Incorporation of an Ionic Conducting Alkali-Metal Halide into a Two-Dimensional Copper Oxide Lattice through a Novel Stepwise Intercalation Route

Dae Hoon Park, Su Gil Hur, Jong-Ho Jun, and Seong-Ju Hwang*

Department of Applied Chemistry and Center for Emerging Wireless Transmission Technology,
College of Natural Sciences, Konkuk University Chungju Campus, Chungju, Chungbuk 380-701, Korea

Received: August 28, 2004; In Final Form: September 22, 2004

A new lithium iodide intercalation complex, $Li_{0.3}I_{1.0}Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$, has been synthesized by applying a novel stepwise intercalation technique. According to X-ray diffraction analysis, lithium iodide species are stabilized between Bi_2O_2 double layers, leading to an increase of basal spacing of $\sim$3.4 Å per host layer. X-ray photoelectron and X-ray absorption spectroscopic analyses reveal that there is little charge transfer between the intercalant lithium iodide layer and host lattice. In this context, the observed minute change of T_c upon Li–I intercalation can be regarded as evidence of the negligible contribution of interlayer coupling to superconductivity. On the other hand, ac impedance analysis demonstrates that the intercalation complex of lithium iodide species shows a Li^+ ionic conductivity in the order of $\sim$10^{-6} Ω^{-1} cm^{-1} at a low temperature of <70 °C. In combination with an excellent electronic conductivity of the host lattice, this material can be a new type of mixed Li^+ ionic–electronic conductor. From the viewpoint of synthesis, the present compound is the first example of the stabilization of an alkali-metal halide in the two-dimensional metal oxide lattice.

Introduction

A remarkable anisotropy in the chemical bonds of a bismuth-based cuprate high-T_c superconductor makes it possible to apply an intercalation technique in high-temperature superconductor research.[1–3] The incorporation of foreign species into a two-dimensional copper oxide lattice provides an opportunity to examine the role of interlayer coupling in high-temperature superconductivity and to develop novel high-T_c superconducting intercalation complexes as well. Such hybrid materials would possess unique advanced functionality created by the synergetic combination of two different properties.[4] In this regard, intense research interest has been concentrated on this subject, and consequently, several intercalation compounds of high-T_c superconducting cuprate have been synthesized. All the reported inorganic intercalates can be classified as two groups depending upon their synthetic methods. The first class of intercalation complexes can be prepared by a direct reaction between host Bi-based cuprates and vaporized guest molecules such as I_2, Br_2, HgX_2 (X = Br, I), etc.[1,2,5] The other type of intercalates can be obtained through the diffusion of transition-metal ions (e.g., Ag^+ and Au^+) into the interlayer space of iodine intercalated bismuth cuprates.[4,6] Regardless of synthetic routes, all the intercalation compounds show a partial electron transfer from the host lattice to the guest layer, resulting in a change of the hole density in the CuO_2 layer. Such a variation of electronic structure prevents us from examining directly the influence of lattice expansion on superconductivity, i.e., the effect of interlayer coupling.[7] Considering the fact that the band gap of ionic molecules such as alkali-metal halide is large enough to suppress an electron transfer from the host lattice, these compounds are expected to be suitable guest species in studying high-temperature superconducting materials. However, to our knowledge, the intercalation complex of alkali-metal halides has

never been successfully prepared for any type of two-dimensional inorganic solid.

Here we report the successful synthesis of lithium iodide intercalated Bi-based cuprate through a novel stepwise intercalation technique. In the present work, instead of an iodine intercalate, a lithium intercalate is used as a secondary host material for subsequent iodine intercalation.[8] The physical properties and chemical bonding nature of the Li–I intercalate have been examined by performing magnetic susceptibility and ac impedance measurements as well as X-ray photoelectron (XPS) and X-ray absorption (XAS) spectroscopic analyses.

