitrogen

As confirmed by XRD, all the compounds under nitrogen synthesis were found to be of single phase. It is noted that after air annealing, only the sample with  $x = 0.2$  has the same composition as those before air annealing. When  $x > 0.2$ , the peak of  $\text{Ca}_2\text{PbO}_4$  appears, indicating that the incorporated Pb is released out of the (Bi,Pb)-2212 phase during air annealing. These results are consistent with the data reported by Crossley *et al.* [6] and the result in part 1.

Fig. 3 shows the O K-edge XANES spectra of  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  for  $0.2 \leq x \leq 0.6$  under nitrogen and air atmosphere. It is noticed that in air-annealed compounds the

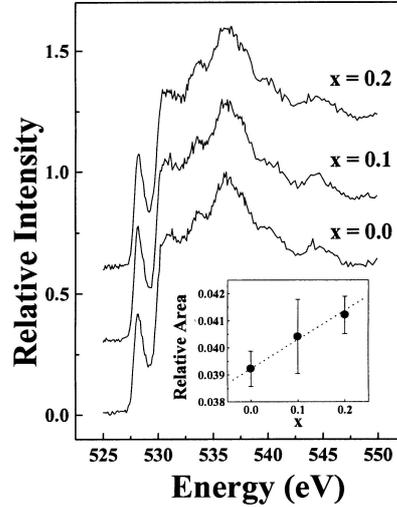


FIG. 2: O K-edge XANES spectra of the series  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$ ,  $0 \leq x \leq 0.2$ . The embedded figure shows the relative area of the pre-edge peak in the spectra.

peak around 530.5 eV is mainly contributed from oxygen in  $\text{Ca}_2\text{PbO}_4$  (as shown in XANES spectrum for standard compound), not from Bi-2212.

Fig. 4 shows the Cu  $L_3$ -edge XANES spectra of  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  for  $0.2 \leq x \leq 0.6$  under nitrogen and air atmosphere. As noted, the Cu  $L_3$ -edge absorption spectra are asymmetric and one shoulders exhibit at the high-energy side of the main peak. The shoulder (as indicated by the dash line in Fig. 4) is ascribed to transition from the  $\text{Cu}(2p_{3/2})3d^9\bar{L}$  ground state into the  $\text{Cu}(2p_{3/2})^{-1}3d^{10}\bar{L}$  excited state (where  $\bar{L}$  denotes a ligand hole in the O  $2p$  orbital). The spectral weight of this shoulder is a direct indicator of total hole concentration on both the in-plane and out-of-plane oxygen of cuprate superconductors.

From the O K-edge and Cu L-edge results, it has been found that when  $x = 0.2$  the hole concentration after air annealing does not change significantly, indicating that the Pb content remains constant during the annealing process. When Pb content is more than 0.2, the hole concentration decreases after air annealing. This might imply that the incorporated Pb is released out of the (Bi,Pb)-2212 phase. Comparing the O K-edge spectra before and after air annealing, the peak at  $\sim 530.5$  eV appears in air-annealed samples. This indicates the presence of  $\text{Ca}_2\text{PbO}_4$  (as shown by arrow in Fig. 3). It confirms that Pb is released out of the (Bi,Pb)-2212 phase after air annealing and forms  $\text{Ca}_2\text{PbO}_4$  in samples with  $x > 0.2$ . From the observation of these spectra, we can conclude that the Pb solubility in  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  can be enhanced by synthesizing under nitrogen atmosphere, which can be increased up to  $x = 0.6$ . After annealing in air, the solubility decreases to  $x = 0.2$  and the excess Pb forms  $\text{Ca}_2\text{PbO}_4$ . Accordingly, the Pb content can be tuned via changing the oxygen content of annealing atmosphere and monitored via XANES spectroscopy.

