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Intercalation route to nano-hybrids: inorganic/organic-high T_c cuprate hybrid materials†

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A systematic application of intercalation techniques to layered superconducting oxides enables us to open a new chapter in the development of nano-hybrids with various functions. Recently we were successful in preparing a new series of inorganic–inorganic nano-hybrids, M–X–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (M = Hg, Ag, Au; X = Br, I; m = 1–3) and organic–inorganic ones, R_2HgI_4–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (R = organic cation). Our synthetic strategies are based on (1) HSAB (hard–soft acid–base) interactions and (2) interlayer complexation concepts. Since the iodine species in $IBi_2Sr_2Ca_{m-1}Cu_mO_y$ are stabilized as I_3^- (soft base) with a charge transfer between host and guest, soft Lewis acids like Ag^+, Au^+, and Hg^{2+} can be further intercalated into the iodine layers inbetween the (Bi–O) double layers. On the other hand, new organic–inorganic nano-hybrids (R_2HgI_4–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$) have also been achieved through the intercalative complex-salt formation reaction between preintercalated HgI_2 molecules and R^+I^- salts in the interlayer space of $Bi_2Sr_2Ca_{m-1}Cu_mO_y$. Compared to the pure compounds the superconducting transition temperatures of the organic-salt intercalates are little changed even with a large basal increment upon intercalation, indicating a two-dimensional nature of the high-T_c superconductivity. From the viewpoint of application, the intercalation of large organic molecules provides a new synthetic route to high-T_c superconducting thin-film and nano-particles by separating superconducting blocks into isolated single sheets.

Introduction

Intercalation techniques have been widely applied not only to the study of chemical and physical properties of low dimensional compounds but also to the development of new nano-hybrid materials that cannot be prepared by conventional solid state methods.[1] The essential advantage of this technique is that it allows some degree of modification in the geometric, chemical, electronic, and optical properties of host and guest. Moreover, the bonding between them also varies broadly from essentially van der Waals dipolar to metallic and ionic. In this respect, intercalation reactions can be considered as effective tools in tailoring the properties of the desired materials and also in the investigation of the physical properties of layered materials.

Since the discovery of high-T_c superconductivity in ceramic cuprate materials, intense research efforts have been made to understand their high-T_c superconductivity, but the mechanism has not yet been established. Concerning the high-T_c superconducting mechanism, one of the most important debating points is on the relationship between the superconductivity and structural anisotropy which is a common feature of high-T_c superconductors. Actually it is expected that the superconductivity can be affected by the interlayer Josephson coupling which depends on the interlayer distance of the CuO_2 layer. On the other hand, instead of Josephson coupling, Wheatley, Hsu, and Anderson considered the coherent hopping of valence bond pairs between CuO_2 planes (WHA model).[2] However, the validity of these theoretical models has remained unconfirmed due to the lack of experimental evidence. If we can control the strength of interlayer coupling, it will be informative in understanding the relation between interlayer coupling and superconductivity. In this regard, the intercalation into high-T_c superconductors is expected to be quite effective because it allows us to control the strength of interlayer coupling. Further, intercalation can also provide useful ways of preparing high-T_c superconducting nano-hybrids with multi-functional properties since it enables us to combine the heterogeneous species into a unified chemical system.[3–10] From the viewpoint of practical application, it can also be expected that the high-T_c superconducting intercalate with a remarkable lattice expansion will be available as a precursor for making superconducting thin-films and nano-particles, because the bulky guest molecule can facilitate the exfoliation of superconducting layers by minimizing the chemical interaction between superconducting blocks.[7]

As mentioned above the advantages of the intercalation technique have attracted us to perform systematic studies on high-T_c superconducting intercalation compounds. Previously we have investigated the bonding character of iodine intercalated in $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (denoted hereafter as Bi2201 for m = 1, Bi2212 for m = 2, and Bi2223 for m = 3, respectively), and found that there is a partial electron transfer from host lattice to intercalant layer.[10] On the basis of such a finding, we can successfully develop a new series of inorganic–inorganic and organic–inorganic superconducting nano-hybrids by applying new synthetic strategies such as soft–hard acid–base interactions and the interlayer complexation concept.

In this paper, we report a systematic approach towards the synthesis of HgX_2-, AgI-, and organic-salt-intercalated $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (m = 1–3), together with the characterization of their physico-chemical properties. Emphasis is especially placed on the synthetic strategies applied to develop the present inorganic–inorganic and organic–inorganic nano-hybrids.

Experimental

All the pure $Bi_2Sr_2Ca_{m-1}Cu_mO_y$(m = 1–3) compounds were prepared by the conventional solid state reaction. At first, the powder reagents Bi_2O_3, PbO, $SrCO_3$, La_2O_3, $CaCO_3$, and CuO were thoroughly mixed with molar ratios of Bi : Sr : La : Cu = 2 : 1.6 : 0.4 : 1 for m = 1, Bi : Sr : Ca : Cu = 2 : 1.5 : 1.5 : 2 for m = 2, and Bi : Pb : Sr : Ca : Cu = 1.85 : 0.35 : 1.9 : 2.1 : 3.1 for m = 3,