Experimental Section

A polycrystalline $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ sample was synthesized by a conventional solid-state reaction and used as a host material for the intercalation of lithium iodide.[9] Lithium intercalate was prepared by reacting the host bismuth cuprate with $\sim$10 molar excess *n*-BuLi solution in hexane at room temperature for several days, leading to the intercalation of 0.3 mol of lithium ions per formula unit of the host material. According to previous reports on Li intercalation into the bismuth cuprate via chemical and electrochemical methods,[5,10] the present content of lithium nearly corresponds to the maximum limit of Li concentration accommodatable for the host lattice. As a next step, the intercalation of iodine was carried out by heating an evacuated silica tube containing the Li intercalate and excess iodine molecules at 170 °C for 1 h. The formation of a single-phase Li–I intercalate was confirmed by using powder X-ray diffraction (XRD) analysis. The chemical composition of the Li–I intercalate was determined to be $Li_{0.3}I_{1.0}Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ by atomic absorption spectroscopy, induced coupled plasma spectrometry, and thermogravimetry. The evolution of superconductivity upon intercalation was examined by dc magnetic susceptibility measurements. Dc magnetic susceptibilities were measured as a function of temperature with a superconducting quantum interference device

* To whom correspondences should be addressed. Phone: +82-43-840-3569. Fax: +82-43-851-4169. E-mail: hwangsju@kku.ac.kr.
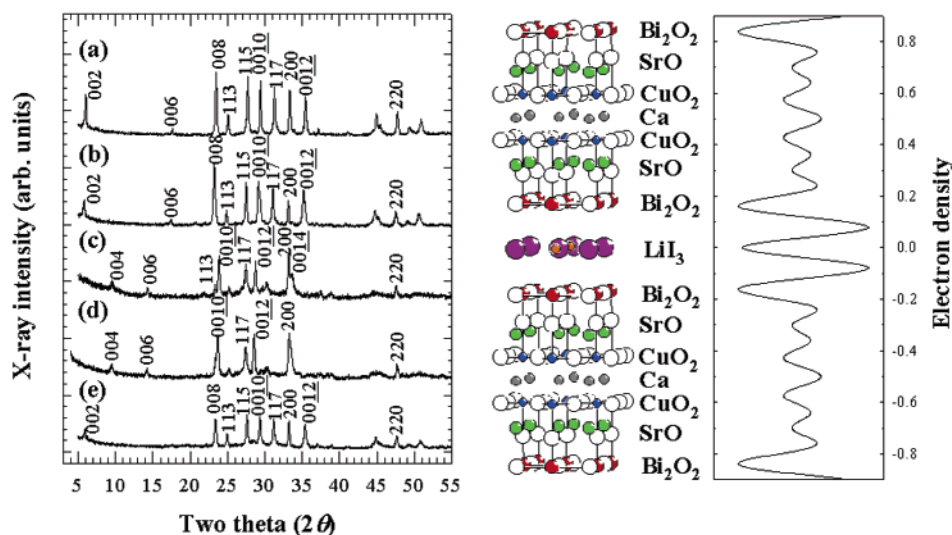
Figure 1. Powder XRD patterns for the (a) pristine $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$, (b) lithium intercalate, (c) lithium iodide intercalate, (d) iodine intercalate, and (e) lithium iodide intercalate after the heat treatment at 500 °C, together with the structural model and experimental 1D electron density map.

