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New Superconducting Intercalation Compounds: $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (X = Br and I)

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Intercalation into high-T_c cuprate superconductor, $Bi_2Sr_2CaCu_2O_y$, continues to be of particular interest since it may provide the means of understanding the mechanism of superconductivity. In previous studies on iodine intercalation into the $Bi_2Sr_2CaCu_2O_y$ phase, it has been argued that the T_c evolution is likely dependent on one of two factors or both, the doped hole concentration and/or interblock electronic coupling.[1−8] But our recent XANES spectroscopic studies on the $IBi_2Sr_2CaCu_2O_y$ phase demonstrated clearly the charge transfer from iodine guest to host lattice with the formation of I_3^-.[9,10] In order to prove the minor effect of interblock coupling, it was necessary to find a bigger guest than iodine which interacts with the interlayer surface of the $Bi_2Sr_2CaCu_2O_y$ host, giving rise to a larger separation of the CuO_2 plane. Therefore, an attempt was made to find a superconducting intercalation system without any remarkable charge transfer effect but with a significantly reduced interblock coupling one. Recently, two groups were successful in preparing the bulk[11] and thick film[12] AgI-intercalated compounds in an ambient atmosphere, which prompted us to investigate the intercalation of mercuric halides into the $Bi_2Sr_2CaCu_2O_y$ host lattice. Here, we report synthesis and characterization of new intercalation compounds of $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (X = Br and I). As expected, in contrast to the previously known iodine intercalation, the present HgX_2 intercalation drops T_c only by a small fraction, even with the remarkable expansion along the *c*-axis ($\Delta \approx 7.2$ Å), which makes this twice as large as the first-staged iodine intercalate ($\Delta \approx 3.6$ Å).

We have prepared new intercalation compounds by the reaction of $Bi_2Sr_2CaCu_2O_y$ with mercuric halide. The polycrystalline $Bi_2Sr_2CaCu_2O_y$[13] pellet and mercuric halides (mole ratio of 1:5) were placed in 8-mm-diameter Pyrex tubes and then vacuum-sealed. Especially on HgI_2 intercalation, 1 mol of free iodine ($P(I_2) \approx 1.5$ atm) was added as a transporting agent. The $HgBr_2$ intercalate could be successfully prepared by heating at 230 °C for 4 h, and the HgI_2 intercalate by two-step heating at 190 °C for 2 h and then at 240 °C for 4 h. After the reaction was finished, the tubes were placed in a temperature gradient in order to prevent the excess mercuric halide from crystallizing on the sample as it cooled. All the processes were performed in an Ar-filled drybox because of the hygroscopic character of the intercalating agents. However, the resulting compounds were surprisingly quite stable in air. To characterize the intercalates, powder X-ray diffraction (XRD), electron probe microanalysis (EPMA), thermogravimetric analysis (TGA), X-ray photoelectron spectroscopy (XPS), magnetic susceptibility, and resistance measurements were carried out.

The TGA results showed that the mercuric halides were deintercalated below 400 °C for both $HgBr_2$ and HgI_2 intercalates and that the total weight losses were in good agreement with the calculated values of $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$.[14] The EPMA experiments were repeated five times,[15] and the average atomic ratio between Hg, X, and Bi was estimated to be 0.5:1:2 in both compounds, which also confirms the stoichiometry obtained from TGA. From the XPS analysis, it was found that the binding energies of Hg $4f_{7/2}$ (100.5 eV for the $HgBr_2$ intercalate and 100.3 eV for the HgI_2 intercalate), Br $3d_{5/2}$ (68.3 eV) and I $3d_{5/2}$ (619.3 eV) agreed well with those observed from HgX_2 reference spectra, which indicates that the oxidation states of intercalated species are corresponding to Hg^{2+}, Br^- and I^-.

The XRD patterns for the pristine $Bi_2Sr_2CaCu_2O_y$, $IBi_2Sr_2CaCu_2O_y$ and $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (X = Br, I) are shown in Figure 1a−d, respectively. Figure 1e represents the XRD pattern of the deintercalated product after the TGA, which shows obviously the reversibility of intercalation reaction. The *c*-axis unit cell parameter for the pristine material is 30.6 Å, while those for $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ and $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ are 43.2 and 44.9 Å, corresponding to an increase of ~12.6 and ~14.3 Å, respectively. Such results suggest that there are two intercalated layers of HgX_2 for each unit cell of $Bi_2Sr_2CaCu_2O_y$, that is, each mercuric halide layer expands the *c*-axis by 6.30 Å for the $HgBr_2$ intercalate and 7.15 Å for the HgI_2 intercalate, respectively. Although the mercuric halide intercalation remarkably expands the *c*-axis in $Bi_2Sr_2CaCu_2O_y$, it has little effect on the in-plane *a* and *b* parameters. The estimated *a* and *b* parameters of $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ from the (020) and (220) diffraction peaks are both 5.4 Å, which are equal to those of the pristine materials.[16]