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respectively and the obtained mixtures were calcined at 800 °C for 12 h in air, and then, the pre-fired materials were pressed into 13 mm disc-shaped pellets and finally sintered with intermittent grinding. Depending upon the composition, different final heating conditions were adopted to obtain the single phase samples. That is, the pure $Bi_2Sr_2CuO_y$(Bi2201) and $Bi_2Sr_2CaCu_2O_y$(Bi2212) compounds were prepared by heating for 40 hours in air at 890 and 860 °C, respectively, whilst the pure $Bi_2Sr_2Ca_2Cu_3O_y$(Bi2223) sample was synthesized by heating at 830 °C for 150 h in a N_2 (99.999%) atmosphere. Since the stoichiometric $Bi_2Sr_2CuO_y$ compound possesses an overdoped hole concentration, some of the Sr^{II} ions (20%) were substituted with La^{III} to induce the highest T_c with an optimum hole concentration.[11] In the case of the Bi2223 phase, both the substitution of Bi^{III} ion with Pb^{II} and heat treatment in a reduced atmosphere were required to obtain a single phase sample,[12] since such conditions make it easier to form Bi2223 through the reaction between the intermediate products Bi2212 and Ca–Sr–Cu–O.[13] The HgX_2-intercalates (X = Br or I) were synthesized by vapor transport reaction between host and guest in a vacuum sealed Pyrex tube. In the case of Bi2201 and Bi2212, their $HgBr_2$-intercalates were easily obtained by heating the pure compounds with excess $HgBr_2$ at 230 °C for 4 h, while their HgI_2-intercalates were prepared by heating the pure samples with excess HgI_2 at 190 °C for 2 h and then at 240 °C for 4 h with one molar equivalent of free iodine as a transport agent.[4] However, the intercalation of HgX_2 into Bi2223 could not be achieved through the direct reaction between host and HgX_2 vapor. In order to overcome such a difficulty, we have used iodine intercalated Bi2223 as a secondary host, which results in the formation of the first-stage intercalate. On the other hand, each AgI-intercalate of Bi2201 and Bi2212 was synthesized by heating a mixture, in the form of a pellet, of the pure compound and Ag metal under an iodine atmosphere [$P(I_2) = 1$ atm]. The heat treatment was carried out in a stepwise manner where the sample was heated in an iodine atmosphere at 170 °C for 3 h and then in air at 190 °C for 10 h. According to the X-ray diffraction (XRD) analysis for the product after the first heat treatment at 170 °C, it was found that no AgI-intercalate exists but the iodine-intercalate is formed together with AgI. Such a finding indicates that the AgI intercalation is accomplished *via* the thermal diffusion of Ag^+ ions into the preintercalated iodine sublattice.[14] However, the AgI-intercalated Bi2223 was not easily prepared by the above method as in the case of HgX_2-Bi2223, which is attributed to the high deintercalation rate of preintercalated iodine compared to the Ag^+ diffusion rate into the lattice. For this reason, we have adopted an alternative synthetic route whereby a mixture of AgI and iodine-intercalated Bi2223 (IBi2223) was heated at 190 °C for 75 h under an iodine vapor pressure of 1 atm. The single phase AgI-intercalate could be finally obtained by both extending the reaction time and imposing an iodine atmosphere to prevent iodine disintercalation during Ag^+ diffusion. Such a difficulty in the intercalation of HgX_2 and AgI into Bi2223 is attributed to the fact that the pure sample cannot suffer from a large elastic deformation upon intercalation owing to its thicker unit block with three CuO_2 layers compared to Bi2201 and Bi2212. This is also partially ascribed to an enhanced attraction between BiO layers induced by the substitution of Bi^{III} with Pb^{II}.[15]

The organic–inorganic hybrids $[(Py\text{-}C_nH_{2n+1}I)_2HgI_4]$–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ ($n = 1$, 2, 4, 6, 8, 10, or 12; $m = 1$–3) were synthesized by the stepwise intercalation route as follows; first, the HgI_2-intercalates were prepared as mentioned above, and then, the intercalation of the organic chain was carried out by the solvent-mediated reaction between the HgI_2-intercalate and alkylpyridinium iodide. The reactants Py-$C_nH_{2n+1}I$ ($n =$ 1, 2, 4, 6, 8, 10, or 12) were prepared by the reaction between equimolar amounts of alkyl iodide and pyridine in diethyl ether. The HgI_2-intercalates were mixed with two molar excess of Py-$C_nH_{2n+1}I$, to which a small amount of pure acetone was added. Each mixture was reacted in a closed ampoule at 40–70 °C for 6 h and washed with a mixture of acetone and diethyl ether in order to remove the excess Py-$C_nH_{2n+1}I$. The resulting products were dried under vacuum. All the samples were air-stable, which made the characterization of their physico-chemical properties easier.

The physico-chemical characterizations were carried out with X-ray diffraction (XRD) and dc magnetic susceptibility measurements along with chemical analysis by electron probe micro-analysis (EPMA) and thermogravimetric analysis (TGA). In the case of the AgI-intercalates, their ionic conductivity was measured in the temperature range 25–270 °C with impedance spectroscopy. The electronic configuration and the crystal structure of the intercalation compounds were investigated by performing X-ray absorption spectroscopic (XAS) analyses, which were carried out on the beam lines 7C and 10B at the Photon Factory, National Laboratory for High Energy Physics (KEK-PF) in Tsukuba. The applied synchrotron X-ray radiation was provided by a storage ring of a 2.5 GeV electron beam with a current of *ca.* 300–360 mA.