(SQUID) magnetometer, where the applied magnetic field was 20 Oe. XPS spectra were recorded by using a PHI 5100 Perkin-Elmer spectrometer. The binding energy (BE) was obtained with an accuracy of 0.8 eV and by charge referencing to the adventitious C 1s peak at 284.6 eV. The XAS experiments were performed at the beam line 7C at the Pohang Light Source (PLS) in Korea. The present XAS data were collected at room temperature from powdered samples in the transmission mode. The X-ray was monochromatized by a silicon 111 double-crystal monochromator detuned to 60% of the maximum intensity to minimize higher harmonics for the I L_I-edge. All the present Cu K- and Bi L_{III}-edge spectra were calibrated carefully by measuring the reference spectrum of Cu metal or Bi metal. The data analysis for the present spectra was performed by standard procedures as reported previously.[11] The ionic conductivity of the Li−I intercalate was measured by complex impedance analysis with a Solartron 1255 frequency response analyzer over a frequency range of 100 Hz to 10 MHz. Judging from the fast electronic conductivity of the host lattice on the order of 10^0-10^3 Ω^{-1} cm^{-1},[12] the applied frequency range allows us to exclude any contribution of an electron conduction in the host lattice and to measure the ionic conductivity of the intercalated Li−I layer only.

Results and Discussion

The powder XRD patterns of the pristine $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ and its lithium iodide intercalate are presented in Figure 1, in comparison with those of lithium and iodine intercalates. The overall feature of the pristine compound remains nearly the same before and after a reaction with *n*-BuLi, which is ascribed to a very weak X-ray scattering power of the lithium ion incorporated. However, a small but distinct shift of the Bragg peaks toward the low-angle side is detected after Li intercalation, evidencing a lattice expansion caused by the incorporation of lithium ions. As shown in Figure 1, the subsequent iodine intercalation for the lithium intercalate gives rise to the further displacement of all the 00*l* reflections toward the lower angle side. From least-squares fitting analysis,[13] the increase of basal spacing upon the Li−I intercalation was determined to be ∼6.8 Å per unit cell (i.e., ∼3.4 Å per host layer), confirming the incorporation of a lithium iodide layer between the Bi_2O_2 double layers. The observed lattice expansion along the *c*-axis is somewhat smaller than that for the iodine intercalate ($\Delta c =$

∼7.0 Å). Such a difference in the lattice expansion can be explained from an electrostatic interaction between lithium cation and iodide anion, leading to the retraction of electron clouds from iodide to lithium. As a consequence, the overlapped 0010/113 and 0014/200 reflections in the pattern of the iodine intercalate are split into the separated features for the lithium iodide intercalate (Figure 1c,d). On the basis of structure factors from the present XRD pattern, we have calculated a one-dimensional electron density map for the intercalation complex of lithium iodide. The simulated result is well consistent with a suggested structural model, evidencing the stabilization of lithium iodide monolayers between Bi_2O_2 double layers (the right panel of Figure 1). However, it should be noted that we could not determine the exact position of the lithium ions from the calculation of the one-dimensional electron density map, since the very small X-ray scattering factor of lithium results in the negligible dependence of the electron density map on its position. On the other hand, the disintercalated product of the lithium iodide intercalate from a heat treatment at 500 °C shows the characteristic XRD features of the host Bi-based cuprate phase, suggestive of the reversibility of the Li−I intercalation (Figure 1e). However, the *c*-axis lattice parameter of this calcined derivative ($c = 30.609$ Å) was estimated to be a little larger than that of the pristine compound but slightly smaller than that of the lithium intercalate.[13] Such a variation of the *c*-axis lattice parameters implies that a fraction of lithium ions still exist in the interlayer space of the bismuth-based cuprate even after the complete removal of the iodine species.

