

# $T_c$ increase of Bi2212 induced by exposure to organic liquids or by photocatalytic effect using $\text{TiO}_2$

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Superconducting transition temperature  $T_c$  of Bi2212 phase ( $T_c = \sim 80$  K) was increased when the samples were exposed to various organic liquids at room temperature. No structure change was observed.  $T_c$  was increased gradually with an exposure time, and was saturated about 30 days later. The increase of  $T_c$  ( $\Delta T_c$ ) was observed to be at most 13 K when exposed to glycerol. The lattice expansion was observed after the exposure to organic liquids, suggesting that the organic molecules are intercalated into the samples. As-prepared Bi2212 samples were observed to be in the overdoping state in the study of Y-substituted samples. It was interpreted that the  $T_c$  increase originates from the decrease of hole concentration caused by the electron donation from intercalated and adsorbed organic molecules to  $\text{CuO}_2$  layers.  $\Delta T_c$  showed an almost linear dependence to the relative polarizability  $\alpha_s$  of organic liquids, which was interpreted by that the organic molecules with the higher  $\alpha_s$  can donate the larger number of electrons. The  $T_c$  increase was also observed by irradiating UV ray (254 nm) to the mixture of Bi2212 and  $\text{TiO}_2/\text{Pt}$ , which was explained to be due to the decrease of hole concentration caused by the charge transfer from  $\text{TiO}_2$  to Bi2212.

**Keywords:** Bi2212 phase; superconducting transition temperature; increase of  $T_c$ ; overdoping; intercalation; organic molecules; relative polarizability; X-ray diffraction; magnetic susceptibility; electrical resistivity; photocatalytic effect; anatase.

## 1. Introduction

Since the discovery of cuprate superconductor of  $(\text{La}_{2-x}\text{Ba}_x)\text{CuO}_4$  with high critical temperature ( $T_c$ ) by Bednorz and Müller<sup>1)</sup>, a lot of high- $T_c$  copper oxides have been found. The Bi-Sr-Ca-Cu-O series is described as  $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4+\delta}$  ( $n = 1, 2, 3$ )<sup>2,3)</sup>. Corresponding to  $n = 1, 2$ , and 3, these oxides are referred to Bi2201, Bi2212, and Bi2223, respectively. Bi2201, Bi2212, and Bi2223 phases exhibit  $T_c$  at  $\sim 20$  K,  $\sim 80$  K, and  $\sim 110$  K, respectively. The schematic crystal structure of Bi2212 phase (pseudo-tetragonal:  $I4/mmm$ ) is shown in Fig. 1. The structure is constructed with  $\text{CuO}_2$  planes separated by Ca atoms and edge-shared BiO double layers; the stacking sequence is Bi-Sr-Cu-Ca-Cu-Sr-Bi<sup>4)</sup>. The BiO layers contain excess oxygen atoms, donating holes to  $\text{CuO}_2$  planes.

It is hardly prepare the stoichiometric Bi2212 samples; about 5 % of Sr sites are usually substituted by Bi ions to give the actual chemical formula of  $\text{Bi}_{2+x}\text{Sr}_{2-x}\text{CaCu}_2\text{O}_{8+\delta}$  ( $x = \sim 0.1$ ). The cation disorder in the Sr site strongly affects the value of  $T_c$ <sup>5)</sup>.

We have previously reported that amorphous Se was selectively crystallized into either of two types of Se crystals (hexagonal Se and  $\alpha$ -monoclinic Se) when exposed to organic fluids at room temperature<sup>6,7)</sup>. Grown crystal type was observed to depend on the relative dielectric constant of organic fluids. Organic molecules play only a catalytic role.

$T_c$  of Bi2212 phase is known to be very sensitive to many structural factors such as lattice modification, nonstoichiometry, substitution of other elements, etc.

In this study, thus, we investigated the change of  $T_c$  of Bi2212 phase by exposing the samples to various organic liquids.

