Electrochemical lithium intercalation into$Bi_2Sr_2CaCu_2O_{8+\delta}$

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1 Introduction

Transition-metal oxides have attracted much interest because of fascinating phenomena such as high-temperature superconductivity in cuprates and oxipnictides, giant magnetoresistance in perovskite Mn oxide, large thermoelectric properties in rock-salt-type layered cobalt oxide, and multiferroic effect in hexagonal Mn oxide. 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 $KTaO_3$. In addition to this study, this FET structure is also used to control superconducting transition temperature TC of $La_{1-x}Sr_xCuO_4$ system. 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.

$Bi_2Sr_2CaCu_2O_{8+\delta}$(Bi2212) is one of the most interesting high TC superconductors with critical temperatures in the range of 70-100 K. Bi2212 has a layered structure consisting of double CuO2 planes sandwiched by BiO-SrO rocksalt-type layers, in which carrier concentration is modified by substitutions of Pb ions into Bi sites or oxygen nonstoichiometry. 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. Fujiwara *et al.* have performed lithium intercalation into Bi2212 by using electrochemical method and found that T_C changes with increasing lithium content [1] 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.

2 Experiment

Polycrystalline sample of Bi2212 was prepared by solid state reaction. Stoichiometric amounts of Bi_2O_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 the positive electrode 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 2h in vacuum.

Electrochemical reaction was performed in a galvanic cell with the electrolyte made of ethylenecarbonate(EC)/diethylcarbonate(DEC) solution containing 1 mol/l LiClO4. As a negative electrode, stainless steel with lithium metal was used. The theoretical capacity of $Li_xBi_2Sr_2CaCu_2O_{8+\delta}$ (Li_xBi2212) was calculated to be $33x$ mAh/g so that the charge/discharge current density of $6.6x$ mA/g was applied for 5h to obtain Li_xBi2212 ($x = 0.2, 0.4, 0.6, 0.8, 1.0$, 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 ˚A 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 CuK-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 (I4/mmm) with lattice parameters of a =3.8134(2)˚A and c = 30.817(6) ˚A,

respectively. A broad peak-like background below 2θ =18° 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 of $Li_xBi2212$. 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.
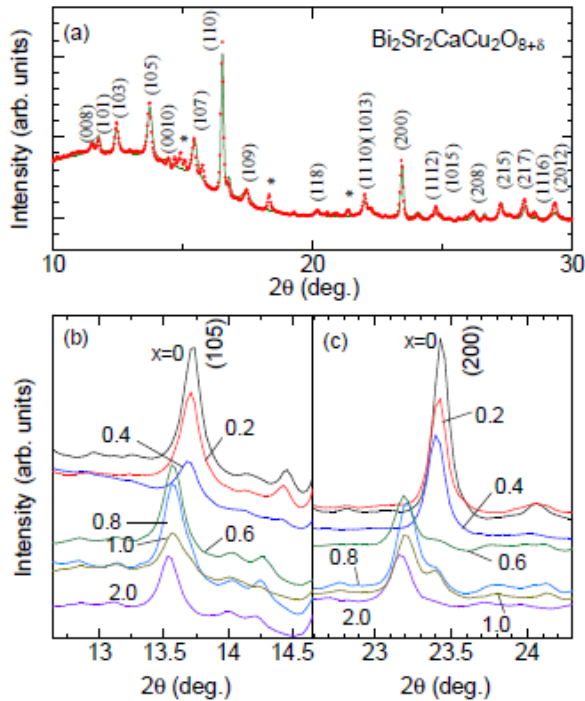

Fig. 1: (a) Synchrotron-radiation powder x-ray diffraction pattern of as-grown Bi2212. (b) and (c) Magnified diffraction patterns of $Li_xBi2212$

Figure 2 shows the temperature dependence of the magnetization for $Li_xBi2212$ 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 $x = 2$. Since the c-axis parameter of the as-grown sample is $c = 30.817(6)$°A, the oxygen content δ is evaluated to be ~ 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.
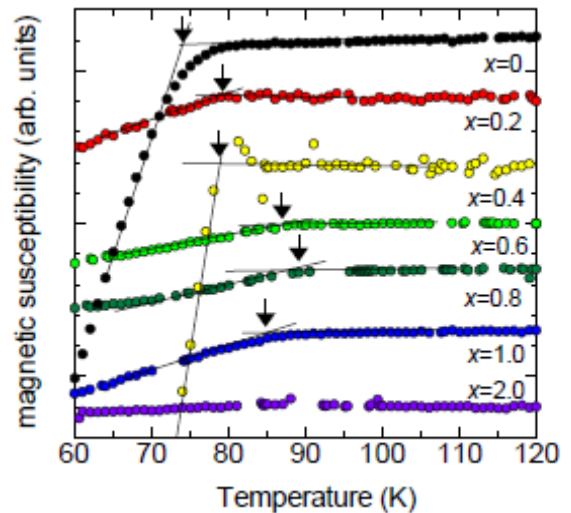

Fig. 2: Temperature dependence of magnetization for $Li_xBi2212$.

