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## EXAFS studies of (Pb,Cd)1212 phase superconductor and (Bi,Cd)1212 phase compound

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We synthesized (Pb,Cd)Sr<sub>2</sub>(Y,Ca)Cu<sub>2</sub>O<sub>7+x</sub> phase superconductor. After substitution of Pb with Bi, the BiCd1212 phase shows no superconductivity. Although previous EXAFS study has shown the local structure environment of the Cu is similar in both compounds, EXAFS results of Bi and Pb here demonstrate that  $\sigma^2$  of Pb-O<sub>in-plane</sub> is larger than that of Bi-O<sub>in-plane</sub>, whereas  $\sigma^2$  of Pb-O<sub>apical</sub> is smaller than that of Bi-O<sub>apical</sub>. The Sr shell features are also different. It appeared that superconductivity needs some disorder in carrier reservoir layer, which is due to the substitutional defect caused by different ionic radii.

**Keywords:** High Tc superconductor; XAFS; disorder; PbCd1212; BiCd1212.

### 1. Introduction

In the history of high-Tc superconductors' synthesis, the chemical substitution has a great help not only in the enhancement of transition temperature but also in the understanding of the high Tc superconducting mechanism. It is interesting to know the influence of local structure changes on the superconducting properties.

We have successfully synthesized (Pb,Cd)Sr<sub>2</sub>(Y,Ca)Cu<sub>2</sub>O<sub>7+x</sub> phase superconductor. After substitution of Pb with Bi, the BiCd1212 phase shows no superconductivity. XRD result was unable to explain this phenomenon. Also, the previous EXAFS studies (Sun, H., 1997) has shown that the local structure of the Cu is similar in both compounds. So, it is worthy to investigate what causes PbCd1212 phase superconducting but not BiCd1212. Here we demonstrate the results of local environment around Pb and Bi determined by the EXAFS, which may help us to answer this question.

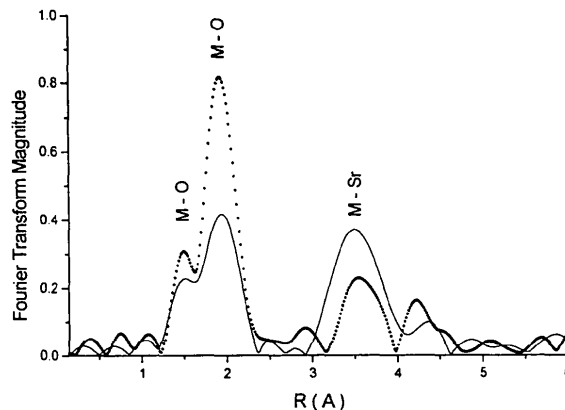
### 2. Experimental

Samples were prepared by sol-gel routine according to nominal composition (M<sub>0.5</sub>Cd<sub>0.5</sub>)Sr<sub>2</sub>(Y<sub>0.7</sub>Ca<sub>0.3</sub>)Cu<sub>2</sub>O<sub>7+x</sub> (M=Pb, Bi). L<sub>III</sub> edge XAFS measurements were performed in transmission at beam line BL-10B of Photon Factory using Si(111) double crystal monochromator.

XAFS was analyzed by use of EXCURV92, incorporated in the Cerious<sup>2</sup> MSI software package. The Energy dependent normalization was carried out after the step normalization and isolation of EXAFS by dividing the energy dependent cross section.