Results and discussion

Iodine intercalation

It is well known that intercalation reactions occur in highly anisotropic lamella structures in which the interlayer binding forces are fairly weak compared to the strong ionocovalent intralayer ones. In this respect, the weak van der Waals interaction between the Bi_2O_2 layers in layered Bi-based cuprate superconductors allows these compounds to be good host materials for intercalation reaction as shown in Fig. 1.[16]

As we were performing our research in this field, some organic and inorganic molecules were reported in the literature to be intercalated into the Bi-based cuprate high-T_c superconductors (Table 1). However, among them, only the iodine intercalation compound has been chemically well defined. From the magnetic susceptibility and four probe resistivity measurements for the iodine intercalates, we found that the T_c is depressed by ≈ 10 K upon iodine intercalation.[10] Since the T_c of cuprate superconductors is closely related to the hole concentration in the CuO_2 plane, we have examined the bonding character of iodine stabilized in the lattice of IBi2212 with Raman and X-ray absorption near edge structure

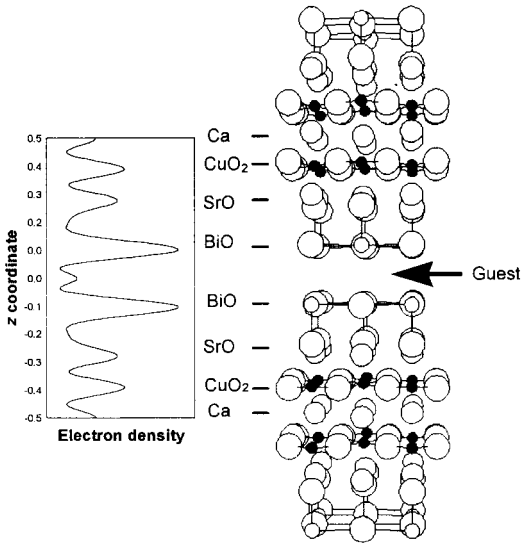

Fig. 1 Mica-like crystal structure of the Bi2212 superconductor, together with a one-dimensional electron density map along the *c*-axis. The guest species can be intercalated inbetween weakly bound Bi_2O_2 double layers.

Table 1 High-T_c superconducting intercalation compounds

Intercalant	Research group	Published in	Year
Iodine[a]	X. D. Xiang *et al.*	*Nature*, **348**, 145	1990
Copper, silver	G. A. Scholz *et al.*	*Solid State Commun.*, **74**, 959	1990
Lithium	T. Okubo *et al.*	*Physica C*, **185–189**, 847	1991
Bromine	Y. Koike *et al.*	*Solid State Commun.*, **79**, 501	1991
IBr	M. Mochida *et al.*	*Physica C*, **212**, 191	1993
Conjugated ring organic molecules	L. S. Grigorian *et al.*	*Physica C*, **205**, 296	1993
Metal–phthalocyanines	L.S. Grigorian *et al.*	*Physica C*, **218**, 153	1993
Hg_2Cl_2	Y. Muraoka *et al.*	*Physica C,* **233**, 247	1994
Fullerene (C_{60})	S. Sathaiah *et al.*	*J. Appl. Phys.*, **81,** 2400	1997

[a]Only the iodine intercalate is chemically well-defined.

Table 2 Previous reports on the iodine intercalated Bi-cuprates, those which are classified, depending upon the author's interpretation of why the T_c is depressed upon iodine intercalation

Charge transfer	Interlayer coupling
J. H. Choy *et al.*, *J. Solid State Chem.*, **102**, 284 (1993)	X. D. Xiang *et al. Nature*, **348**, 145 (1990)
D. Pooke *et al. Physica C*, **198,** 349 (1992)	X. D. Xiang *et al. Science*, **254**, 1487 (1991)
T. Huang *et al. Phys. Rev. B*, **49**, 9885 (1994)	P. V. Huong *et al. Phys. Rev. B*, **48,** 9869 (1993)
Y. Koike *et al. Physica C*, **208,** 363 (1993)	J. Ma *et al. Physica C*, **227,** 371 (1994)
M. A. Subramanian, *J. Solid State Chem.*, **110,** 193 (1994)	M. Biagini, *Phys. Rev. B*, **52,** 7715 (1995)
C. K. Subramaniam *et al. Physica C*, **249,** 139 (1995)	

(XANES) spectroscopies. The Raman spectroscopic results indicated that the intercalated iodine is stabilized as a triiodide molecular ion (I_3^-),[17] which was also confirmed by the I L_I-edge XANES analysis.[10] Further evidence on the hole donation from the intercalated iodine layer to the superconducting CuO_2 layer could be obtained from the thermoelectric power and the Cu K-edge XANES analyses.[18] From these experimental findings, it was suggested that the T_c evolution upon iodine intercalation is due to the hole overdoping to the CuO_2 sheets (Table 2).[10,19] However, on the basis of WHA model, other groups explained the T_c decrease for the first- and second-stage iodine intercalated compounds by the weakening of the interblock coupling due to the lattice expansion.[2,20] In fact, since it is impossible to separate both effects of intercalation, that is, lattice expansion effects and charge transfer ones, for the iodine intercalate, the origin of the T_c variation upon intercalation has remained controversial, as demonstrated in Table 2. In order to solve this problem, a new intercalation system, where the lattice expansion is larger than that of iodine intercalate, was required.

Metal halide intercalation

From the Raman and XANES studies on the iodine intercalate, it becomes clear that the guest iodine plays a role as electron acceptor, that is, soft Lewis acid, with the host Bi-based superconductor as electron donor, soft Lewis base. It is therefore concluded that the driving force of iodine intercalation into Bi-based cuprates is a charge transfer between host and guest, and that an electronegative element or molecule can be incorporated into this superconducting lattice. Based on this understanding, we have tried to intercalate various kinds of soft (hard) Lewis acids which are classified in Table 3.[21] And as a result, we were successful in developing a new type of high-T_c superconducting compound, M–X–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ (M = Hg, Ag, Au; X = Br, I; m = 1–3), where a superconducting layer and an insulating/superionic conducting one are regularly interstratified.