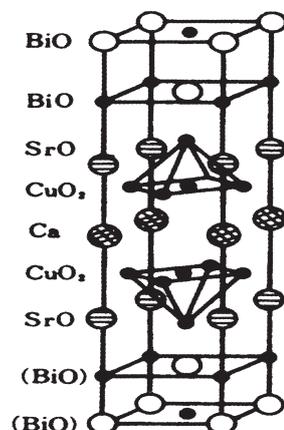


Figure 1. Schematic crystal structure of Bi2212 phase.

## 2. Experiments

Bi2212 samples were prepared by following manners. Mixture of  $\text{Bi}_2\text{O}_3$  (Wako chemical Ltd., 99.99% in purity),  $\text{SrCO}_3$  (Wako chemical Ltd., 99.99% in purity),  $\text{CaCO}_3$  (Nacalai tesque, 98.0% in purity), and  $\text{CuO}$  (Wako chemical Ltd., 99.99% in purity) with the atomic ratio of  $\text{Bi} : \text{Sr} : \text{Ca} : \text{Cu} = 4 : 3 : 3 : 4$ , was mixed thoroughly and was pressed into a pellet, followed by heating at 1027 K for 1 day in air atmosphere. The obtained pellet was ground and pelletized again, followed by annealing at 1047 K for 2 days. The sample was finally annealed at 1123 K for 2 days, after grinding and palletization, and then was slowly cooled to room temperature. Y substituted samples of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$  were prepared by similar ways using  $\text{Y}_2\text{O}_3$  (Rare metallic, 99.999% in purity).

Pelletized samples of Bi2212 were immersed in various organic liquids at room temperature for more than 30 days. The examined organic liquids are cyclohexane, benzene, toluene, diethyl ether, acetophenone, acetone, ethanol, benzonitrile, methanol, *t*-butyl alcohol, acetonitrile, ethylene glycol, and glycerol.

The samples were identified by powder X-ray diffraction (XRD) method using a diffractometer with monochromated  $\text{CuK}\alpha$  radiation (RIGAKU; Rint 2500). The surfaces of the pellets were observed by scanning electron microscopy (SEM) using a CL-SEM (JEOL JSM-5410CL). Electrical resistivity ( $\rho$ ) measurements were performed for these pellets

using dc four-probe method from 2 K to 300K. Magnetic susceptibility  $\chi$  was measured using a SQUID magnetometer (MPMS XL5, Quantum Design) under 0.1 T from 2 K to 300 K. The experimental procedures are schematically shown in Fig. 2. The pellet was cut in half. A half of as-prepared pellet was used for the physical measurements. Another half pellets was used for the measurements after being exposed to organic liquids.

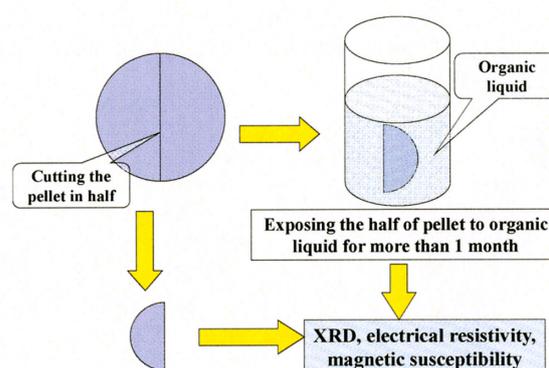


Figure 2. Experimental procedures. The pelletized sample was cut in half. A half of pellet of as-prepared sample was used for several kinds of measurements, and another half of pellet was exposed to organic liquids, followed by the measurements.

## 3. Results

### 3-1 XRD and SEM observations

Figure 3 shows XRD patterns of as-prepared sample of Bi2212 and the sample obtained by being immersed in methanol for 44 days. There is no structure change after the exposure to methanol; both samples are of the pseudo-tetragonal phase.

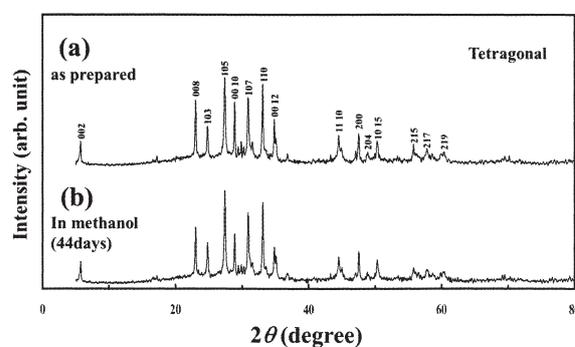


Figure 3. XRD patterns of Bi2212 phase: (a) as-prepared, (b) after 44 days of exposure to methanol.