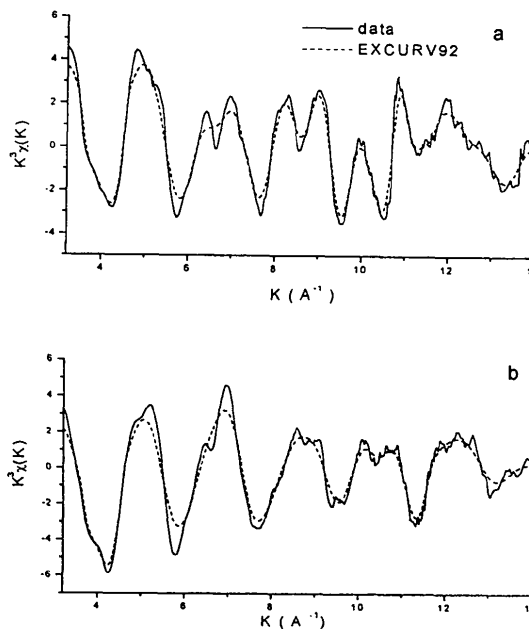
### 3. Results and Discussion

The PbCd1212 phase has the superconducting transition temperature of 77 K, while the BiCd1212 sample showed no superconductivity down to 2K. XRD pattern of as-prepared samples, with few of peaks of impurity, can be fitted using a space group of P4/mmm with tetragonal unit cell of a=3.81 Å and c=11.90 Å for PbCd1212 phase, and a=3.82 Å and c=11.88 Å for BiCd1212 phase.



**Figure 1**

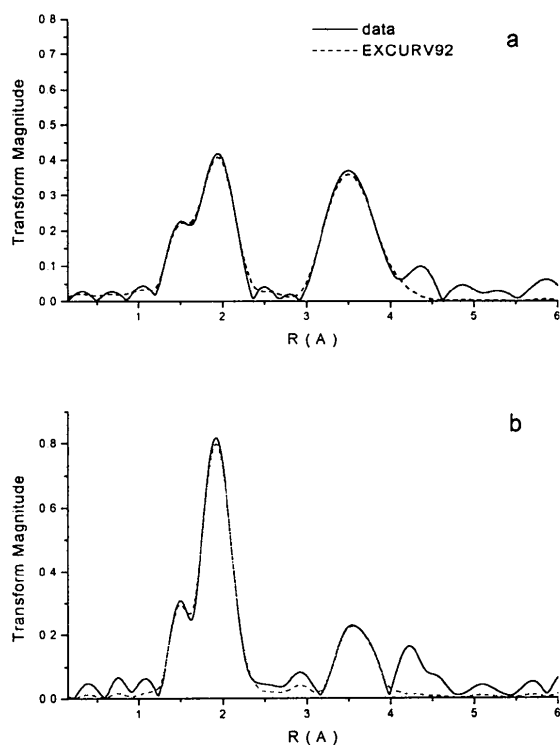
Comparison of Fourier transform magnitude of  $K^3\chi(k)$  using  $\Delta K = 3-14 \text{ \AA}^{-1}$  data for both of Pb (solid) and Bi (dotted) L<sub>III</sub> edges. O shell and Sr shell are indicated (M = Pb or Bi).



**Figure 2**

Refinement fit for  $K^3\chi(K)$  of (a) Pb L<sub>III</sub> edge and (b) Bi L<sub>III</sub> edge.

Because Pb and Bi are neighbor atoms in atomic number and their phase shift and back-scattering amplitudes are almost similar, we compare their radical distribution function (Figure 1). It is obvious that there is a big difference in the local structure of the two compounds. Fitting results are presented in Figure 2, Figure 3 and Table 1.



**Figure 3**  
Refinement fit for RDF around (a) Pb and (b) Bi.

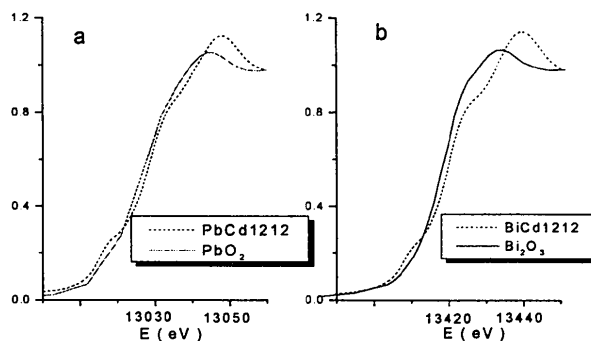
**Table 1**

EXAFS fitting results table for Pd1212 and Bi1212. Estimated standard deviations are given in brackets.