According to the XRD (Cu-Kα radiation) analyses, the lattice expansion along the c-axis (Δd) upon intercalation is estimated to be $\approx$6.3 Å for $HgBr_2$-intercalates and $\approx$7.2 Å for HgI_2 ones, which indicates that the halogen bilayers are stabilized in the interlayer space of Bi-based cuprates. According to the dc magnetic susceptibility measurements, all the metal halide-intercalates are found to exhibit bulk superconductivity with a slight T_c depression of only 6–14% compared to the corresponding pure materials. Their superconducting transition temperatures (T_c's) are summarized in Table 4, together with lattice parameters. It was previously suggested that the T_c evolution upon intercalation might be due to a change in hole concentration in the CuO_2 planes[10,19] and/or due to the weakening of interblock electronic coupling.[2,20] Taking into account the hybrid structure of these intercalates where the electronically insulating metal halide layer is regularly interstratified between the superconducting lattices, the interblock electronic coupling is expected to be

Table 3 List of Lewis soft acid–base compounds (ref. 18)

Lewis acid	Lewis base
$Co(CN)_5^3$, Pd^{2+}, Pt^{2+}, Cu^+, *Ag^+*,[a] *Au^+*,[a] Cd^{2+}, Hg_2^{2+}, *Hg^{2+}*,[a] CH_3Hg^+, BH_3, $Ga(CH_3)_3$, $GaCl_3$, $GaBr_3$, GaI_3, Tl^+, $Tl(CH_3)_3$, CH_2, carbenes, HO^+, RO^+, RS^+, RSe^+, Te^{4+}, RTe^+, Br_2, Br^+, *I_2*,[a] I^+, ICN, O, Cl, Br, I, N, M^0 (metal atoms), π-acceptors; trinitrobenzene, quinones, *etc.*	H^-, R^-, C_2H_4, C_5H_6, CN^-, RNC, CO, SCN^-, R_3P, $(RO)_3P$, R_3As, R_2S, RSH, RS^-, $S_2O_3^{2-}$, *I^-*, *I_3^-*

[a]All the elements intercalated into $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ belong to the soft Lewis acid group and are denoted as *italic* characters.

Table 4 Lattice parameters and superconducting transition temperatures of $Bi_2Sr_2Ca_{m-1}Cu_mO_y$ and their metal halide-intercalates

Compound		Metal halide	a/Å	c/Å	Δd/Å	T_c/K	ΔT_c/K
$m=1$	Pure		5.39	24.2		29	
	Intercalate	$HgBr_2$	5.40	36.8	6.3	27	−2
		HgI_2	5.39	38.4	7.1	25	−4
$m=2$	Pure		5.40	30.70		78	
	Intercalate	$HgBr_2$	5.39	43.3	6.1	71	−7
		HgI_2	5.40	45.0	7.2	68	−10
$m=3$	Pristine		5.40	40.0		105	
	Intercalate	HgI_2	5.42	51.0	7.0	97	−8

a: in-plane lattice parameter, c: out-of-plane lattice parameter, Δd: lattice expansion along c-axis per each metal halide layer, $\Delta T_c = T_c$ (intercalate) $- T_c$ (pure).

extremely weak. In this respect, the maintenance of superconductivity upon intercalation of metal halides allows us to conclude that interlayer coupling is not a main factor for superconductivity. It is also suggested that the present T_c evolution upon intercalation should be understood in terms of the charge transfer between guest and host block.

In this regard, we have performed XANES analysis for these intercalates in order to investigate the evolution of electronic configuration of host and guest upon intercalation. A comparison of the I L_I-edge XANES spectra for HgI_2-intercalates with that for the unintercalated HgI_2 as a reference indicates clearly that there is a partial electron transfer from host block to guest HgI_2 layer. The Br K-edge XANES analysis for $HgBr_2$-intercalate also reveals a partial electron transfer from host lattice to $HgBr_2$ layer. From these XANES results, it becomes obvious that there is also a charge transfer between host and guest for all the metal halide intercalates, related to the T_c evolution upon intercalation, and that the intercalation of metal halide is surely a kind of Lewis acid–base reaction.

The intracrystalline structures of intercalated metal halide layers have also been investigated by performing extended X-ray absorption fine structure (EXAFS) analysis. In the case of AgI-intercalates, the experimental Ag K-edge EXAFS spectra are well fitted to the calculated data from a two-shell model where there is a displacement of Ag toward a face of the iodine tetrahedron, which is strikingly similar to the local structure of super-ionic conducting α-AgI.[22] On the basis of this structural information, we have carried out ionic conductivity measurements for AgI-intercalates, and found that these compounds have a high ionic conductivity ($\sigma_i = 10^{-1.4}$–$10^{-2.6}$ $\Omega^{-1}cm^{-1}$ at 270 °C) with uniform activation energies ($\Delta E_a = 0.22 \pm 0.02$ eV), which are similar to those of other two-dimensional Ag^+ superionic conductors.[23,24] Such ionic conductivity enables us to intercalate electrochemically the Ag^+ ion into the lattice of IBi2212 with the electrochemical cell –Ag|AgI_6WO_4|IBi2212–, where the contact between electrolyte and electrodes was improved through heat treatment. The ionic conduction in these compounds may attract special interest since the materials exhibit both high electronic and ionic conductivities with ionic transfer numbers of $t_i =$ 0.02–0.60. Although it is rarely observed that a material possesses both high electronic conductivity and a high ionic one, the mixed conductivity of the AgI derivatives originates from their unique crystal structures consisting of an ionic conducting AgI layer and an electronic conducting host.