We have calculated one-dimensional electron density along the *c*-axis, $\varrho(z)$, from the Fourier transform of the structure factors, F_{00l} (Figure 2). The latter is based on the data from the calculated intensities best fit to the observed intensity. One-dimensional Fourier maps show clearly the intercalation of mercuric halides between the double Bi_2O_2 layer (Br is at z = 1.12 Å and I is at z = 1.73 Å). From the tilting angles[17] and

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(13) The starting composition of this material is Bi:Sr:Ca:Cu = 4:3:3:4, corresponding to the conventional preparation method.

(14) Anal. Calcd (observed) for $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_8$: 17.3 (17.0). Anal. Calcd (observed) for $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_8$: 20.8 (21.2).

(15) Anal. Calcd (found) for $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_8$: Hg, 9.60 (10.44); Br, 7.65 (7.69); Bi, 40.0 (39.59); Sr, 12.58 (10.77); Ca, 5.75 (5.41); Cu, 12.16 (12.16); O, 12.26 (13.94) (by difference). Anal. Calcd (found) for $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_8$: Hg, 9.18 (9.10); I, 11.62 (12.80); Bi, 38.28 (38.13); Sr, 12.04 (11.17); Ca, 5.51 (5.66); Cu, 11.64 (11.32); O, 11.73 (11.82) (by difference).

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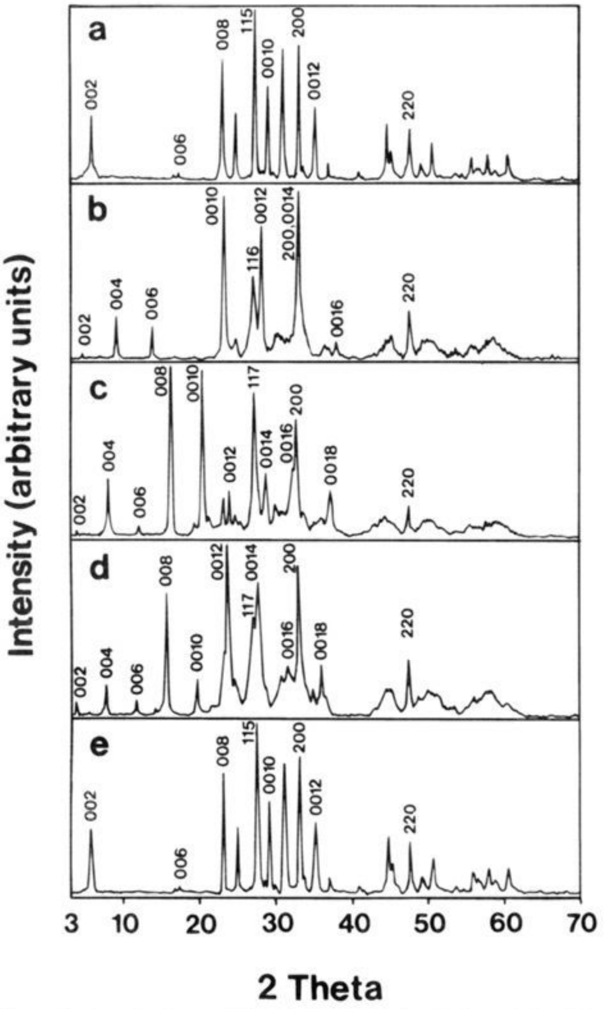

Figure 1. Powder X-ray diffraction patterns for (a) the pristine $Bi_2Sr_2CaCu_2O_y$, (b) $IBi_2Sr_2CaCu_2O_y$, (c) $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$, (d) $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_y$, and (e) the deintercalated phase after TGA of b, c, and d samples. All the reflections could be indexed on the basis of the double-slab tetragonal unit cell.

cross-sectional areas[18] of mercuric halides, the number of guest molecules per unit cell of $Bi_2Sr_2CaCu_2O_y$ could be estimated to be 1 for both cases (corresponding to 0.5 per formula $Bi_2Sr_2CaCu_2O_y$), which is well consistent with stoichiometry determined from TG and EPMA.

