Electrochemical lithium intercalation into Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$

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Abstract. We have prepared Li-intercalated Li$_x$Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ($x=0-2.0$) samples by using electrochemical method, and performed synchrotron x-ray diffraction, Cu K-edge x-ray absorption fine structure (XAFS), and magnetic susceptibility measurements. With increasing $x$, $a$- and $c$-lattice parameters monotonically increase, which shows lithium intercalation into Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. Accompanied by the lithium insertion, the valence of Cu ion changes from Cu$^{2+}$/Cu$^{3+}$ to Cu$^{1+}$/Cu$^{2+}$ to realize charge neutrality. This change of the valence was detected by Cu K-edge XAFS measurement. A clear increase of spectral weight that corresponds to $1s \rightarrow 4p_{\pi} (3d^{10}L_{\pi})$ was observed at around 8982 eV with $x$. The superconducting (SC) transition temperature $T_C$ significantly changes from 74 K for $x = 0$ to 90 K for $x = 0.8$, which is attributed to modified density of states by the decrease of hole concentration. A volume fraction of the superconducting phase was 1-2 % for $x \geq 0.6$, implying phase separation where Li-rich non SC phase and Li-poor SC phase coexist. Such a phase separation is universally seen in electrode active materials.

1. Introduction

Transition-metal oxides have attracted much interest because of fascinating phenomena such as high-temperature superconductivity in cuprates and oxipnictides [1], giant magnetoresistance in perovskite Mn oxide [2], large thermoelectric properties in rock-salt-type layered cobalt oxide [3], and multiferroic effect in hexagonal Mn oxide [4]. In these materials, carrier concentration is one of the most important parameter for controlling these properties, which is mainly tuned by chemical doping and/or oxygen nonstoichiometry.

Recently, another doping, namely electrostatic doping has been demonstrated using field-effect transistors (FET) that uses a liquid electrolyte as a gate insulator. When electric field is applied for the FET, a Helmholtz electric double layer occurs at the surface. The accumulated charge carrier can exhibit superconductivity even in insulating material KTaO$_3$ [5]. In addition to this study, this FET structure is also used to control superconducting transition temperature $T_C$ of La$_{1-x}$Sr$_x$CuO$_4$ system [6]. In spite of the clear control of the superconductivity, there...
are two disadvantages shown below; (1) atomically flat surface is essential; (2) in principle, bulk properties such as magnetization, and thermodynamic properties can not be detected.

$\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}(\text{Bi2212})$ is one of the most interesting high $T_C$ superconductors with critical temperatures in the range of 70-100 K. Bi2212 has a layered structure consisting of double CuO$_2$ planes sandwiched by BiO-SrO rocksalt-type layers [7], in which carrier concentration is modified by substitutions of Pb ions into Bi sites or oxygen nonstoichiometry [8]. In addition to the chemical doping, iodine and lithium ions have been found to be intercalated owing to the layered structure weakly connected by Van der Waals interaction [9, 10, 11]. Fujiwara et al. have performed lithium intercalation into $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ by using electrochemical method and found that $T_C$ changes with increasing lithium content [10] implying that lithium intercalation changes the electronic structure of Bi2212. Thus, bulk properties of superconductors can be tuned by the electrochemical intercalation, which will be another way to control superconductivity. We have prepared Li-intercalated Li$_x$Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ($x=0$-2.0) samples by using electrochemical method, and performed synchrotron x-ray diffraction, Cu $K$-edge x-ray absorption fine structure (XAFS), and magnetic susceptibility measurements. We have succeeded in detecting the modification of the valence of Cu ion using XAFS, which is consistent with structural and magnetic properties. The superconducting (SC) transition temperature $T_C$ significantly changes from 74 K for $x=0$ to 90 K for $x=0.8$, which is attributed to modified density of states yielded by the lithium intercalation.

2. Experiments

Polycrystalline sample of $\text{Bi}_2\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta}$ was prepared by solid state reaction. Stoichiometric amounts of $\text{Bi}_2\text{O}_3$, SrCO$_3$, CaCO$_3$ and CuO were mixed, and the mixture was sintered at 780 °C for 12 h. Then, the product was finely ground, and sintered at 820 °C for 24 h. The final product was again finely ground, and mixed with a binder polymer [polyvinylidene difluoride (PVDF)] to be Bi2212:PVDF=95:5 (weight ratio). Then, the mixture as an active material for electrodes was again finely ground, and mixed with a binder polymer [polyvinylidene difluoride (PVDF)] to be Bi2212:PVDF=95:5 (weight ratio). Then, the mixture as an active material for electrodes was coated using a spin coater on an indium tin oxide (ITO) transparent electrode where the surface was beforehand cleansed by UV. Finally, the positive electrode was dried at 120 °C for 2 h in vacuum.