On the other hand, the Hg L_{III}-edge EXAFS fitting results indicate that the intercalated mercuric halide is stabilized as a linear molecule with bond distances of ≈2.46 Å for $HgBr_2$-intercalates and ≈2.65 Å for HgI_2 ones, respectively. These intracrystalline structures of intercalated mercuric halides are quite similar to the local structures of free HgX_2 vapors.[25] In this respect, the present EXAFS results clarify that these HgX_2-intercalates are the first examples of two-coordinated mercuric halide molecular solids stabilized in an ionocovalent solid matrix. As shown in Fig. 2, we suggest a structural model for mercuric halide intercalates, based on the present Hg L_{III}-edge EXAFS results and one-dimensional electron density calculations.

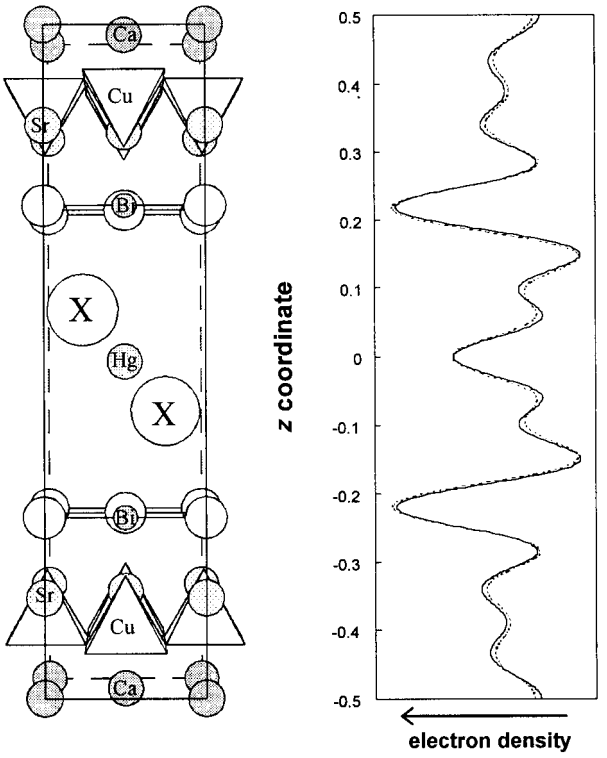

Fig. 2 One-dimensional electron density mappings along the *c*-axis of $(HgX_2)_{0.5}Bi_2Sr_2CaCu_2O_y$, together with the structural model; (—) experimental, (---) calculated.

Organic-salt intercalate

The intercalation of organic chain molecules into the layered superconductor has been expected to be one of the most effective methods to investigate the relationship between the structural anisotropy and high-T_c superconductivity, because it allows us to freely regulate the distance between the superconducting cuprate blocks by controlling the carbon number in the organic intercalant. For this reason, many attempts have been made to intercalate the organic molecule into a superconducting lattice, on the basis of the HSAB concept. But, every trial was found only to fail, which might be due to a severe geometric hindrance of the bulky organic molecule. In this respect, we have adopted a new synthetic strategy using interlayer complexation reaction. Taking into account the coordinately unsaturated state of mercury in HgX_2-intercalates,[5] it is reasonable to expect that the intercalated mercuric halide species could be further ligated by organic/inorganic ligands in the interlayer space of Bi-based cuprates. Based on this synthetic strategy, we were successful in intercalating organic salts into Bi-based compounds. The formation of single phase stage-1 intercalates was confirmed not only by powder XRD analyses but also by a cross-sectional view of the high-resolution electron microscope (HREM) images. The XRD analyses for the organic-salt-intercalate (Py-$C_nH_{2n+1})_2HgI_4$–$Bi_2Sr_2Ca_{m-1}Cu_mO_y$ indicate that the basal increment ranges from 10.8–31.6 Å depending on the length of the alkyl chain. The basal spacing of organic-salt-intercalate is plotted in Fig. 3 as a function of carbon number in the organic chain, where the basal increment (Δd) is linearly proportional to the number of carbon atoms (n) in each alkyl chain over the range $n = 4$–12. From the slope of $\Delta d/n$ (= 2.42 Å), it is suggested that the bilayered alkyl chains are stabilized inbetween Bi_2O_2 layer with a tilt angle of ≈70° with respect to the basal plane as illustrated in Fig. 3.

The HREM image of the cross-section of the organic–inorganic hybrid [(Py-$C_{12}H_{25})_2HgI_4$–Bi2212] obtained by ultramicrotomy is represented in Fig. 4. It appears to feature well-aligned planes with a periodic arrangement of dark lines and bright ones, where the discrete bright lines represent the intercalated organic bilayers. The basal spacing estimated by the present HREM image ($d \approx 48$ Å) is consistent with that from XRD analysis.