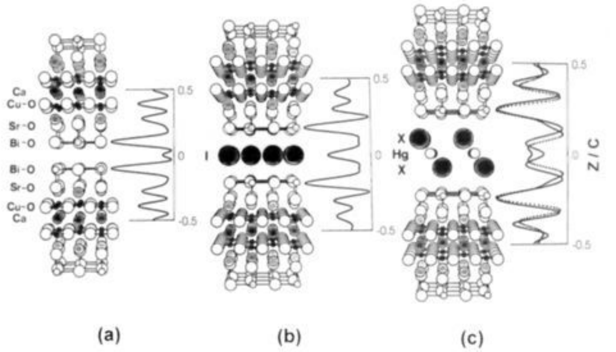

Figure 2. Schematic structures and one-dimensional Fourier maps for (a) $Bi_2Sr_2CaCu_2O_y$, (b) $IBi_2Sr_2CaCu_2O_y$, and (c) $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$. In the Fourier map on c, the solid line and dotted line represent $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ and $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$, respectively.

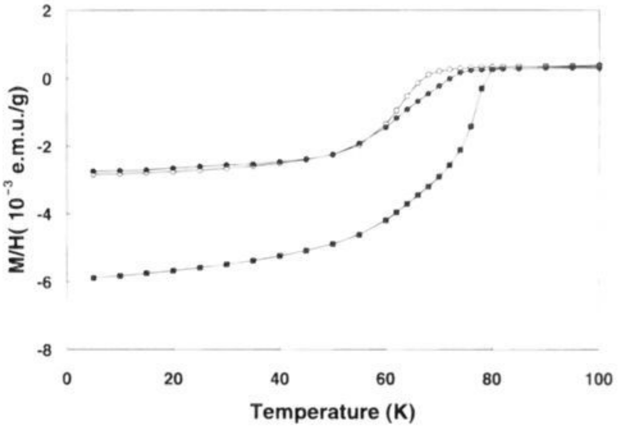

Figure 3. Zero-field-cooled magnetization, *M*, in a field H of 20 Oe, as a function of temperature for the pristine $Bi_2Sr_2CaCu_2O_y$ (■), $(HgBr_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (●), and $(HgI_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (○). The respective onset transition temperatures of these compounds are 76, 71, and 68 K.

Figure 3 shows magnetic susceptibilities for the pristine $Bi_2Sr_2CaCu_2O_y$ and $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ as a function of temperature. The intercalation compounds are also superconducting, with T_c values of 71 ($X = Br$) and 68 K ($X = I$), respectively, slightly lower than that of the pristine $Bi_2Sr_2CaCu_2O_y$($T_c \approx 76$ K). The magnitudes of the fractional diamagnetic shielding at $T = 5$ K were estimated to be 20.7% ($X = Br$) and 21.4% ($X = I$), indicative of the bulk superconductivity of these new compounds. No obvious observation of two or more distinct transitions indicates the homogeneity of intercalation compounds.

Resistance measurements were performed by using a conventional four probe method. The T_c values were depressed by 6 and 7 K upon $HgBr_2$ and HgI_2 intercalation, respectively, which is well consistent with magnetic property measurements.

In summary, we have synthesized new intercalation compounds of $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$ (X = Br and I) and confirmed superconducting behavior for these compounds. Furthermore, it was found that the intercalation of HgX_2 into $Bi_2Sr_2CaCu_2O_y$ does not alter the hole carrier concentration on the CuO_2 layers to any significant degree, and despite the large lattice expansion along the *c*-axis, the superconducting transition temperature drops only by a small fraction, indicating that at least the effect of interblock electronic coupling may be negligible in this system. In order to clarify the superconducting properties, XANES and EXAFS studies are under way.

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[17] If the Hg−Br and the Hg−I distances in the intercalation compounds were the same as in the molecular solid (2.4 and 2.6 Å), the HgX_2 molecular axis should be tilted at an angle of ~62° ($X = Br$) and ~48° ($X = I$) with respect to the *c*-axis.

[18] 8.5 × 3.7 Å^2 for $HgBr_2$ and 9.5 × 4.3 Å^2 for HgI_2, where 8.5 and 9.5 Å correspond to the lengths of the linear X−Hg−X molecule of $HgBr_2$ and HgI_2 and 3.7 and 4.3 Å to van der Waals diameters of Br_2 and I_2, respectively.