The temperature-dependent dc magnetic susceptibilities of the pristine $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ and its lithium iodide intercalate are plotted as a function of temperature in Figure 2, in comparison with those of the iodine intercalate. Only a slight depression of T_c ($\Delta T_c \leq 3$ K) is discernible after the intercalation of lithium iodide, which is smaller than the T_c decrease upon the iodine intercalation ($\Delta T_c = 8$ K). It is well-known that the Bi-based cuprate shows a parabola-type T_c dependence on the hole density of the CuO_2 layer.[12,14] That is, T_c becomes greater with increasing hole density in a hole-underdoped region, reaches a maximum at an optimum hole concentration, and subsequently decreases with an increase of the hole density in a hole-overdoped region. According to the previous report on the relation between T_c and hole concentration in a cation-substituted Bi-based cuprate system,[9,14] the present host com-
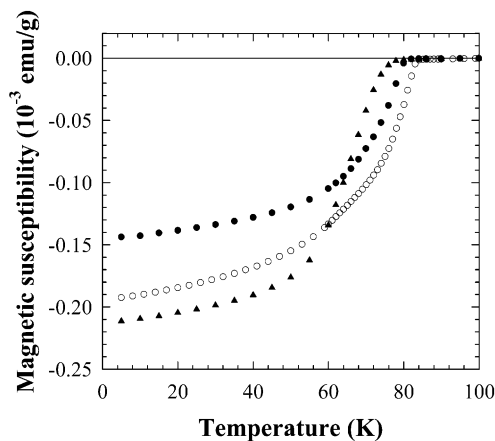
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Figure 2. Temperature-dependent dc magnetic susceptibility of the pristine $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ (open circles) and its lithium iodide (closed circles) and iodine (closed triangles) intercalates.

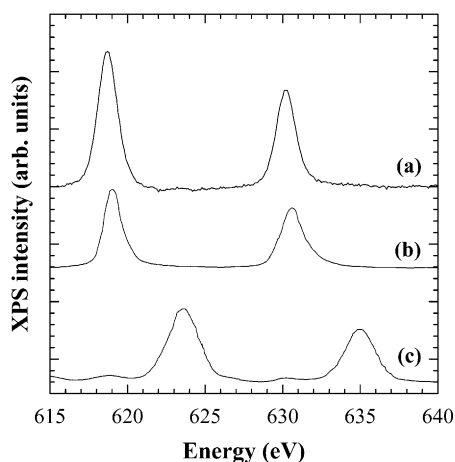**Figure 3.** I 3d XPS spectra for (a) the lithium iodide intercalate, (b) KI, and (c) KIO_4.

position of $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ corresponds to an optimum hole concentration with a maximum T_c. Therefore, any direction of charge transfer between the host and guest, if any, should lead to the depression of T_c due to the deviation of the hole density from an optimum value. On the other hand, there is another factor depressing T_c, i.e., the weakening of interlayer interaction caused by lattice expansion.[7] Therefore, the observed lowering of T_c upon the intercalation is considered to be the net effect of both factors. Considering that the effect of charge transfer cannot relieve the decrease of T_c induced by the weakening of the interlayer coupling, the observed small T_c change can be regarded as strong evidence of the negligible contribution of the interlayer interaction to the superconductivity of layered cuprates.

To investigate the possibility of charge transfer between the host and guest, we have carried out an I 3d XPS spectroscopic investigation for the Li−I intercalate and some references.[15] As can be seen from Figure 3, a set of spin doublets appears commonly for the lithium iodide intercalate and the references KI and KIO_4. A comparison with the reference spectra demonstrates that the BE of the lithium iodide intercalate (618.7 eV) corresponds to that of negatively charged iodide anion (618.0−619.5 eV).[16] In contrast to the iodine intercalate exhibiting the presence of two different oxidation states of iodine,[9] no evidence on the existence of highly oxidized periodate species can be observed for the lithium iodide intercalate. It should be mentioned that, due to a small BE difference between neutral iodine (619.9 eV) and negatively
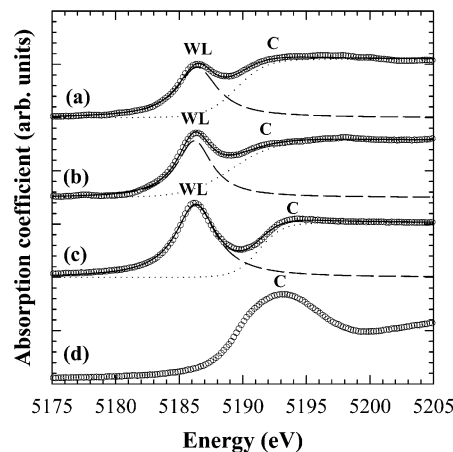