Calculated lattice parameters were  $a = 0.3823$  nm and  $c = 3.084$  nm for as-prepared sample. After the exposure to methanol liquid, the sample showed a slight increase of both  $a$  and  $c$ . No detectable change was also observed in XRD patterns for the other organic liquids. TEM observations showed no apparent change of ED patterns<sup>8)</sup>.

Figure 4 represents SEM image of the surface of the pellet of as-prepared Bi2212 sample, showing that the pellet consists of many thin plate like crystals with the surface area smaller than  $10^{-12}$  m<sup>2</sup>.

Figure 5 exhibits SEM image of powdered Bi2212 phase obtained by 30 days of exposure to methanol. No significant change, such as exfoliation, was observed in the morphology of particles.

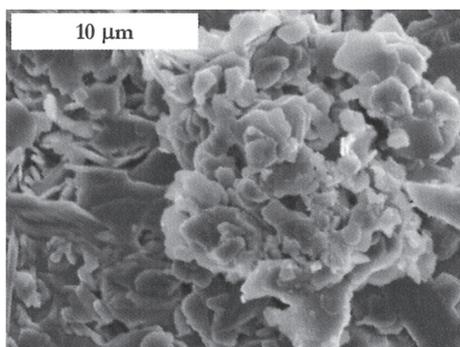


Figure 4. SEM image of the surface of the pellet of as-prepared Bi2212.

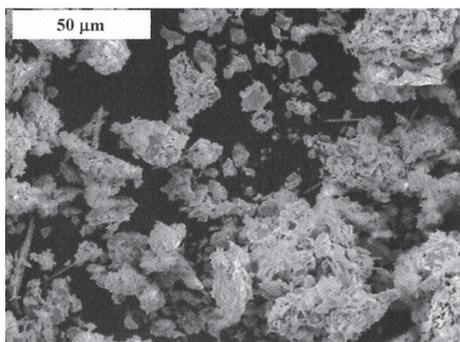


Figure 5. SEM image of powdered Bi2212 sample obtained by being exposed to methanol for 30 days.

### 3-2 Increase of $T_c$ induced by exposure to organic liquids ( $\rho$ and $\chi$ measurements)

Figure 6 shows temperature variations of electrical resistivity  $\rho$  for the half pellets of as-prepared Bi2212 sample and of another half pellets obtained by 31 days of exposure to methanol liquid at room temper-

ature. The figure clearly shows the increase of  $T_c$  by the exposure to methanol; the as-prepared sample exhibits  $T_c$  (onset) at  $\sim 80$  K, and the methanol-treated sample at  $\sim 89$  K.

$T_c$  was observed to increase gradually with an exposure time:  $T_c = 81$  K, 82 K, and 85 K after 3 h, 6 h, and 24 h of exposure, respectively. Samples showed no more increase after about 30 days of exposure.  $T_c$  was also increased when the pellet was partially dipped in methanol liquid, indicating that the methanol liquid was soaked through into the inside of the pellet by capillary action, which is compatible with the SEM image of pelletized sample containing many voids as shown in Fig. 4.

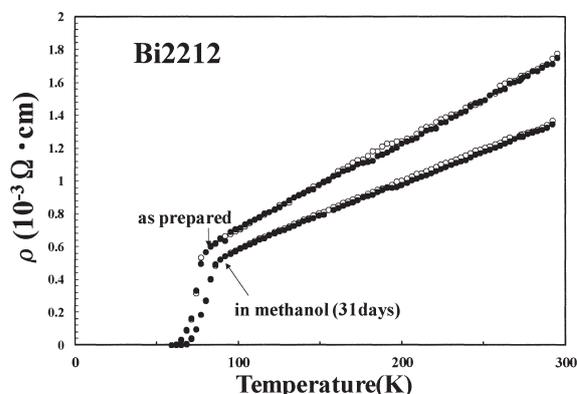


Figure 6. Electrical resistivity ( $\rho$ ) of Bi2212 (as-prepared and obtained by 31 days of exposure to methanol).