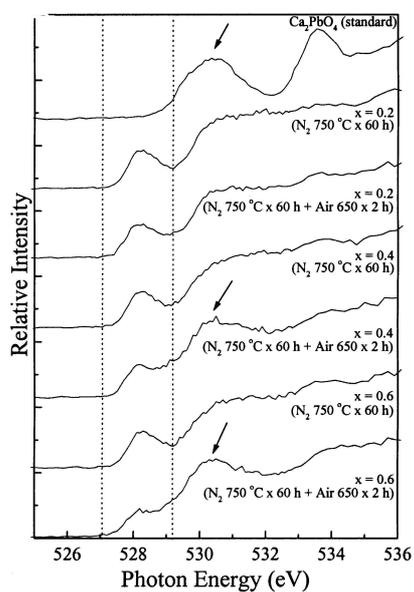


FIG. 3: O K-edge XANES spectra of the series  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$ ,  $0.2 \leq x \leq 0.6$ . The peak indicated by arrows originates from oxygen signal of  $\text{Ca}_2\text{PbO}_4$ .

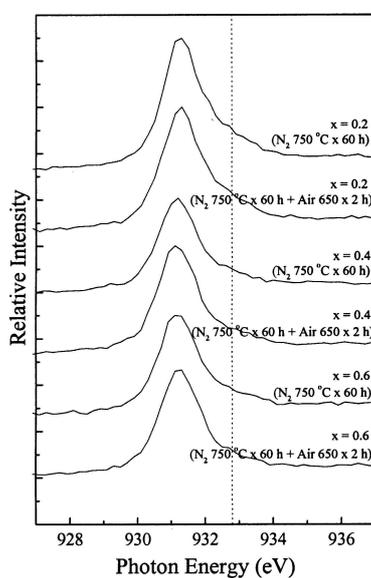


FIG. 4: Cu  $L_3$ -edge XANES spectra of the series  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$ ,  $0.2 \leq x \leq 0.6$ . The shoulder is indicated by the dash line.

#### IV. CONCLUSION

We have successfully synthesized the  $(\text{Bi}_{2-x}\text{Pb}_x)\text{Sr}_2\text{CaCu}_2\text{O}_y$  [(Bi,Pb)-2212] series of high- $T_c$  superconductors by solid state reaction in air and nitrogen. By using X-ray absorption near-edge structure (XANES) spectroscopy with synchrotron radiation, Pb is found to have the valence of 2+ in air-treated samples. Moreover, the Pb content can be tuned via changing the oxygen content of annealing atmosphere and the hole concentration will increase with ascending Pb content. The results lead us to conclude that the substitution of  $\text{Pb}^{2+}$  in the  $\text{Bi}^{3+}$  sites of the (Bi,Pb)-2212 system causes the compounds to be in the over-doped state.

#### Acknowledgments

We thank National Science Council under the contract No. of NSC 92-2113-M-002-036 (Taiwan) for the financial support.

#### References

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- [1] P. J. Majewski, S. Kaesche, and F. Aldinger, *J. Am. Ceram. Soc.* **80**, 1174 (1997).
  - [2] H. Fujii, H. Kumakura, and K. Togano, *Jpn. J. Appl. Phys.* **39**, 2591 (2000).
  - [3] V. Manivannan, J. Gopalakrishnan, and C.N.R. Rao, *Phys. Rev. B* **43**, 8686 (1991).
  - [4] I. Chong, Z. Hiroi, M. Izumi, J. Shimoyama, Y. Nakayama, K. Kishio, T. Terashima, Y. Bando, and M. Takano, *Science* **272**, 770 (1997).
  - [5] R. S. Liu, I. J. Hsu, J. M. Chen, and R. G. Liu, *Physica C* **341-348**, 383 (2001).
  - [6] A. L. Crossley, Y. H. Li, A. D. Caplin, and J. L. MacManus-Driscoll, *Physica C* **314**, 12 (1999).
  - [7] T. Motohashi, Y. Nakayama, T. Fujita, K. Kitazawa, J. Shimoyama, and K. Kishio, *Phys. Rev. B* **59**, 14080 (1999).
  - [8] I. J. Hsu, R. S. Liu, J. M. Chen, R. G. Liu, L. Y. Jang, J. F. Lee, and K. D. M. Harris, *Chem. Mater.* **12**, 1115 (2000).
  - [9] J. Fink, N. Nucker, E. Pellegrin, H. Romberg, M. Alexander, and M. Knupfer, *J. Electron Spectrosc. Relat. Phenom.* **66**, 395 (1994).
  - [10] J. L. Tallon, G. V. M. Williams, and J.W. Loram, *Physica C* **338**, 9 (2000).