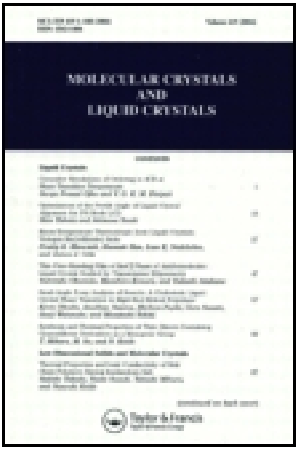


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# Iodine Intercalation of $Bi_2Sr_2Ca_{(n-1)}Cu_nO_y$(N=2,3) Superconductors by Using Reactants $I_2$ or $FeI_2$

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# Iodine Intercalation of $Bi_2Sr_2Ca_{(n-1)}Cu_nO_y$(N=2,3) Superconductors by Using Reactants $I_2$ or $FeI_2$

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The change of superconductivity induced by intercalation is very interesting We have investigated on intercalation into Bi2212 single crystal and Bi2223 polycrystalline superconductors using $FeI_2$ or $I_2$ as reactant. The iodine intercalation by using $FeI_2$ as a reactant into Bi2223 phase is reported for first time as long as we know. In iodine intercalation into Bi2212 by using $FeI_2$ as reactant, the critical tem $T_{Conset}$ in out-of-plane measurement has suddenly decreased on X=0.95. Similar changes of $T_{Conset}$ with higher X have been observed independent of directions and reactants. $T_{Conset}$ of $I_xBi_2Sr_2CaCu_2O_y$ intercalated by $FeI_2$ is a little lower than one of $I_xBi_2Sr_2CaCu_2O_y$ intercalated by $I_2$. This is likely due to the change of hall concentration induced by reduction of host In iodine intercalation into Bi2223, the smaller change of $T_{Conset}$ with increasing amount of intercalant is likely due to the number of $CuO_2$ planes between ntercalant layers.

*Keywords:* Iodine intercalation; Bi2212 single crystal; Bi2223; $FeI_2$; $T_{Conset}$

## INTRODUCTION

Bi-based copper oxide superconductors with layered structures have a chemical property of taking in another elements between Bi-O double layers. This property is called intercalation, and these elements and superconductors are called intercalant and host, respectively. In general, an intercalation leads to the expansion along the c-axis, the change of temperature dependence or anisotropy in electrical conductivity[1-3]. Bi based superconductors have a drastic feature in their electrical transport anisotropy. The normalstate in-plane resistivity typically varies linearly with temperature, whereas the out-of-plane resistivity varies like a one of semiconductors. In addition, the out-of-plane resistivity is changed like one of metals after intercalation[4-6].

The change of superconductivity induced by intercalation is very interesting. We have investigated on intercalation into Bi2212 single crystal and Bi2223 polycrystalline superconductors using some halogens and halides. In previous paper, we reported iodine intercalation into Bi2212 by using $FeI_2$ as a reactant[7]. In our recent work, we have succeeded in iodine intercalation into Bi2223 superconductors by using $FeI_2$ as a reactant. In these intercalations, it needs oxygen for separation of $I_2$ from $FeI_2$. It is likely that oxygen was released from host material, because intercalation was carried out in vacuum sealed pyrex tubes. This will lead differences of change of superconductivity between $FeI_2$ and $I_2$. We have investigated on the influence to the superconductivity of $Bi_2Sr_2 \cdot Ca_{(n-1)}Cu_nO_y$(n=2,3) due to the iodine intercalation into Bi2212 single crystal and Bi2223 polycrystalline superconductors by using $FeI_2$ and $I_2$ as reactant.

## EXPERIMENT

Bi2212 single crystal and Bi2223 polycrystalline superconductors were prepared using the ingredients $Bi_2O_3$, PbO, $SrCO_3$, $CaCO_3$ and CuO. In the process of preparation of Bi2212 single crystal, at first feed and seed rods were sintered by ordinary solid state reaction with the ratio of Bi:Sr:Ca:Cu=2.2:1.8:1:2, then single crystal was grown in air at a rate of 1mm/h by travelling solvent floating zone(TSFZ) method. Bi2223 polycrystalline was prepared by ordinary solid state reaction process with the ratio of Bi:Pb:Sr:Ca:Cu=1.84:0.34:1.91:2.03:3.06. At first, mixed powder was calcined in a gold boat at 800℃ for 16h and then ground and pelleted at 396MPa. Then pellet was sintered at 845℃ for 120h in air.