Electrochemical reaction was performed in a galvanic cell with the electrolyte made of ethylenecarbonate(EC)/diethylcarbonate(DEC) solution containing 1 mol/l LiClO$_4$. As a negative electrode, stainless steel with lithium metal was used. The theoretical capacity of Li$_x$Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ was calculated to be 33 mAh/g so that the charge/discharge current density of 6.6x mA/g was applied for 5 h to obtain lithium intercalated Li$_x$Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$ ($x=0.2, 0.4, 0.6, 0.8, 1.0,$ and 2.0). The cut-off voltage was from 1.5 to 3.7 V. Lithium content $x$ was evaluated using the current density.

Synchrotron powder x-ray diffraction measurements with wavelength of 0.7749 Å were carried out at the BL-8A at the Photon Factory, KEK, and the structural refinements were performed by Rietveld analysis (RIETAN-FP). X-ray absorption fine structure(XAFS) measurement was performed using the BL-9C at the photon Factory, KEK. The Cu$K$-edge was recorded by a Lytle detector in fluorescent yield mode with a Si(111) double-crystal monochromator and was normalized by the intensity at 9300 eV. The magnetization was measured from 5 to 120 K by a commercial superconducting quantum interference device (SQUID, Quantum Design MPMS). The lithium intercalated sample was treated in a glove box filled with Ar gas, and was sealed by adhesive tape for these measurements. We would like to note that the same sample was used for the three different measurements.

3. Results and Discussion

Figure 1(a) shows the synchrotron powder x-ray diffraction pattern of as-grown Bi2212 sample and Rietveld fitting (green line). Almost all the peaks were well fitted by tetragonal symmetry.
Figure 1. (Color online) (a) Synchrotron powder x-ray diffraction pattern of as-grown Bi2212 sample, the magnified diffraction patterns in the range of (b) 12.6-14.7° and (c) 22.6-26.3° for \( x = 0 - 2.0 \).

(\( I4/mmm \)) with lattice parameters of \( a = 3.8134(2) \) Å and \( c = 30.817(6) \) Å, respectively. A tiny amount of CuO and Bi\(_{0.5}(\text{Sr, Ca})_{0.5}\)O\(_2\) was observed as impurity phases [12]. A broad peak-like background below \( 2\theta = 18^\circ \) is attributed to Kapton tape which wrapped the sample to prevent its exposure to the air. Figures 1(b) and (c) show the magnified x-ray diffraction patterns in the range of 12.6-14.7° and 22.6-26.3°. With increasing \( x \), both the peaks clearly shift to the lower angles implying that the lattice parameter increases. This can be attributed to lithium intercalation into Bi2212 whose layers are weakly connected by Van der Waals interaction.

Figure 2 shows the temperature dependence of the magnetization for \( \text{Li}_x\text{Bi}_{2}\text{Sr}_2\text{CaCu}_2\text{O}_{8+\delta} \) \( (x = 0 - 2.0) \) in the temperature range of 60-120 K. With increasing \( x \), the superconducting transition temperature \( T_C \) (onset) increases, shows the maximum of 90 K at \( x = 1 \), and finally vanishes at \( x = 2 \). This tendency is qualitatively explained by hole concentration per Cu site. According to P. H. Duvigneaud \textit{et al.}, c-axis lattice parameter has a correlation with both the oxygen content \( \delta \) and \( T_C \) [13]. Since the c-axis parameter of the as-grown sample is \( c = 30.817(6) \) Å, the oxygen content \( \delta \) is evaluated to be \( \sim 0.17 \) implying that the present sample is in the overdoped region. With increasing \( x \), the hole concentration would decrease due to the charge neutrality. Thus, the lithium intercalated sample experiences the under-doped region through the optimum-doped region with the maximum \( T_C \) of 90 K.

Figure 3 shows Cu K-edge spectra for \( x = 0 - 2.0 \) samples. The inset shows the raw spectral data in the range between 8960 and 9020 eV. Characteristic shoulder and peak structures are seen at around 8982 and 8993 eV, respectively, which are consistent with previous works [11, 14, 15]. (we indicate these features as \( A \) and \( B \), respectively.) According to the polarized Cu K-edge x-ray-absorption-near-edge structure for the Bi2212 single crystal performed by Bianconi \textit{et al.}
Figure 3. (Color online) Cu K-edge spectra for \( x = 0 - 2.0 \) samples. The inset shows the raw spectral data in the range between 8960 and 9020 eV.