		N	R(Å)	$2\sigma^2$ (Å <sup>2</sup> )
PbCd1212	Pb-O(2)	2	1.95(2)	0.011(2)
	Pb-O(3)	4	2.121(5)	0.039(5)
	Pb-Sr	8	3.62(2)	0.026(5)
BiCd1212	Bi-O(2)	2	1.90(1)	0.018(4)
	Bi-O(3)	4	2.190(4)	0.012(2)
	Bi-Sr	8	3.81(2)	0.033(7)

In the fitting procedure, the coordination number is fixed. Six oxygen atoms surround Pb or Bi to form an octahedron. Two are apical oxygens, Bi(Pb)-O(2) and other four in-plane, Bi(Pb)-O(3). The main difference lies in the value of  $\sigma^2$ . Oxygen in plane of rocksalt PbCdO layer obviously has a larger disorder compared with that of BiCdO layer, whereas the apical oxygen of PbCdO layer shows more order than that of BiCdO layer. More, the Sr shell disorder is larger than that of Pb1212. The difference in disorder in rocksalt layer is so obvious but the reason is unclear.

Fig.4 shows the  $L_{III}$  edges XANES of Pb and Bi.  $L_{III}$  edge of Bi shifts to high energy region by about 5 eV compared to the  $Bi_2O_3$ , while that of Pb moves about 3eV compared to the  $PbO_2$ .



**Figure 4**  
XANES of (a) Pb and (b) Bi  $L_{III}$  edge. Solid line ( $PbO_2$  and  $Bi_2O_3$ ) and Dashed line (samples).

Typically edge shift by about 5-7eV at  $L_{III}$  edge means a valence change of 1. However there is no bismuth oxide standard of the +4 valence state, here we can only conclude from XANES results that the oxidation state of Bi in Bi1212 compound is 4. In the view of the effective ionic radii, for CN=6, Bi(III) radius is 1.03 Å and Pb(IV) radius is 0.78 Å, but Cd(II) radius is 0.95 Å (Shannon,R.D., 1976). There is no data about the Bi(IV) ionic radius. In general, as oxidation state increase, the radius will decrease. We estimate, from Shannon's data base of the effective ionic radii, that Bi(IV) radius is around 0.9 Å, which is close to the ionic radius of Cd(II). Therefore, we speculate that the larger difference between ionic radius of Pb(IV) and Cd(II) would give rise to the substitutional defect, which lead to the larger disorder in PbCdO layer.

Copper oxide can be viewed consisting of the conducting layer and carrier reservoir layer, corresponding to CuO layer and (Pb/Bi)CdO layer, respectively. From EXAFS results, it appears that the disorder in rocksalt layer is necessary to the superconducting properties.

The existence of a strong interplay between superconducting properties and crystal structure, lattice distortions, defects, or local vibrational properties are well known. XAFS has played a relatively important role in the study of disorder effects in high  $T_c$  superconductor. Most works are concentrated in the  $CuO_2$  plane. (Haskel, D.,1998; Sperandini F., 1998; Currie, D.B., 1998). As to our knowledge, few of EXAFS investigations have been presented on rocksalt layer of our system. IR and Raman spectroscopy has been used to study the effect of vibration mode of Pb1212. Yu (1994) found that the increase of  $Pb-O(3)_{in-plane}$  and  $Pb-O(2)_{apical}$  disorder is associated with the insulator to superconductor transition. Huang (1993) reported the neutron powder diffraction results on  $YSr_2AlCu_2O_7$  superconductor showing that the O(3) in rocksalt layer has small disorder.

In summary, it is concluded that the structural difference between superconducting Pb1212 and non superconducting Bi1212 lies in the difference in degree of disorder. The difference in disorder may be due to the substitutional defect. Larger in-plane disorder of PbO layer results in the generation of hole-carriers easily. On the other hand, larger order in both apical oxygen and SrO layer makes it easier for the conduction of carriers. These two factors may play a major role in superconductivity in PbCd1212 sample and no superconductivity in BiCd1212.

To elucidate the relation between the disorder and the superconductivity, further research is needed, such as the local structure of Cd in both of these compounds.

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