Host and reactant were placed in 8mm-diameter pyrex tubes and then vacuum sealed at 0.3Torr. The length of pyrex tube after sealing was about 8cm. Intercalation using $FeI_2$ was carried out at 150-161℃ for 24-144h with the temperature gap between host and reactant parts. Intercalation by $I_2$ was carried out at 150℃ for 24-48h.

To characterize the intercalates, surface scanning or powder X-ray diffraction(XRD) with CuK $\alpha$ radiation, analysis of composition by fluorescent X-ray analysis microscope(0.1mm $\phi$ ), weight change measurements before and after intercalation and resistance measurements by four-probe method with 1-5mA, were carried out. From XRD patterns, lattice parameter was decided with the angle $20 \leqq 2\theta \leqq 35^\circ$.

## RESULT AND DISCUSSION

Fig.1 shows the X-ray diffraction patterns of Bi2212 pristine and $I_XBi_2Sr_2CaCu_2O_y$. Diffraction pattern (a) shows Bi2212 pristine phase. Patterns (b) and (c) show the intercalated phases by using $I_2$ and $FeI_2$ as reactant, respectively. The value of X

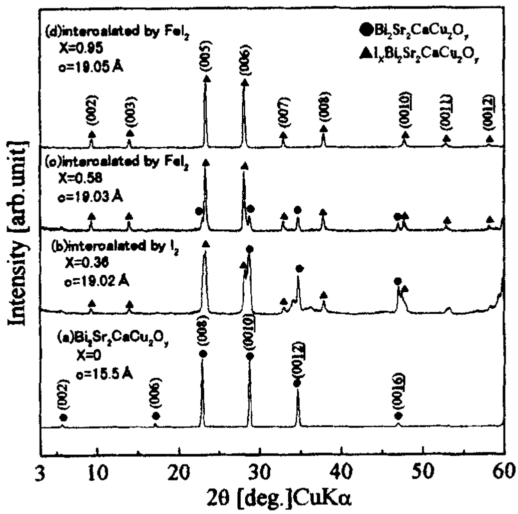


FIGURE 1 XRD patterns for $Bi_2Sr_2CaCu_2O_y$ single crystal and $I_xBi_2Sr_2CaCu_2O_y$ intercalated by $FeI_2$ or $I_2$.

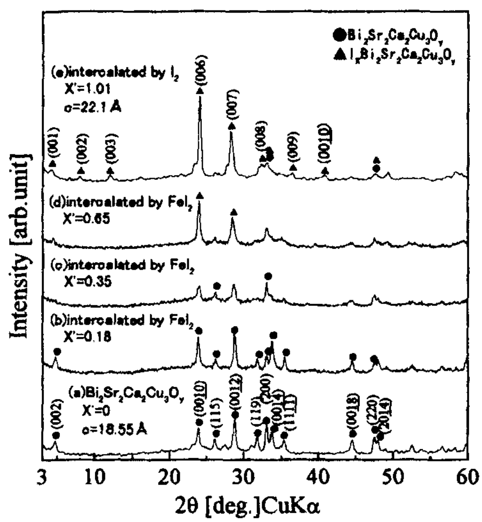


FIGURE 2 XRD patterns for $Bi_2Sr_2Ca_2Cu_3O_y$ and $I_x Bi_2Sr_2Ca_2Cu_3O_y$ intercalated by $FeI_2$ or $I_2$.