Figure 4. Experimental I L_I-edge XANES spectra (open circles) for (a) the lithium iodide intercalate, (b) the iodine intercalate, (c) I_2, and (d) LiI, and their fits (solid lines) to the sum of the Lorentzian (dashed lines) and sigmoidal (dotted lines) functions.

charged iodide anion, we are unable to conclusively assign the iodine oxidation state of the lithium iodide intercalate on the basis of the XPS results. In this regard, we have applied I L_I-edge X-ray absorption near edge structure (XANES) spectroscopy for determining the oxidation state of iodine, since an XANES feature in the I L_I-edge can provide a quantitative measure for the density of the unoccupied I 5p state.

The I L_I-edge XANES spectrum of the Li−I intercalate is displayed in Figure 4, together with those of the iodine intercalate, I_2, and LiI. Except for LiI with an I $5p^6$ electronic configuration,[17] all the present samples show a white line (WL) peak corresponding to $2s \rightarrow 5p$ transition, together with another peak (C) at higher energy related to a transition from the 2s orbital to the continuum state.[18] A closer inspection reveals that the intensity of the WL peak is slightly smaller for the Li−I intercalate than for the reference iodine and the iodine intercalate. Since the intensity of the WL peak reflects sensitively the density of unoccupied final states,[19] the observed depression of this feature indicates that the unoccupied I 5p orbital is partially filled with the electron transferred from the host lattice. For a quantitative analysis, we have evaluated the area of the WL feature by convoluting the spline spectra with Lorentzian and sigmoidal functions; see Figure 4. The net charges of intercalated iodine species calculated from the relative peak areas with respect to neutral iodine are summarized in Table 1. The area of the WL peak was found to be smaller for the Li−I intercalate by ∼30% than for neutral I_2. Hence, the iodine oxidation state of the lithium iodide intercalate can be assigned as a negatively charged $I^{-0.3}$ state.

The effects of the Li−I intercalation on the electronic structures of CuO_2 and BiO layers have also been examined by using XANES spectroscopy. The Cu K- and Bi L_{III}-edge XANES spectra of the pristine compound and its lithium iodide intercalate are presented in Figures 5 and 6, respectively, in comparison with those of some references. As shown in Figure 5, the Cu K-edge positions of the Bi-based cuprates appear to be higher than those of the references $La_2Cu^{II}O_4$ and $Nd_2Cu^{II}O_4$ but lower than that of the reference $La_2Cu^{III}_{0.5}Li_{0.5}O_4$, indicating the mixed oxidation state of copper (Cu^{II}/Cu^{III}) in these compounds. The Li−I intercalation has little influence on the energy of the edge jump as well as on the position of fine features, highlighting that the hole density in the CuO_2 layer is insignificantly changed by the intercalation of lithium iodide. Like the Cu K-edge region, there is no marked shift of the Bi L_{III}-edge position upon the Li−I intercalation, indicative of a

TABLE 1: Lorentzian and Sigmoid Line Fitting Results of I L_I-Edge XANES Spectra for I_2 and Lithium Iodide and Iodine Intercalates

	Lorentzian line[a]			sigmoid line[b]					
	a_0	w (eV)	E_0 (eV)	b_0	b_1 (eV)	E_1 (eV)	WL area[c] (eV)	no. of holes	iodine oxidation state
I_2	1.37	3.88	5186.30	1.02	0.92	5191.25	8.35	1.00	0
Li−I intercalate	0.95	3.85	5186.41	1.10	1.15	5189.49	5.73	0.69[d]	−0.31
iodine intercalate	1.06	3.33	5186.21	1.08	1.71	5189.13	5.59	0.67[d]	−0.33