In relation to the intercalation mechanism of organic intercalates, the intracrystalline structures of the intercalated Hg–I species have been investigated by EXAFS analysis on the Hg L_{III}-edge for the HgI_2-intercalate and the organic-salt one. The k^3 weighted Fourier transforms (FT's) of Hg L_{III}-

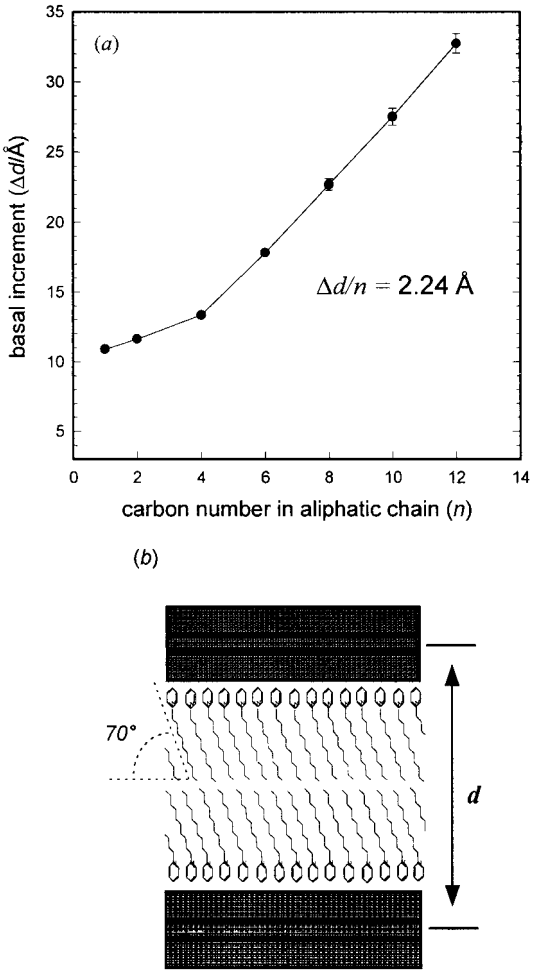

Fig. 3 (a) The relation between the basal spacing and the alkyl chain length in organic–inorganic nano-hybrids $(Py\text{-}C_nH_{2n+1})_2HgI_4$–Bi2212. (b) Schematic illustration of most probable structure of Bi2212 intercalated with *n*-decylpyridinium derivatives It is suggested that complex anion HgI_4^{2-} is sandwiched inbetween the *n*-alkylpyridinium cation but omitted here for simplicity.

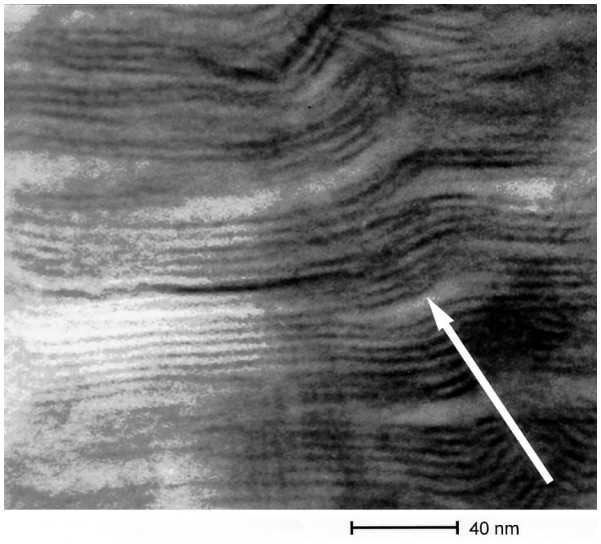

Fig. 4 A cross-sectional HREM image of $(Py\text{-}C_{12}H_{25})_2HgI_4$–Bi2212. The superconducting cuprate layers of 15.4 Å thick are bent by the mechanical strain upon thin-sectioning, where the arrow indicates the cutting direction.

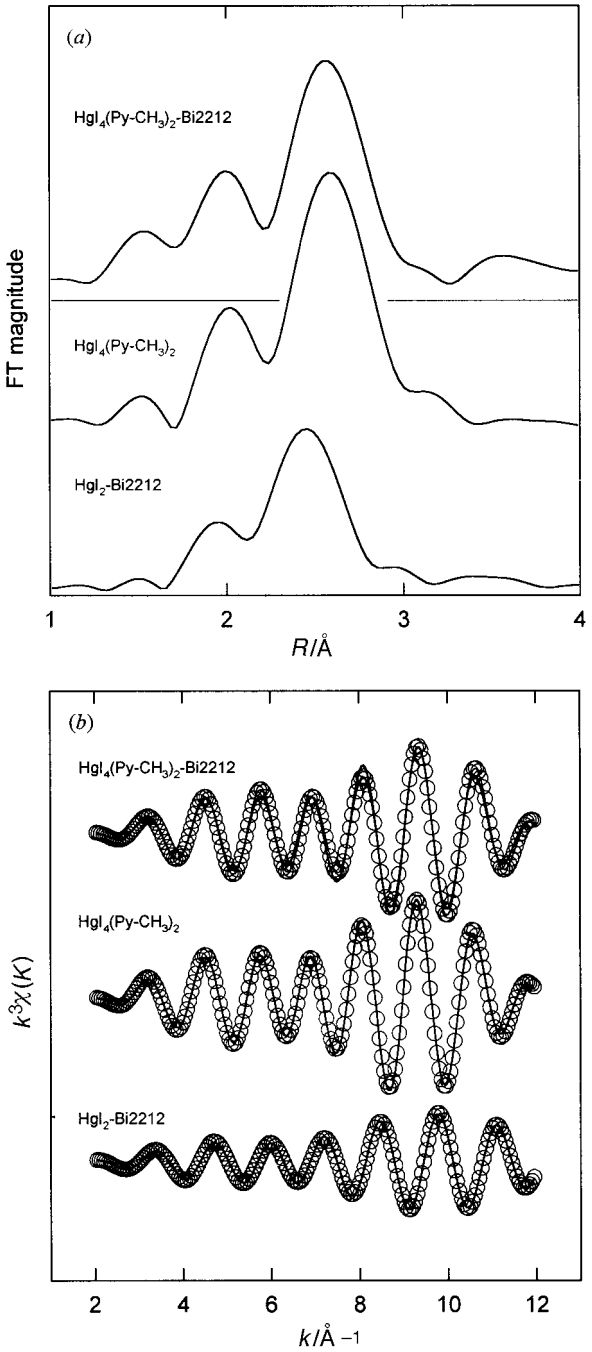

Fig. 5 (a) Fourier transformation of k^3 weighted Hg L_{III}-edge EXAFS spectra and (b) their inverse Fourier transforms for HgI_2–Bi2212, $(Py\text{-}CH_3)_2HgI_4$–Bi2212 and $(Py\text{-}CH_3)_2HgI_4$. The solid line and open circle represent the experimental and calculated data, respectively.