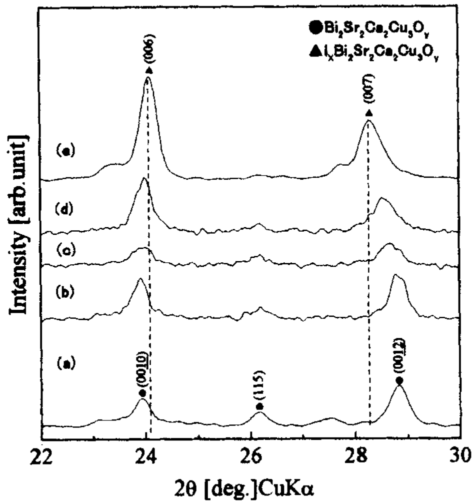


FIGURE 3 Expanded pattern of fig.2.

was determined by fluorescent X-ray analysis. From the patterns (b) and (c), it is found that Bi2212 phase coexists with intercalated one and the ratio of peak intensities for Bi2212 and intercalated phases reverses with increasing X. Similar results have been also obtained in iodine intercalation by $I_2$. From the comparison with X and one of calculated value from ratios of peak intensity, it has been found that there is the error of about $\pm 0.2$ in X. Although the error is slightly big, the value of X has been determined by fluorescent X-ray analysis. Because the size of samples of Bi2212 single crystal for XRD and resistance measurements is about $1.5\text{mm} \times 3\text{mm} \times 30\,\mu\text{m}$, it is very difficult to decide X from weight change measurements before and after intercalation. Thus, X of $I_XBi_2Sr_2CaCu_2O_y$ has been determined by fluorescent X-ray analysis.

Fig.2 shows X-ray diffraction patterns of Bi2223 polycrystal and $I_XBi_2Sr_2Ca_2Cu_3O_y$. Fig.3 is the expanded pattern of Fig.2. Diffraction pattern (a) shows Bi2223 phase, patterns (b)~(d) show the intercalated phases by $FeI_2$ and (e) shows intercalated phase by $I_2$. Pattern (e) has been added to confirm the iodine intercalation with $FeI_2$, because there is upper limit of X in the intercalation by $FeI_2$. In order to distinguish the X value determined by fluorescent X-ray analysis from the one determined by weight change measurement, X' value are used for latter. The peaks of $I_XBi_2Sr_2Ca_2Cu_3O_y$ are gradually appearing with increasing X'. The observed shift of peaks on $2\theta = 24$ and $28°$ is due to the overlap with the broad peaks of Bi2223 and $I_XBi_2Sr_2Ca_2Cu_3O_y$ phases.

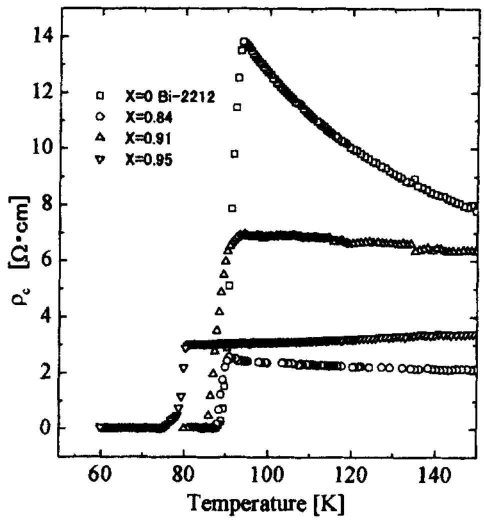


FIGURE 4 Out-of-plane resistivity vs temperature curves for $Bi_2Sr_2CaCu_2O_y$ single crystal and $I_xBi_2Sr_2CaCu_2O_y$ intercalated by $FeI_2$.

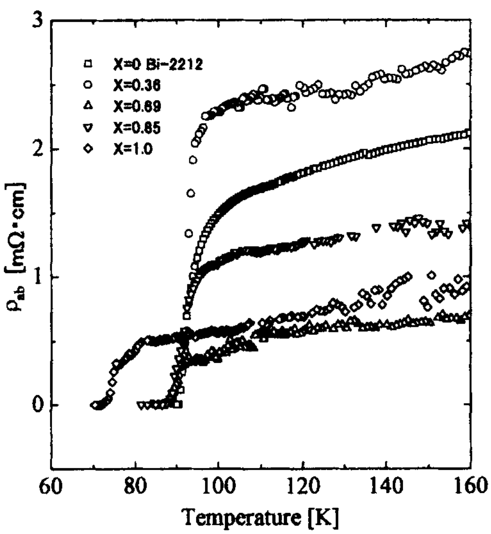


FIGURE 5 In-plane resistivity vs temperature curves for $Bi_2Sr_2CaCu_2O_y$ single crystal and $I_xBi_2Sr_2CaCu_2O_y$ intercalated by $I_2$.