[a] The symbols a_0, w, and E_0 represent the maximum amplitude, the full width at half-maximum (fwhm), and the energy at a_0 of the Lorentzian line, respectively, determined by fitting the following Lorentzian equation to the normalized XANES data: $f(E) = a_0[(w/2)^2/((w/2)^2 + (E - E_0)^2)]$, where $a_0 = c/[\pi(w/2)]$, c being the amplitude constant. [b] The symbols b_0, b_1, and E_2 represent the step, the fwhm, and the inflection position of the sigmoid line in energy, respectively, determined by fitting the following sigmoid step function to the normalized XANES data: $f(E) = b_0/[1 + \exp\{-(E - E_1)\}/b_1]$. [c] The WL area was calculated by integrating the Lorentzian line. [d] The amount of holes was estimated by imposing spectral weight to the area of each WL peak.
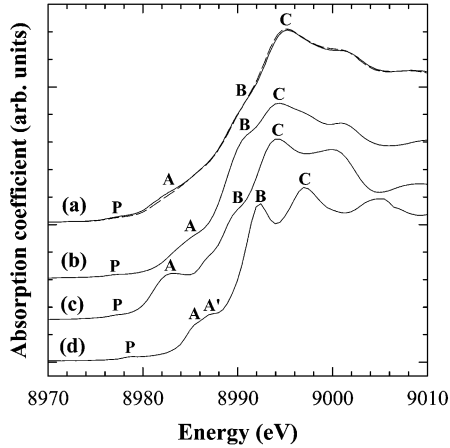

Figure 5. Cu K-edge XANES spectra for (a) the pristine $Bi_2Sr_{1.4}La_{0.1}$-$Ca_{1.5}Cu_2O_y$ (solid lines) and its lithium iodide intercalate (dashed lines), in comparison with the reference spectra of (b) La_2CuO_4, (c) Nd_2CuO_4, and (d) $La_2Cu_{0.5}Li_{0.5}O_4$.
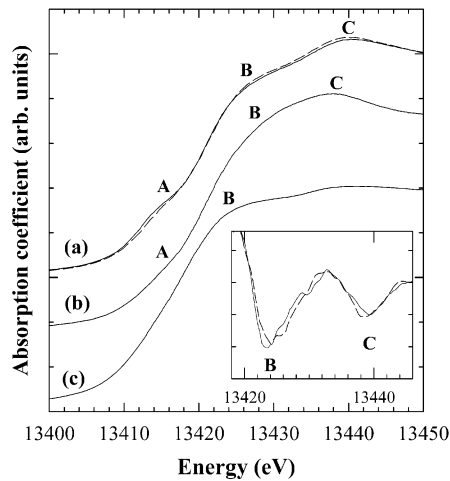

Figure 6. Bi L_{III}-edge XANES spectra for (a) the pristine $Bi_2Sr_{1.4}$-$La_{0.1}Ca_{1.5}Cu_2O_y$ (solid lines) and its lithium iodide intercalate (dashed lines), in comparison with the reference spectra of (b) Bi_2O_3 and (c) Bi metal. The inset represents the second-derivative spectra for the pristine $Bi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ (solid lines) and its lithium iodide intercalate (dashed lines) in the energy range of 13418−13446 eV.

negligible variation in the oxidation state of Bi; see Figure 6. Contrary to the small shift of the edge jump, the energy difference between peaks B and C is slightly decreased after the Li−I intercalation, as can be seen clearly from the inset of Figure 6. According to the previous Bi L_{III}-edge XANES study for Bi-based cuprates and some references,[20] peaks B and C are attributed to $2p_{3/2} \rightarrow 6d_{t_{2g}}$ and $2p_{3/2} \rightarrow 6d_{e_g}$ transitions, respectively. On the basis of this assignment, the peak splitting
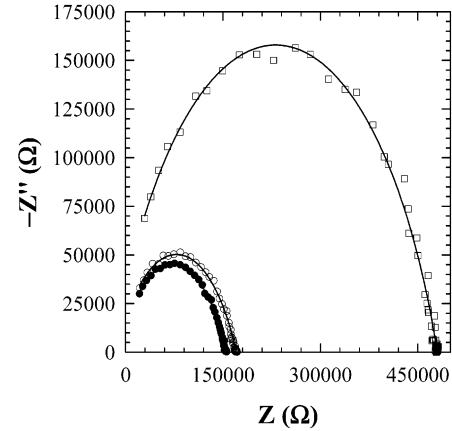