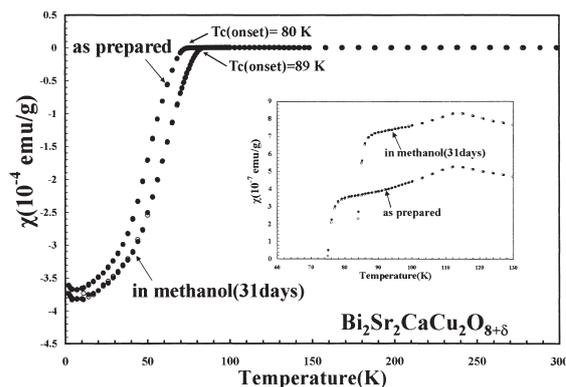


Figure 7. Magnetic susceptibility ( $\chi$ ) of Bi2212 before and after exposure to methanol liquid.

Figure 7 exhibits temperature dependences of magnetic susceptibility  $\chi$  for the Bi2212 sample same as that used in the  $\rho$  measurements.  $T_c$  increased to 89 K after 31 days of exposure to methanol, compatible

with the  $\rho$  measurements. The volume fraction of superconductivity was scarcely changed after the exposure, indicating that the sample was uniformly affected by the exposure treatment. Enlarged  $\chi$  data around  $T_c$  are shown in the inset of Fig. 7, where the increase of  $T_c$  is more clearly shown. A broad peak around 120 K would be due to the  $T_c$  of possibly co-existing Bi2223 phase. The  $T_c$  of Bi2223 was scarcely changed by being exposed to methanol. The amount of Bi2223 phase is negligibly small, because no anomaly was observed in the  $\rho$  measurements.

The same treatments were carried out on the Bi2212 samples using other organic liquids. The increase of  $T_c$  (onset) ( $\Delta T_c$ ) was observed for almost examined organic liquids.  $\Delta T_c$  after 30 days of exposure was 1 K, 3 K, 2 K, 0 K, 4 K, 5 K, 5 K, 5 K, 9 K, 6 K, 6 K, 5 K, and 13 K for cyclohexane, benzene, toluene, diethyl ether, acetophenone, acetone, ethanol, benzonitrile, methanol, *t*-butyl alcohol, acetonitrile, ethylene glycol, glycerol, respectively.  $T_c$  was not influenced by H<sub>2</sub>O.

$T_c$  showed the sample dependence. Figure 8 gives temperature dependences of  $\chi$  for the sample different from that shown in Fig. 6 and 7. After 30 days of exposure to methanol,  $\Delta T_c$  was observed to be 12 K, which is higher than that of other samples.

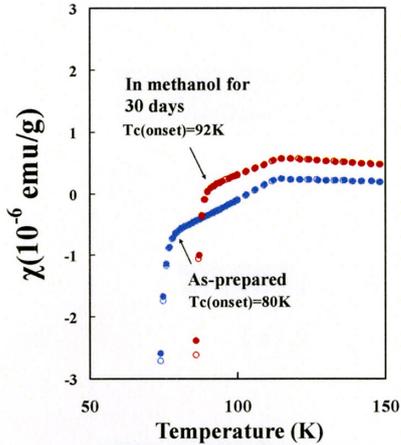


Figure 8. Temperature variations of  $\chi$  for as-prepared Bi2212 and the sample obtained by being exposed to methanol for 30 days.

### 3-3 $T_c$ increase due to exposure to the vapor of methanol

Figure 9 shows the  $\chi$  data for the Bi2212 after ex-

posure to methanol vapor for 30 days at room temperature.  $T_c$  increased by 5 K after the exposure. The  $\Delta T_c$  is lower than that in the liquid, which may be owing to the lower molecular density of methanol gas as compared with the liquid.

