

# Chimie Douce Reaction to Layered High- $T_c$ Superconducting / Super-ionic Conducting Heterostructures

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We have developed new type of superconducting-superionic conducting nanohybrids,  $\text{Ag}_x\text{I}_y\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=1$  and  $2$ ) by applying the *chimie douce* reaction to the superconducting Bi-based cuprates. These nanohybrids can be achieved by the stepwise intercalation whereby the  $\text{Ag}^+$  ion is thermally diffused into the pre-intercalated iodine sublattice of  $\text{IBi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ . According to the X-ray diffraction analysis, the Ag-I intercalates are found to have a unique heterostructure in which the superionic conducting Ag-I layer and the superconducting  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  layer are regularly interstratified with a remarkable basal increment of  $\sim 7.3$  Å. The systematic XAS studies demonstrate that the intercalation of Ag-I accompanies the charge transfer between host and guest, giving rise to a change in hole concentration of  $\text{CuO}_2$  layer and to a slight  $T_c$  change. The Ag K-edge EXAFS result reveals that the intercalated Ag-I has a  $\beta$ -AgI-like local structure with distorted tetrahedral symmetry, suggesting a mobile environment for the intercalated  $\text{Ag}^+$  ion. In fact, from ac impedance analyses, we have found that the Ag-I intercalates possess a fast ionic conductivity ( $\sigma = 10^{-11} \sim 10^{-20} \Omega^{-1}\text{cm}^{-1}$  at  $270^\circ\text{C}$ ) with a uniform activation energy ( $\Delta E_a = 0.22 \pm 0.02$  eV). More interesting finding is that these intercalates exhibit high electronic conductivities as well as ionic ones ( $t_i = 0.02 \sim 0.60$ ) due to their interstratified structure consisting of superionic conducting and superconducting layers. In this respect, these new intercalates are expected to be useful as an electrode material in various electrochemical devices.

**Key words :** Chimie douce, Nanohybrid,  $\text{Ag}_x\text{I}_y\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ , Charge transfer, Ionic conductivity, Interstratified structure

## I. Introduction

In chemistry, the term "*chimie douce*" describes the soft chemistry by which the solid state compound is formed under milder reaction conditions such as the heat treatment below  $300^\circ\text{C}$ , compared to the conventional solid state reaction conditions. Among the *chimie douce* reaction, the intercalation reaction has attracted much research interest due to its usefulness for probing the chemical and physical properties of layered materials.<sup>1)</sup> In particular, its application to high- $T_c$  superconductors provides an effective method not only to engineer the physical properties of host superconductor but also to investigate the mechanism responsible for high- $T_c$  superconductivity and to develop new superconducting materials and devices.<sup>2-8)</sup>

Previously we have performed systematic studies on the iodine intercalated  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=2$  and  $3$ ) and found that the guest iodine plays a role of an electron acceptor, that is, Lewis acid.<sup>6,7)</sup> Based on this finding, attempts have been made to intercalate various guest species with Lewis acidity. Recently we have successfully developed new type of high- $T_c$  superconducting compounds of  $\text{M-X-Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  ( $\text{M-X}=\text{HgI}_2, \text{HgBr}_2$ , and  $\text{AgI}$ ) in which superconducting and insulating/superionic

conducting layers are regularly interstratified.<sup>2-8)</sup> The new metal salt intercalates exhibit a remarkable expansion of the crystal lattice along the  $c$ -axis, which is almost twice as large as that for the iodine intercalate, along with a slight charge transfer. Therefore, these new compounds are expected to provide a direct information on the effect of interlayer coupling upon the superconductivity. Especially, the Ag-I intercalate is expected to possess an ionic conductivity as well as an electronic one due to its unique hybrid structure consisting the ionic conducting Ag-I layer and superconducting  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  one.

In this paper, we report the syntheses and physico-chemical properties of Ag-I intercalated superconductors. We have performed the X-ray absorption spectroscopic (XAS) studies for these intercalates in order to examine the effect of intercalation on the electronic and geometric structures of host and guest.

## II. Experimental

The pristine Bi-based cuprate compounds,  $\text{Bi}_2\text{Sr}_2\text{Ca}_n\text{Cu}_{n-1}\text{O}_y$  ( $n=1$  and  $2$ ) were prepared by standard solid state reaction and their Ag-I intercalates were synthesized by the heat-treatment of polycrystalline mixture of silver

metal and pristine powder with an iodine vapor pressure of 1 atm.<sup>4,6</sup> The contents of intercalated silver and iodine could be controlled by changing the starting ratio of Ag and pristine material. The characterizations of physico-chemical properties were carried out with powder X-ray diffraction (XRD) and dc magnetic susceptibility measurements along with electron probe micro analysis (EPMA). The ionic conductivities of the Ag-I intercalates were measured in the temperature range of 25–270°C by employing two different techniques of pulsed method or ac impedance and dc polarization methods. The XAS 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 providing a 2.5 GeV electron beam at a current of ca. 300–360 mA.

