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X-Ray Absorption Spectroscopic Study of New High- T_c Superconducting Intercalation Compound of $(\text{HgX}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ ($\text{X} = \text{Br}, \text{I}$)

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Abstract. We have systematically performed X-ray absorption spectroscopic (XAS) studies on the new mercuric halide intercalated superconductors, $(\text{HgX}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, with $\text{X} = \text{Br}$ and I , in order to investigate the electronic and crystal structures of these compounds. According to the $\text{I L}_{1,2}$ - and Br K -edge X-ray absorption near edge structure (XANES) spectroscopic analyses, it is found that a small amount of electron is transferred from the intercalant HgX_2 to the host lattice, resulting in the negatively charged state of $(\text{HgX}_2)^\delta$. The Cu K -edge extended X-ray absorption fine structure (EXAFS) analysis reveals that the bond distance of $(\text{Cu-O}_{\text{axial}})$ is slightly shortened upon intercalation, reflecting the oxidation of CuO_2 layer, which is well consistent with the $\text{I L}_{1,2}$ - and Br K -edge XANES results. On the other hand, the present Hg L_{111} -edge EXAFS results indicate that the mercury is coordinated with two bromide or iodide ligands with bond length of 2.46 Å for the HgBr_2 -intercalate and 2.65 Å for the HgI_2 -one, respectively. This is the first example of linear molecular salt of HgX_2 stabilized in the solid lattice.

1. INTRODUCTION

Since the intercalation reaction provides an effective method to modify the chemical and physical properties of host materials, it has been extensively applied to the studies of two-dimensional solids. Recently it has become an important and increasingly used method for developing new high- T_c superconductors as well as for studying the high- T_c superconductivity of layered cuprate compound.[1-2] More recently we have successfully synthesized new type of high- T_c superconducting compounds of M-X-Bi-Sr-Ca-Cu-O ($\text{M} = \text{Hg}, \text{Ag}$ and $\text{X} = \text{Br}, \text{I}$) with hybridized crystal lattice of a superconducting and an insulating/superionic conducting layer.[1-2] Among these new series of intercalates, the HgX_2 -derivatives have attracted much interest due to their very small T_c depression even with large basal increment. In order to understand the relation between T_c /lattice expansion or T_c /hole concentration, a systematic study on the chemical bonding nature and crystal structure of these intercalates, closely related to the superconducting properties of high- T_c materials, is urgently needed.

In this work, we have performed the X-ray absorption spectroscopic studies for the HgX_2 intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, in order to investigate the evolution of the electronic and geometric structure of guest and host upon intercalation.

2. EXPERIMENTAL

The HgX_2 intercalated $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ compounds were prepared by heating the $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ pellet and mercuric halide (mole ratio of 1:5) in a vacuum sealed Pyrex tube as described previously.[1] The formation of the first staged intercalate was monitored by the X-ray diffraction (XRD) with a Philip PW1050 spectrogoniometer using Ni-filtered $\text{Cu K}\alpha$ radiation. The amount of guest species introduced into the host lattice was determined by thermogravimetric analysis (TGA) using DuPont 2000 Thermal Analysis Station. The evolution of superconductivity upon intercalation was examined by the dc magnetic susceptibility and the resistivity measurements. X-ray absorption experiments were carried out on the beam lines 7C and 10B at the Photon Factory, National Laboratory for High Energy Physics (KEK-PF) in Tsukuba with a storage ring running at 2.5 GeV with a stored current of ca. 260 ~ 370 mA.

3. RESULTS AND DISCUSSION

According to the XRD analyses, the c-axis unit cell parameter is determined to be 30.6 Å for the pristine, while 43.2 Å and 44.9 Å for $(\text{HgBr}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ and $(\text{HgI}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, corresponding to an increase of ~12.6 Å and ~14.3 Å, respectively. Since there are two intercalated layers of HgX_2 for each unit cell of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$, the lattice expansion per mercuric halide layer is 6.30 Å for HgBr_2 intercalate and 7.15 Å for HgI_2 one, those which are almost twice as large as that upon iodine intercalation (3.6 Å). The figure 1 shows the dc magnetic susceptibilities of the pristine $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ and their intercalates as a function of temperature. Distinct diamagnetic transitions, indicating the advent of superconductivity, are observed at the temperature of 71 K for the HgBr_2 intercalate and 68 K for the HgI_2 one, respectively, those which are slightly lower than that for the pristine $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ ($T_c \approx 76$ K) but higher than that for the iodine intercalate ($T_c \approx 63$ K). Only a slight T_c depression ($\Delta T_c = 5 \sim 8$ K) upon HgX_2 intercalation compared to iodine one ($\Delta T_c = 13$ K) suggests strongly that

there exists different interaction between host lattice and guest layer. In this respect, we have carried out the I L₁- and Br K-edge XANES analyses which are very sensitive even to a small modification of electronic structure of halogen layer.