edge EXAFS spectra and their Fourier filtered spectra are shown in Fig. 5(a) and 5(b). From the results of EXAFS curve fitting, the coordination number of Hg was found to increase from two in the HgI_2-intercalate[5] to four in the organic-salt one, which is consistent with the reference compound $(Py\text{-}C_nH_{2n+1})_2HgI_4$.[7] The above result clarifies that the intercalation of organic molecules occurs through the interlayer complexation between intracrystalline HgI_2 and *n*-alkylpyridinium iodide, resulting in the formation of bis(*n*-alkylpyridinium)tetraiodomercurate, $(Py\text{-}C_nH_{2n+1})_2HgI_4$. For this reason, the major driving force of organic-salt-intercalation is assigned as a negative enthalpy change during the formation of the tetraiodomercurate complex anion (HgI_4^{2-}); $HgI_2+2I^-\rightarrow HgI_4^{2-}$, $\Delta H=-95.8$ kJ mol^{-1}.[26]

According to the dc magnetic susceptibilities for pure Bi2212 and its organic-salt-intercalates, all the organic-salt intercalates are found to exhibit high-T_c superconductivity with the onset T_c of 80–81 K, which is higher than those for the iodine-intercalate (T_c = 63 K, Δd = 3.6 Å) and for the HgI_2 one (T_c = 68 K, Δd = 7.2 Å), even slightly higher than that for pure Bi2212 (T_c = 78 K). Considering the large separation between the superconducting blocks and the small coherence length along the *c*-axis in the pure compounds,[27] the high-T_c superconductor interstratified with organic layers can be regarded as a two-dimensional cuprate superconductor with negligible interlayer electronic coupling. Although similar Josephson (S–I–S) coupled multilayers could be fabricated by the sequential deposition of alternate layers of superconducting layers and non-superconducting ones,[28,29] the present organic–inorganic nano-hybrids are believed to be the most suitable model compounds for studying the two-dimensional high-T_c superconductivity, due to completely insulating nature of hydrocarbon molecules in the intercalant layer.[30,31] Moreover, their facility to modify the interlayer distance of superconducting layers allows us to examine systematically the relationship between interlayer distance and the physical properties of layered superconductors.

Application of intercalation to the nano-engineering of high-T_c superconductors

From the viewpoint of application, the intercalation of *n*-alkylchain derivatives can provide a new way of engineering high-T_c cuprates, since it is possible to obtain ultra-fine superconducting particles by exfoliating them into individual sheets. That is, a remarkable lattice expansion upon intercalation leads to a minimization of chemical binding between superconducting blocks, and therefore the superconducting blocks can be separated from each other by applying an appropriate physico-chemical treatment, as illustrated in Fig. 6. In fact, we were successful in preparing the superconducting colloid suspension by the exfoliation of organic-salt-intercalates. At first, an amorphous superconducting film could be realized by dip-coating the colloid suspension with the Ag substrate and the superconducting Bi2212 thin-film was obtained by heating this film at 800 °C for 6 h. As shown in Fig. 7, the sharp (00*l*) XRD peaks are clearly detected for the heat-treated film, indicating that the single phase Bi2212 grains are well aligned along the *c*-axis. The crystal structures of exfoliated particle and as-coated film have also been examined by performing electron diffraction (ED) analyses [Fig. 8(a) and (b)]. While the ED pattern of each exfoliated particle exhibits the characteristic atomic arrangement of $[100]_{Bi2212}$ and $[010]_{Bi2212}$, clarifying the retention of the oxide lattice even after exfoliation, the ED pattern of as-coated film represents concentric circles together with some spot patterns,

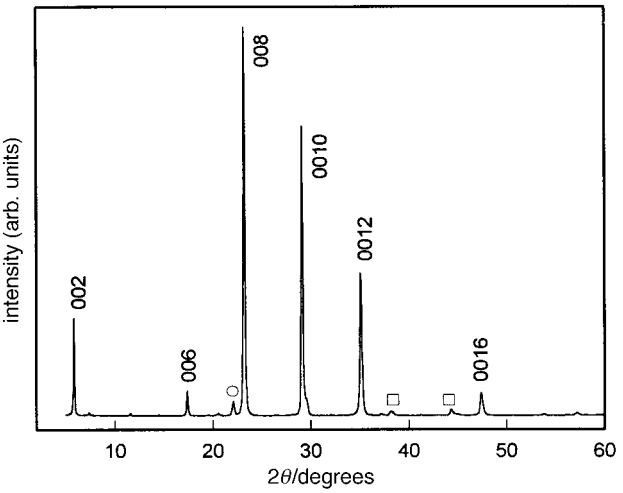

Fig. 7 XRD patterns for superconducting thin film after heat treatment. The XRD reflections originated from other phases are denoted as open squares for Ag substrate and as open circles for impurity Bi2201.