### III. Results and Discussion

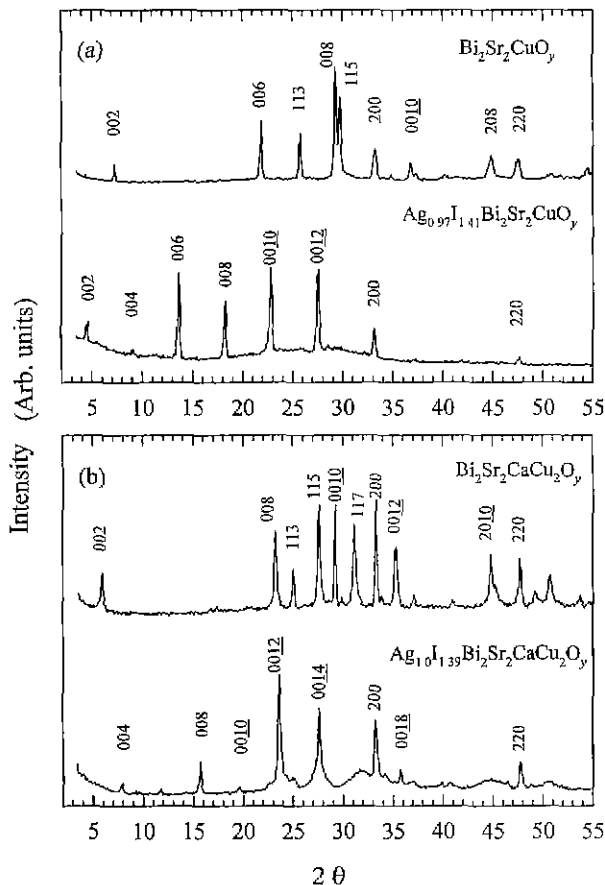
From the EPMA analyses, Ag compositions ( $x$ ) of  $\text{Ag}_{1-x}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  and  $\text{Ag}_{1-x}\text{Bi}_2\text{Sr}_2\text{CuO}_y$  are found to be in the range of 0.76–1.17, depending on the initial mixing ratio of Ag to pristine ( $x$ ). In the region of  $x \leq 1.45$ , the Ag and I concentrations are directly proportional to the  $x$  ratio while they remain constant over the range of

$x \geq 1.45$ .

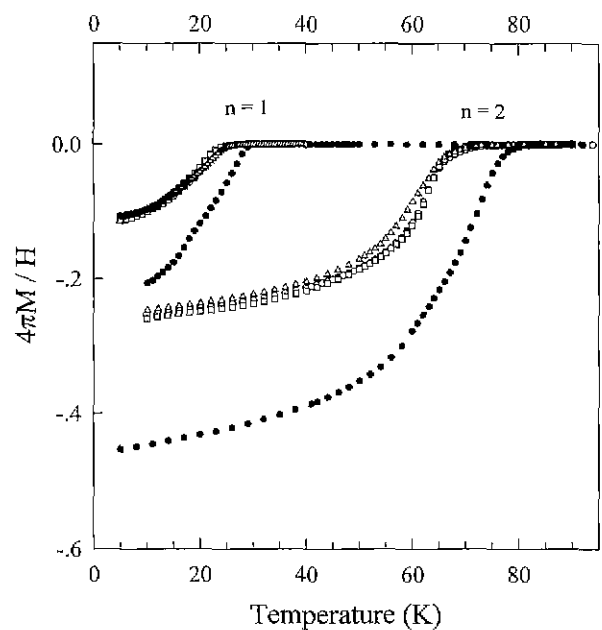
According to the XRD patterns (Fig. 1) for the  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  ( $n=1$  and 2) and their Ag-I intercalates,  $\text{Ag}_{0.97}\text{I}_{1.41}\text{Bi}_2\text{Sr}_2\text{CuO}_y$  and  $\text{Ag}_{1.00}\text{I}_{1.39}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$ , the  $c$ -axis unit cell parameters of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  are determined to be 24.43 Å for  $n=1$  and 30.73 Å for  $n=2$ , respectively, whereas those for the intercalates are 38.82 Å and 45.40 Å corresponding to the lattice expansions of  $\sim 14.6$  Å. For each unit cell of  $\text{Ag}_x\text{I}_y\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ , there are two intercalated Ag-I layers; each Ag-I layer expands the  $c$ -axis by  $\sim 7.3$  Å, which is approximately twice as large as that for iodine intercalates ( $\Delta d \approx 3.6$  Å). On the other hand, the Ag-I intercalation has little effect on the in-plane  $a$  and  $b$  parameters ( $\approx 5.40$  Å).