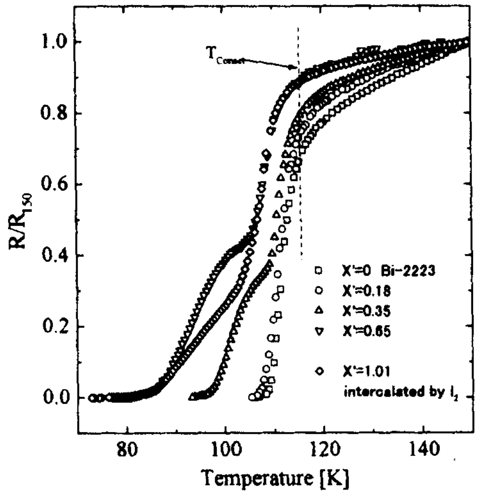


FIGURE 6 Temperature dependence of resistance for $Bi_2Sr_2Ca_2Cu_3O_y$ and $I_XBi_2Sr_2Ca_2Cu_3O_y$ intercalated by $FeI_2$ or $I_2$.

Fig.4 and Fig.5 show the temperature dependence of out-of-plane resistivity for $I_XBi_2Sr_2CaCu_2O_y$ intercalated by $FeI_2$ and in-plane resistivity for $I_XBi_2Sr_2CaCu_2O_y$ intercalated by $I_2$, respectively. The out-of-plane resistivity becomes metallic as the X value increases. In both out-of-plane and in-plane directions, the critical temperature $T_{Conset}$ has suddenly decreased on X=0.95 and 1.00, respectively. These sudden changes of $T_{Conset}$ with higher value of X have been observed independent of directions and reactants.

Fig.6 shows the temperature dependence for $I_XBi_2Sr_2Ca_2Cu_3O_y$ intercalated by $FeI_2$ or $I_2$. Although transition widths greatly increase with increasing X', $T_{Conset}$ has a little change with increasing X'. In iodine intercalation into Bi2212 polycrystal, $T_{Conset}$ greatly decrease with increasing X[8-10]. This difference between Bi2223 and Bi2212 polycrystal is likely due to the number of $CuO_2$ planes between intercalant layers.

Fig.7 shows the dependence of $T_{Conset}$ on X for $I_XBi_2Sr_2CaCu_2O_y$ and $I_XBi_2Sr_2Ca_2Cu_3O_y$. $T_{Conset}$ of $I_XBi_2Sr_2CaCu_2O_y$ intercalated by $FeI_2$ is a little lower than one of $I_XBi_2Sr_2CaCu_2O_y$ intercalated by $I_2$. This is likely due to the change of hall concentration induced by releasing of oxygen from host material in intercalate reaction.

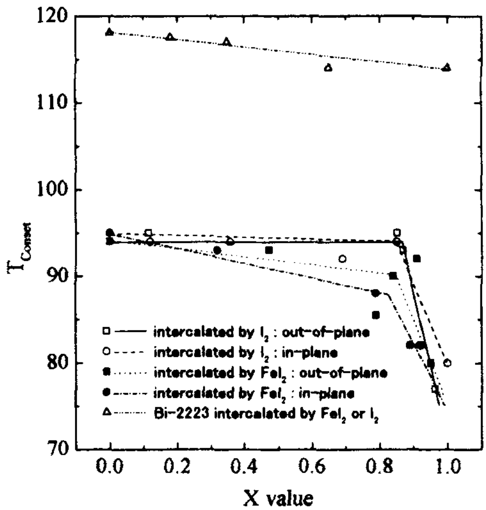


FIGURE 7 Dependence of critical temperature($T_{Conset}$) on X for $I_XBi_2Sr_2CaCu_2O_y$ and $I_XBi_2Sr_2Ca_2Cu_3O_y$.

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