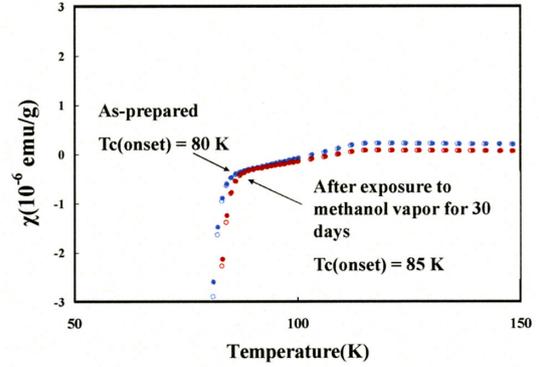


Figure 9.  $\chi$  data for the Bi2212, as-prepared and obtained by exposure to methanol vapor for 30 days at RT.

### 3-4 Y-substitution for Ca in Bi2212

$T_c$  of cuprate superconductors is known to depend on the hole concentration. The maximum  $T_c$  is observed at the optimum-doping concentration<sup>9)</sup>. The hole number dependence of  $T_c$  of Bi2212 phase was investigated in the Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+δ</sub> system<sup>10)</sup>. The hole concentration in this system decreases with increasing  $x$ . The concentration  $x$  for optimum-doping was observed to be  $\sim 0.2$  ( $T_c = \sim 100$  K)<sup>10)</sup>. This means that the as-prepared samples of Bi2212 are in the overdoping state, leading us to consider that the increase of  $T_c$  caused by the exposure to organic liquids would be due to the decrease of hole concentration. In order to confirm this speculation, we have observed the  $T_c$  change of Y-substituted samples by exposing the samples to organic liquids.

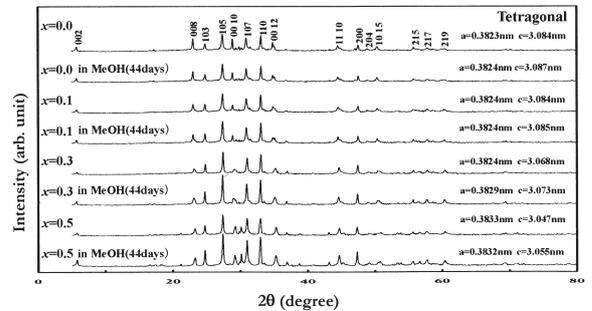


Figure 10. XRD patterns for Bi<sub>2</sub>Sr<sub>2</sub>Ca<sub>1-x</sub>Y<sub>x</sub>Cu<sub>2</sub>O<sub>8+δ</sub>, (samples as-prepared and obtained by exposure to methanol for 44 days for each composition  $x$ ).

XRD patterns for Y-substituted samples (as-prepared and after 44 days of exposure to methanol for each composition  $x$ ) are shown in Fig. 10. After the exposure, the lattice expansion was observed for all samples. Especially, the  $c$ -axis was more expanded than the  $a$ -axis, e.g. for the sample of  $x = 0.3$ ,  $a = 0.3824$  nm and  $c = 3.068$  nm before the exposure, and  $a = 0.3829$  nm and  $c = 3.073$  nm after 44 days of exposure.

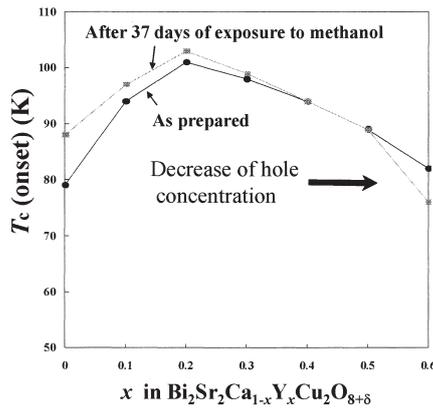


Figure 11.  $T_c$  of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$  (as-prepared, and after 37 days of exposure to methanol) as a function of  $x$ .