Figures 2a and 2b present the I L₁-edge XANES 2nd derivative spectra of the HgI₂ intercalate and the reference HgI₂, and the Br K-edge XANES 2nd derivative spectra for the HgBr₂ intercalate and the reference HgBr₂, respectively. All the present spectra exhibit the white line peak A, corresponding to the transition from 2s (1s) level into 5p (4p) state. It has been well known that the intensity of the peak A is proportional to the density of unoccupied 5p (4p) state.[3] Therefore, the depression of the pre-edge peak A upon intercalation indicates that the intercalant layer receives the electron from the host lattice. Another evidence of charge transfer between host and guest can be obtained from the Cu K-edge EXAFS analysis. From the curve-fitting analysis, it is found that the out-of-plane (Cu-O) bond distance of the pristine (2.36₄ Å) is remarkably decreased upon intercalation (2.34₈ Å for HgBr₂ intercalate and 2.33₈ Å for HgI₂ one), reflecting the oxidation of CuO₂ layer which is closely related with T_c evolution.

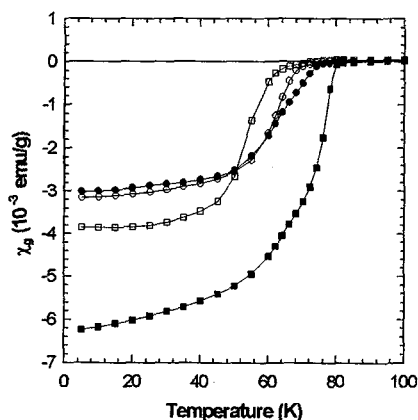


Figure 1: Zero-field-cooled magnetic susceptibilities of 20 Oe, as a function of temperature for the pristine $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (■), $(\text{HgBr}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (●), $(\text{HgI}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (○), and $\text{IBi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (□).

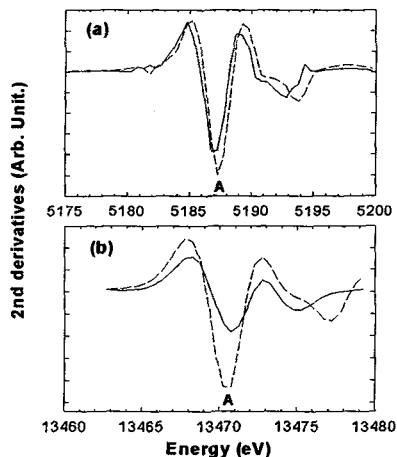


Figure 2: (a) I L₁-edge XANES 2nd derivative spectra for HgI₂ (—) and $(\text{HgI}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (---). (b) Br K-edge XANES 2nd derivative spectra for HgBr₂ (—) and $(\text{HgBr}_2)_{0.5}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ (---).

On the other hand, we have performed the Hg L_{III}-edge EXAFS analysis in order to determine the intracrystalline structure of intercalated HgX_2 . According to the curve fitting results, the coordination number of mercury in HgX_2 intercalate is found to be two for both intercalates, which indicates that the intercalated mercuric halide species are stabilized as linear molecule as in the gaseous state.[4] The (Hg-X) bond distances are also determined to be 2.46₂ Å for the HgBr₂ intercalate and 2.64₇ Å for the HgI₂ one, which are slightly longer than those for the HgX_2 vapor phase ($d(\text{Hg}-\text{Br}) = 2.44$ Å and $d(\text{Hg}-\text{I}) = 2.61$ Å), indicating the interaction between host and guest.[4]

4. CONCLUSION

In this work, we have elucidated clearly that a small fraction of electron is transferred from the host lattice to the intercalated HgX_2 layer, which allows us to conclude that the charge transfer mainly contributes to the T_c evolution upon intercalation. In addition, we have also found that the intercalant HgX_2 is stabilized as a linear molecule as in the vapor state.

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