The high- $T_c$  superconducting properties of the pristines and their Ag-I intercalates have been confirmed by measuring the mass-normalized  $\chi_{dc}$  data as a function of temperature, as shown in Fig. 2. For the compounds with  $n=1$ , the onset  $T_c$ 's of the intercalates are decreased by 4–5 K with respect to  $T_c=29$  K of the pristine material, and for those with  $n=2$ , the onset  $T_c$  is 80 K for  $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  and 67 K for the intercalates. For the intercalates, diamagnetic shielding fractions at  $T=10$  K are  $\sim 13\%$  ( $n=1$ ) and  $\sim 25\%$  ( $n=2$ ), indicative of the bulk superconductivity.

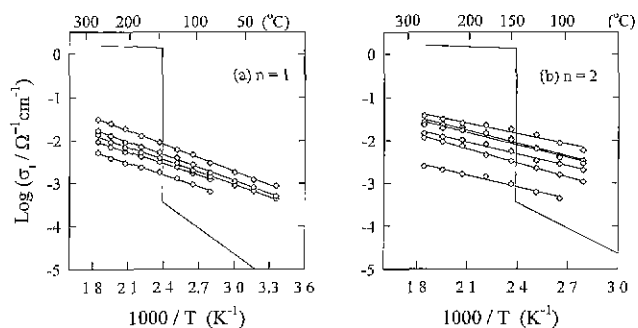
In order to investigate the evolution of electronic structure upon intercalation, we have carried out XAS experiment. According to the I  $L_{\Gamma}$  and Ag K-edge X-ray absorption near edge structure (XANES) spectra, it is demonstrated that there is little difference between the electronic structures of AgI and of the intercalated Ag-I



**Fig. 1.** Powder X-ray diffraction patterns for the pristines,  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  and their Ag-I intercalates (a)  $n=1$  and (b)  $n=2$ .



**Fig. 2.** dc magnetic susceptibilities of pristines (●) and their Ag-I intercalates. For the intercalate with  $n=1$ ,  $x=0.76$  (○), 0.97 (□), 1.15 (△); for  $n=2$ ,  $x=0.76$  (○), 1.00 (△), 1.17 (□).

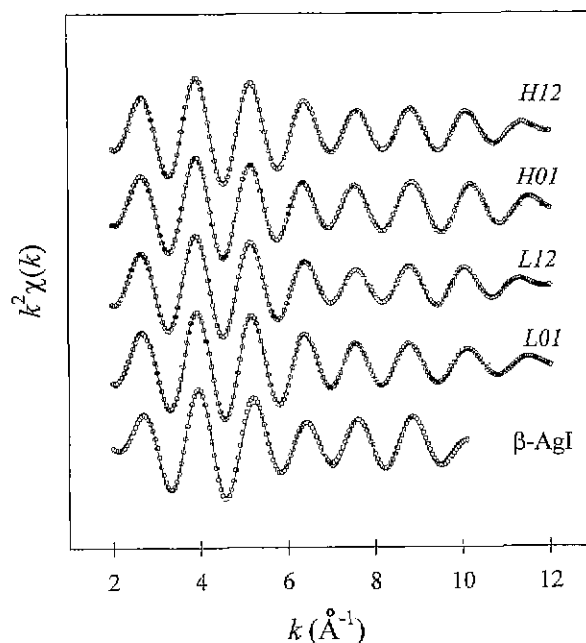


**Fig. 3.** Ionic conductivity of the  $\text{Ag}_x\text{I}_w\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$ , (a)  $n=1$  and (b)  $n=2$ . In both graphs, the solid line represents the ionic conductivity of reference AgI.