Figure 7. Impedance spectra of the lithium iodide intercalate at 25 °C (□), 55 °C (○), and 65 °C (●) and their fits (−).

between B and C can be regarded as an indicator for the strength of the crystal field around Bi. In this context, the observed decrease in energy difference upon the Li−I intercalation reflects the weakened crystal field of Bi, which can be explained on the basis of the change of the crystal structure. That is, the intercalation of lithium iodide between the Bi_2O_2 double layer causes the replacement of one of the axial oxygens in the BiO_6 octahedra with iodine; see the right panel of Figure 1. Since the electronegativity of iodine is quite lower than that of oxygen, the strength of the crystal field around the bismuth ion is decreased upon the intercalation.

On the basis of the above XAS results, we are able to conclude that the intercalation of lithium iodide has little effect on the oxidation states of Cu and Bi, which is in good agreement with the presence of an electronically neutral ($Li^+_{0.3}I^{-0.3}$) layer. In light of this, the observed small change of T_c is attributable to the weak contribution of interlayer coupling to the super-conductivity of Bi-based cuprate (i.e., less than 3% of T_c).

As mentioned in the Introduction, the synergetic combination of two chemical species can create new useful properties. In the present intercalation compound of lithium iodide, the existence of lithium ions in the two-dimensional interlayer space suggests the possibility of Li^+ ionic conductivity. Actually, lithium iodide exhibits Li^+ ionic conductivity as a pure form or as a composite form with a polymer or other halides.[21,22] In this regard, we have performed ac impedance analysis for studying the ionic conductivity of the intercalate. As shown in Figure 7, the intercalation complex of lithium iodide has Li^+ ionic conductivity on the order of $10^{-7}-10^{-6}$ Ω^{-1} cm^{-1} at a low temperature of <70 °C.[23] As the measuring temperature increases, the ionic conductivity of the intercalate becomes greater, which is typical behavior of ionic conductors, but not of a metallic bismuth cuprate lattice. Now we are applying the

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present stepwise intercalation technique to metal halide intercalation compounds with a larger lattice expansion of $\sim$7 Å per host layer,[11] to probe the relationship between Li^+ ionic conductivity and interlayer distance.

Conclusion

In this work, we have synthesized for the first time a new Li^+ ionic conducting−high-temperature superconducting intercalation complex of $Li_{0.3}IBi_2Sr_{1.4}La_{0.1}Ca_{1.5}Cu_2O_y$ through a novel stepwise intercalation method. To our knowledge, this compound is the first example of an alkali-metal halide intercalation complex. Moreover, the absence of detectable charge transfer between the host and guest makes this intercalate a useful model compound for studying the role of interlayer interaction in a high-temperature superconductor. The present stepwise intercalation technique would enable Li^+ ions to be incorporated into the more expanded interlayer space of metal salt intercalated bismuth cuprates. Such Li^+-containing compounds are supposed to show an improved Li^+ ionic conductivity as well as an excellent electronic conductivity from the host lattice, since the expanded interlayer space provides more efficient pathways for Li^+ ion conduction. In addition, this type of compound can also be an effective precursor for the exfoliation reaction of superconducting bismuth cuprate through H_2 gas evolution as in $LiMoS_2$.[24] This expectation is based on the conjecture that the expanded interlayer distance would allow the introduction of water molecules into the gallery space and hence the hydroxylation reaction of the intercalated Li^+ ion, leading to the interlayer evolution of hydrogen gas and the separation of individual superconductor nanosheets.

References and Notes

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