Figure 3 shows Cu K-edge spectra for $Li_xBi2212$. 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. We will call these features as A and B, respectively. Based on the polarized Cu K-edge x-ray-absorption-near-edge structure for the Bi2212 single crystal, Bianconi *et al.*[2] assigned shoulder A (B) to the transition from 1s to out-of-plane $4p\pi$ (in-plane $4p\sigma$) state. With increasing in x, the spectral weight of the shoulder A increases while that of the peak B decreases. The increased spectral weight of A indicates decrease of the Cu valence.
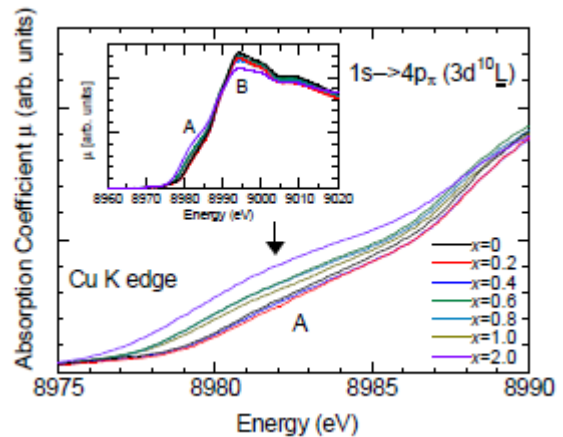

Fig. 3: Cu K-edge spectra for $Li_xBi2212$. The inset shows the overall spectral feature.

Figure 4 summarizes (a) lattice constants, (b) integrated spectral weight of A, (c) T_C and volume fraction of superconductivity, against x. a- and c-axis lattice parameters increase with increasing x, exhibit jumps at around $x = 0.6$, and again slightly than those for $x = 0$, respectively [(a)]. 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. The x dependence of the integrated spectral weight is similar to that of c-axis lattice parameter [(b)]. With increasing x, T_C increases and shows the maximum of 90 K at $x = 1$, and then finally vanishes at $x = 2$ [(c)]. The volume fraction of superconductivity, however, was low except for the $x = 0.4$ sample. These results indicates that the electrochemical doping a promising method to control superconductivity.
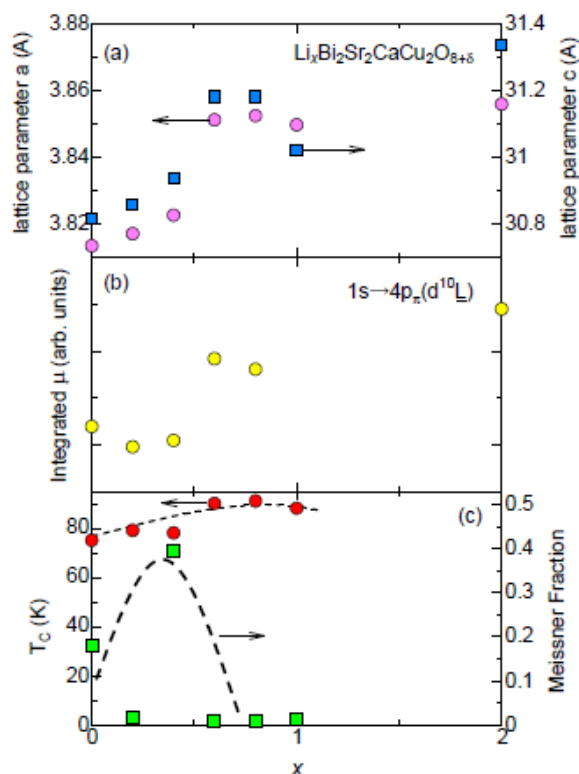
Fig. 4: (a) a- and c-axis lattice constants, (b) integrated spectral weight of A, (c) Tc and Meissner fraction, against x.

References
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