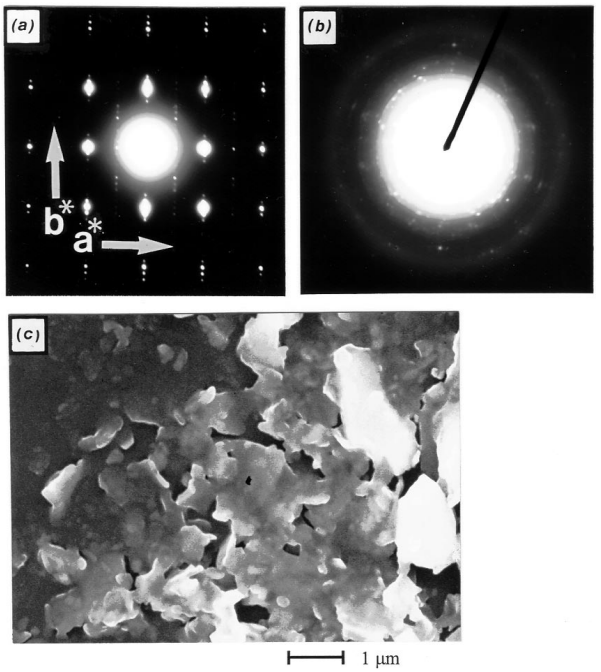

Fig. 8 Electron diffraction patterns for (a) individual particles after exfoliation and (b) as-coated films. (c) Scanning electron micrograph of the substrate surface after dip-coating.

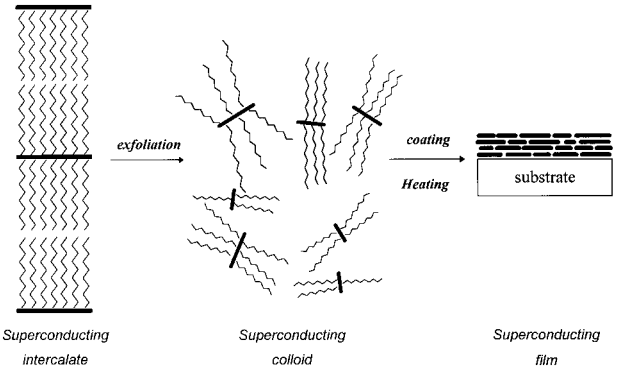

Fig. 6 Schematic diagram for the synthesis of superconducting thin films using intercalation techniques.

suggestive of face-to-face stacking of the exfoliated cuprate sheets. For the as-coated film, the surface morphology has been investigated by obtaining a scanning electron micrograph (SEM), which reveals that the superconducting layers are stacked parallel to the surface [Fig. 8(c)].

Compared to the conventional methods for fabricating superconducting thin-films such as RF-sputtering, chemical vapor deposition, *etc.*, the present method *via* an intercalation complex is believed to be quite simple and economic. In addition to thin-films, this method can also be applied to the preparation of superconducting tapes and wires, by performing continuous dip-coating and heating processes. Moreover, since Bi-based cuprate superconductors have a high critical field (H_{c2}), enough for high-field application, the present intercalation/exfoliation route would be quite useful in fabricating advanced high-magnetic-field equipment.

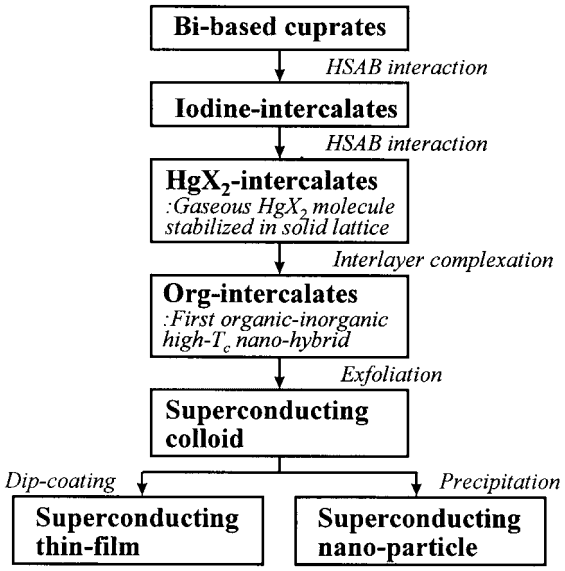

Fig. 9 Flow chart of the synthetic strategy for developing new inorganic–inorganic and organic–inorganic nano-hybrids.

Conclusion

In this paper, a new type of inorganic–inorganic and organic–inorganic high-T_c superconducting nano-hybrids are presented for the first time by adopting unique synthetic strategies of HSAB intercalation and interlayer complexation conceps, as plotted in Fig. 9. As expected, the systematic XANES/EXAFS analyses clarify that the intercalation of metal halides is surely a kind of Lewis acid–base reaction and that the intercalation of organic molecules is achieved through interlayer complexation. For the organic-salt intercalates, the relationship between basal increment and superconducting property has been systematically investigated, which indicates that the superconductivity of high-T_c cuprates is governed by the intrinsic property of the CuO_2 plane. Since the present organic-salt intercalates are also weakly coupled Josephson (S–I–S) multilayers with a controllable thickness of insulating layer, they are expected to be most suitable for studying two dimensional superconducting properties. Moreover, these compounds have a potential applicability for the nano-engineering of high-T_c superconductors such as nano-particles and ultra-thin-films. From the viewpoint of material design, the present novel method of stepwise intercalation provides a new synthetic route to a variety of nano-hybrids.

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