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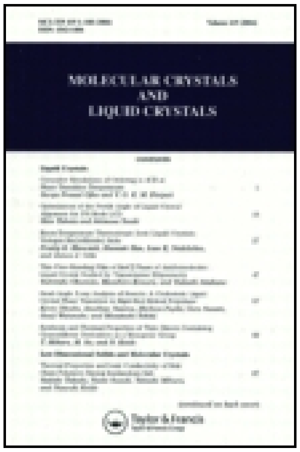

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Intercalation Route to New Hybrid Organic-Inorganic Superconductors

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Recently, we have successfully synthesized new type of high-T_c superconductors of $(HgX_2)_{0.5}Bi_2Sr_2Ca_{m-1}Cu_mO_y$(X=Br, I, and m = 1, 2) by means of intercalation technique. From the X-ray diffraction(XRD) and X-ray absorption spectroscopy(XAS) analyses, we found that the intercalated mercuric halides are stabilized as the isolated gaseous molecules in the interlayer space of superconducting lattice, leading to an increase of basal spacing. A small amount of charge transfer between guest molecule and host lattice could be observed upon intercalation with a slight depression of T_c. For the extension of metal halide intercalation into high-T_c, superconductor, we have developed new type of hybridized superconducting nanohybrid with periodic stacking of organic and superconducting layer by stepwise synthetic approach, where organic compounds are stabilized in the form of organic-inorganic complex salt in-between Bi-O double layers of Bi-based high- T_c cuprates. The synthetic strategy proposed here can be applicable to many other layered systems.

Keywords: intercalation; tetraiodomercurate; interblock complexation; interlayer distance..

INTRODUCTION

The intercalation of mercuric halide molecules into $Bi_2Sr_2CaCu_2O_y$ leads not only to an increase of basal spacing (Δd = 6-7Å) but also to a slight charge transfer from host lattice to guest molecule resulting in $(HgX_2)^{\delta-}$, which was confirmed by XRD and XAS analysis for the intercalates[1,2]. Further more, the existence of molecular $HgBr_2$ in-between the two-dimensional superconducting lattice was also proved by the Raman spectroscopic study on $HgBr_2$-Bi2212. According to the magnetic susceptibility measurement, all the HgX_2 intercalates are superconducting with a slight depression of T_c (ΔT_c = 5-7 K) compared to the iodine intercalate (Δd = 3.6 Å, ΔT_c = 13 K)[3] Such a T_c change is strongly related to the variation of hole concentration upon intercalation. The iodine intercalate also showed spectroscopic evidence of electronic charge transfer from host lattice to intercalant layer leading to I_3^-.[4]

Based on this finding, more recently, we have intercalated organic compounds into the Bi-based cuprates in the form of the complex organic salt containing aromatic rings, $(Ar\text{-}R)_2HgI_4$. In this study, new type of high-T_c intercalation compounds are investigated.

EXPERIMENTAL SECTION

The pristine $Bi_2Sr_2CuO_x$ (Bi2201) and $Bi_2Sr_2CaCu_2O_y$ (Bi2212) were synthesized by conventional solid state reaction with the nominal composition of $Bi_2Sr_{1.6}La_{0.4}CuO_x$ and $Bi_2Sr_{1.5}Ca_{1.5}Cu_2O_y$. First, the polycrystalline Bi2212 or Bi2201 pellet, mercuric iodide, and free iodine(mol ratio of 1:5:1) were placed in a Pyrex tubes and then vacuum sealed. The $(HgI_2)_{0.5}Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m=1, 2) were prepared by two step heating at 190 °C for 2 hours and then 240 °C for 4 hours. Second, HgI_2 intercalates were mixed with two molar equivalents of iodide salt of aromatic base $Ar^+\text{-}R$ I^- ($R = -CH_3$) which was prepared by reacting molar equivalents of

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alkyliodide and aromatic base in diethyl-ether. Then, the polar solvent like acetone was slightly added into this mixture in order to expedite the intercalation reaction. The solvent containing mixture was reacted in a closed ampoule at 40 -70°C for 6 hours and washed with a mixed solvent of acetone and diethyl-ether in order to remove the excess reactant Ar^+-R I^- and a small amount of complex salt $(Ar\text{-}R)_2HgI_4$ expelled from the Bi_2O_2 double layer. The resulting products were dried in vacuum. The samples are stable in air, which makes the characterizations of their physico-chemical properties easier.

RESULT AND DISCUSSION

According to the electron probe microanalysis (EPMA) and elemental analyses for C, H, and N, the chemical formula of organic-salt intercalates were determined to be $[(Ar\text{-}R)_2HgI_4]_{0.35}Bi_2Sr_2CaCu_2O_y$. The formation of stage-1 organic intercalates were confirmed by powder X-ray diffraction analysis. The superconducting properties of the intercalates were examined by dc SQUID magnetometer. XAS analyses were performed to investigate the local structure of intercalated Hg species.

Powder X-ray Diffraction

Fig. 1 shows powder X-ray diffraction pattern for Bi2212 and its intercalates. From the least square fittings to XRD patterns, it is found that all the intercalates are single-phasic. Each intercalated organic spacer layer expands the unit cell along the c-axis by 10.8 Å(~70%), but makes little effect on the in-plane *a* and *b* parameters (both 5.4 Å) estimated from (020) and (220) diffraction peaks are not changed before and after the intercalation.