Figure 4. (Color online) (a) \( a \) - and \( c \) -axis lattice parameters, (b) integrated spectral weight at around 8982 eV, (c) \( T_C \) and Meissner fraction as a function of \( x \).

[14], the shoulder \( A \) is assigned to the 1s to out-of-plane 4p state \((3d^{10}_L)\), while the peak \( B \) is assigned to the 1s to in-plane 4p\(_\sigma\) state \((3d^{10}_L)\), where underline and L denote the hole state and ligand, respectively. Combined with the calculation using the muffin-tin potential with different cluster size, these features are well fitted and interpreted [14] as follows: the shoulder \( A \) feature is determined by an unoccupied high-energy conduction band, where the final-state electron is delocalized over a large cluster involving also the positions of the Sr and Ca ions. On the other hand, the peak \( B \) feature is given by the multiple scattering of the photoelectron by O and Cu ions in the four neighbor Cu sites in the CuO\(_2\) plane. Thus, looking at the spectral data shown in Fig. 3, the spectral weight of the shoulder \( A \) at 8982 eV increases and that of the peak \( B \) decreases with increasing \( x \), which implies decrease of the multiple scattering of photoelectron in CuO\(_2\) plane and modification of positions of the Sr and Ca ions by lithium intercalation. The decrease of the multiple scattering may be due to modified CuO\(_2\) plane by the lithium intercalation and/or decrease of ligand hole concentration. Note that CuO with monovalent Cu ion has a peak at 8980 eV that is close to 8982 eV of the peak \( A \) [11]. Thus, the increased spectral weight of the shoulder \( A \) may also be interpreted by increased proportion of Cu\(^+\). Furthermore, the peak \( B \) position for \( x = 1 \) shifted to lower energies by 0.5 eV compared with that for \( x = 0 \), which shows the valence of Cu ion decreases. A similar behavior is observed in insulating Bi\(_2\)Sr\(_2\)YCuO\(_{8+\delta}\) [14].

Figure 4 summarizes (a) lattice parameters, (b) integrated spectral weight at 8982 eV, (c) \( T_C \) and volume fraction of superconductivity as a function of \( x \). As shown in Fig. 4(a), \( a \) - and \( c \) -axis lattice parameters increase with increasing \( x \), exhibit jumps at around \( x = 0.6 \), and again slightly
increase up to $x = 2$. $a$- and $c$-axis lattice parameters for $x = 2$ were larger by 1.5 and 2 % than those for $x = 0$, respectively. As shown in Figs. 1(b) and (c), small shoulder-like peaks are observed at around 13.7 and 23.4°, respectively, which indicates phase separation. Such a phase separation is generally seen in electrode materials where several phases can exist in a narrow composition range. The phase separation is related to the discontinuous jump in the lattice parameters. As shown in Fig. 4(b), $x$ dependence of the integrated spectral weight at 8982 eV is similar to that of $c$-axis lattice parameter, which indicates a strong correlation between $c$-axis lattice parameter and the shoulder A feature. This is consistent with the discussion stated in the previous paragraph. With increasing $x$, $T_C$ increases and shows the maximum of 90 K at $x = 1$, and then finally vanishes at $x = 2$. On the other hand, volume fraction of superconductivity of the intercalated sample was low except for the $x = 0.4$ sample, which again indicates phase separation where lithium-rich and -poor phases coexist. These results clearly shows that the electrochemical intercalation will give an original way to control superconductivity.

4. Summary
We have investigated the electrochemical lithium intercalation into Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$, and found that lattice parameters, integrated spectral weight of x-ray absorption fine structure, and magnetization systematically change with the intercalated lithium content $x$. The increased lattice parameters and the enhanced spectral weight at 8982 eV show indirect evidences of the lithium intercalation into Bi$_2$Sr$_2$CaCu$_2$O$_{8+\delta}$. We have also succeeded to control the superconducting transition temperature $T_c$ and the volume fraction of superconductivity by introducing lithium ions. $T_C$ significantly changes from 74 K for $x = 0$ to 90 K for $x = 0.8$, which can be attributed to the decrease of the hole concentration/Cu ion. A volume fraction of the superconducting phase was 1-2 % for $x \geq 0.6$ implying phase separation where Li-rich non SC phase and Li-poor SC phase coexist.

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