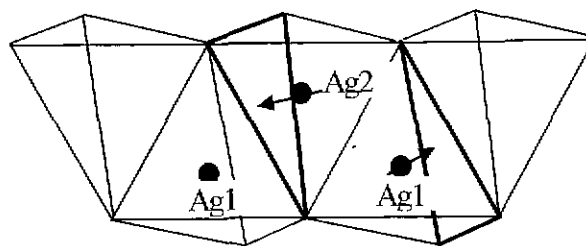
species, indicating the oxidation states of  $\text{Ag}^-$  and I. Considering the stoichiometry of intercalated layer,  $\text{Ag}_x\text{I}_w^{w-x}$  ( $w > x$ ), it is sure that the intercalation of  $\text{Ag}_x\text{I}_w^{w-x}$  gives rise to a partial oxidation of the pristine  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}$  lattice, leading to a  $T_c$  depression.

Figs. 3a and 3b show the measured  $\sigma_1$ 's of  $\text{Ag}_x\text{I}_w\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_y$  with  $n=1$  and 2, respectively. The ionic conductivity increases with increasing Ag content ( $x$ ) in the intercalates, which can be interpreted as a consequence of an increase in the intrinsic  $\text{Ag}^+$  concentration in the intercalates with larger  $x$  values. Comparing the  $\sigma_1$  of  $\text{Ag}_{1.17}\text{I}_{1.54}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  with those of several  $\text{Ag}^+$  superionic conductors, it is found that this intercalate has a  $\sigma_1$  high enough to be classified as a superionic conductor. Moreover, the ionic conduction in Ag-I intercalate is of special interest, since it is accompanied by an electronic conductivity of  $\sim 10^{-1} (\Omega\text{cm})^{-1}$  in the metallic host layer. The ionic transference number,  $t_i (= \sigma_i / \sigma_{\text{total}})$  in  $\text{Ag}_{1.17}\text{I}_{1.54}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  is estimated as 0.40 at  $270^\circ\text{C}$ , where the  $\sigma_i$  and  $\sigma_e$  are  $10^{-14} (\Omega\text{cm})^{-1}$  and  $10^{-12} (\Omega\text{cm})^{-1}$ , respectively, confirming the mixed conductivity of this system.

In order to elucidate the mobile nature of  $\text{Ag}^+$  ion in the intercalates from the viewpoint of structural environment, the Ag  $K$ -edge extended X-ray absorption fine structure (EXAFS) has been studied for  $\text{Ag}_{0.76}\text{I}_{1.20}\text{Bi}_2\text{Sr}_2\text{CuO}_y$  (L01),  $\text{Ag}_{0.76}\text{I}_{1.17}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (L12),  $\text{Ag}_{1.15}\text{I}_{1.53}\text{Bi}_2\text{Sr}_2\text{CuO}_y$  (H01), and  $\text{Ag}_{1.17}\text{I}_{1.54}\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_y$  (H12). As represented in Fig. 4, the Fourier filtered  $k^2\chi(k)$  EXAFS spectra at the Ag  $K$ -edge are compared with the best fits. From the nonlinear curve fitting, the (Ag-I) species of L01 and L12 are found to be stabilized in tetrahedral symmetry with the bond distances,  $R_{\text{Ag-I}}$ , of 2.78 $_7$  Å and 2.78 $_8$  Å, respectively, which is similar to the  $\beta$ -AgI case. In contrast to both intercalates, the model with a displacement of Ag toward a face of the iodine tetrahedron gives the best fits for the intercalates of H01, H12, as observed in  $\alpha$ -AgI.<sup>9</sup> Such a displacement of  $\text{Ag}^+$  ion from the center of  $T_d$  toward a face is interpreted as a result of Coulombic interaction among  $\text{Ag}^+$  ions. Since this repulsive interaction forces  $\text{Ag}^+$  ion to move toward the crystal site with lower potential energy, the direction of  $\text{Ag}^+$  displacement in the Ag-



**Fig. 4.** Fourier-filtered Ag  $K$ -edge EXAFS for H12, H01, L12, L01 and  $\beta$ -AgI. (O : calculated, -- : experimental)



**Fig. 5.** Illustration of the displacement of  $\text{Ag}^+$  ion in H01 and H12, suggested from the EXAFS results.

concentrated compound implicates the most favorable conduction pathway. In this respect, it is suggested that the  $\text{Ag}^+$  ion in the intercalated Ag-I sublattice migrates along the line of  $\cdots\text{T}_d\text{-O}_h\text{-T}_d\text{-O}_h\text{-T}_d\cdots$ , even though the occupancy of the octahedral site ( $\text{O}_h$ ) is relatively low compared to  $\text{T}_d$ , as illustrated in Fig. 5. In fact, such a conduction pathway including  $\text{O}_h$  has been already proposed for most of the ionic conducting AgI-related compounds.<sup>10</sup>

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