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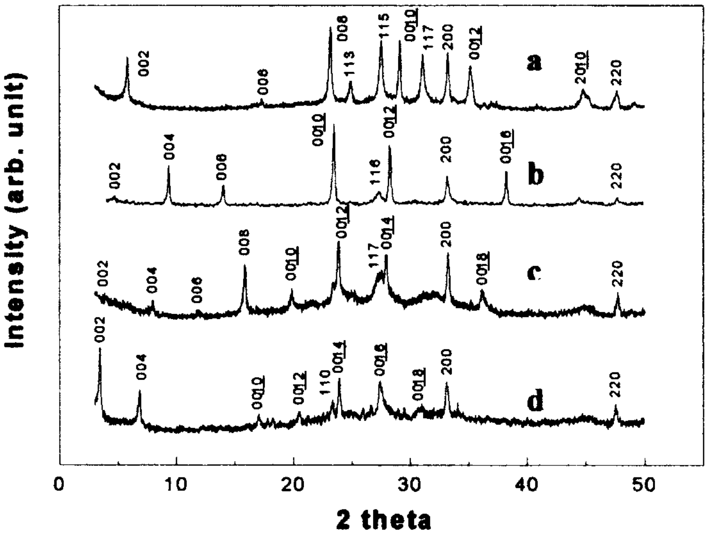

FIGURE 1 Powder X-ray diffraction patterns for the pristine Bi2212 and its intercalates. From the powder X-ray diffraction patterns, the basal spacing could be determined to be 15.3, 18.9, 22.5, and 26.1 Å for Bi2212(a), IBi2212(b), HgI_2-Bi2212(c), and $[(Ar\text{-}R)_2HgI_4]$-Bi2212(d), respectively

X-ray absorption spectroscopy(XAS)

The local structure around mercury in the intercalated layer was investigated by performing the Hg L_{III}-edge extended X-ray absorption fine structure(EXAFS) analysis for the mercuric iodide intercalates and the organic-salt ones together with the reference compounds, free HgI_2 and $(Ar\text{-}R)_2HgI_4$. From the Hg L_{III}-edge EXAFS analysis for HgI_2-Bi2212 and $(Ar\text{-}R)_2HgI_4$-Bi2212, we have found that the two coordinated Hg in the former changes to four coordinated one in the latter, indicating the formation of tetrahedral anion[5] HgI_4^{2-}. This result indicates that the complexation

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reaction occurs in the interlayer space inbetween the superconducting block. In order to explore the change in oxidation state of CuO_2 plane, the Cu K-edge X-ray absorption near edge structure(XANES) analysis was performed for the pristine Bi2212 and its organic intercalate, but no appreciable differences could be seen in both spectra, indicating that the electronic structure of superconductive CuO_2 plane is not changed after the interlayer complexation reaction.

dc-magnetic susceptibility

According to the zero-field-cooled (ZFC) dc magnetic susceptibilities of the pristine Bi2212 and its intercalates, no T_c depression could be observed for the organic intercalate $(Ar\text{-}R)_2HgI_4$-Bi2212($T_c \approx 81$ K), whose phenomenon is obviously distinguished from IBi2212 and HgI_2-Bi2212. For Bi2212 and its intercalate, interlayer distance between CuO_2 planes and T_c are summarized in Table I

TABLE I Interlayer distance and T_c for Bi2212 and its intercalates

Compound	Interlayer distance(Å)	T_c(K)
Bi2212	12	78
IBi2212	16	65
HgI_2-Bi2212	20	68
$(Ar\text{-}R)_2HgI_4$-Bi2212	23	81

It is worthy to note here that the evolution of T_c upon intercalation does not depended on the interlayer distance, but depend on the nature of the intercalant. We also measured the magnetic susceptibility for the Bi2201 and its intercalates, where T_c variation shows the same trends as the Bi2212

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series. In this respect, we could conclude that T_c is mainly dependent on the charge carrier density of CuO_2 plane[6], rather than the interlayer coupling effect[7].

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References

[1.] J. H.Choy, N. G. Park, S. J.Hwang, D. H. Kim, and N. H.Hur, *J. Am. Chem. Soc.* **116**,11564 (1994).
[2.] J. H. Choy, S. J. Hwang, and N. G. Park, *J. Am. Chem. Soc.* **119**,1624(1997).
[3.] X. -D. Xiang, S.McKernan, W. A.Vareka, A. Zettl, J. L. Corkill, T.W. Barbee III, and M. L.Cohen, *Nature* **348**, 145 (1990).
[4.] J. H. Choy, S. G. Kang, D. H. Kim, and N. H. Hur, in Superconducting materials, edited by J. Etourneau, J, -B. Torrance, and H. Yamauchi, (IITT International, Paris, 1993), P335.
[5.] M. Körfer, H. Fuess, and J. W. Bats, *Z. Anorg. Allg. Chem.* **354**,104 (1986).
[6.] M. Di Stasio, K. A. Muller, and L. Pietronero, *Phys. Rev. Lett.* **64**, 2827 (1990).
[7.] J. M Wheatly, T. C. Hsu, and P. W. Anderson, *Nature* **333**, 121(1988).
[8.] R. Arnek, and D. Poceva, *Acta Chem. Scand.*, Ser. A, **30**, 59 (1976).