Figure 11 shows  $x$  dependences of  $T_c$  (onset) of  $\text{Bi}_2\text{Sr}_2\text{Ca}_{1-x}\text{Y}_x\text{Cu}_2\text{O}_{8+\delta}$  as-prepared and obtained after 37 days of exposure to methanol, which were observed by  $\rho$  and  $\chi$  measurements.  $T_c$  of as-prepared samples shows the maximum value at  $x = 0.2$ , which is compatible with the earlier works<sup>10</sup>. After exposure to methanol, the maximum of  $T_c$  was also observed at  $x = 0.2$ , while slightly higher than that of as-prepared sample. For  $x > 0.2$ ,  $\Delta T_c$  decreased with increasing  $x$ , and became negative at  $x = 0.6$ . If the curve after the exposure to methanol is moved to the right by  $x \sim 0.05$ , two curves seem to be nearly overlapped. Based on these results, we can speculate that the  $T_c$  increase induced by the exposure to methanol is due to the decrease of hole concentration.

### 3-5 Intercalation and adsorption of organic molecules

Figure 12 exhibits XRD patterns of Bi2212 phase: (a) as-prepared sample, (b) pelletized sample after 30 days of exposure to methanol, (c) powdered sample after 30 days of exposure to methanol. (d) fine powder sample after 30 days of exposure to methanol.

Calculated lattice parameters are  $a = 0.3820$  nm,  $c = 3.074$  nm for (a),  $a = 0.3821$  nm,  $c = 3.075$  nm for (b),  $a = 0.3825$  nm,  $c = 3.077$  nm for (c), and  $a = 0.3828$  nm,  $c = 3.086$  nm for (d). Both parameters increased by the methanol treatments. It is noticed that the expansion rate of  $c$  axis is larger than that of  $a$  axis by about twice, suggesting that the methanol molecules are intercalated in the samples. The intercalation can be also supported by the observation that the expansion rate increased with decreasing the particle size. This would be due to that the smaller sized particles have larger surface area, which can accommodate the organic molecules much rapidly

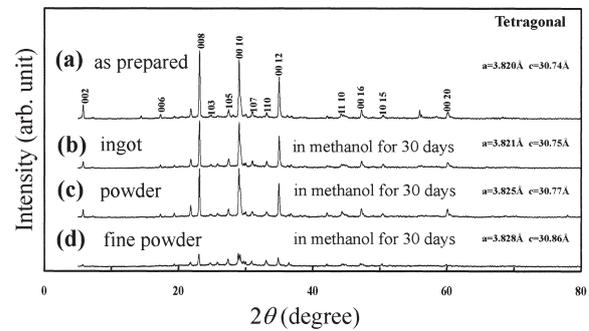


Figure 12. XRD patterns of Bi2212: (a) as-prepared sample, (b) pelletized sample in methanol for 30 days, (c) powdered sample in methanol for 30 days, (d) fine powder sample in methanol for 30 days.

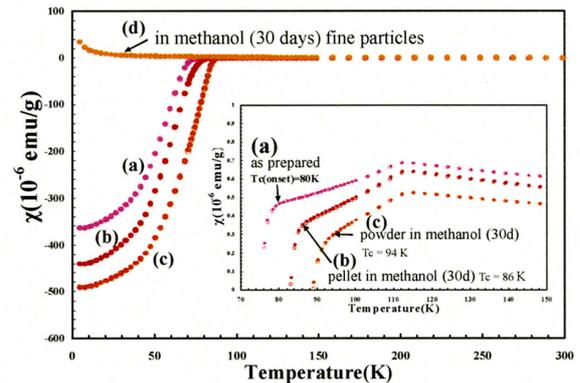


Figure 13.  $\chi$  of Bi2212 phase: (a) as-prepared sample, (b) pelletized sample exposed to methanol for 30 days, (c) powdered sample after 30 days of exposure to methanol, (d) fine powder sample exposed to methanol for 30 days.

Figure 13 gives temperature variations of magnetic susceptibility  $\chi$  for the same samples as those shown

in Fig. 12. The  $T_c$  was increased as the particle size is diminished, which would be due to that the number of intercalated and adsorbed methanol molecules increased with diminishing the particle size accompanied by the increasing surface area. No superconductivity was observed in the fine powder sample, indicating the sample was brought into the underdoping state to a large extent, or the structure was slightly broken by too much intercalated methanol molecules.

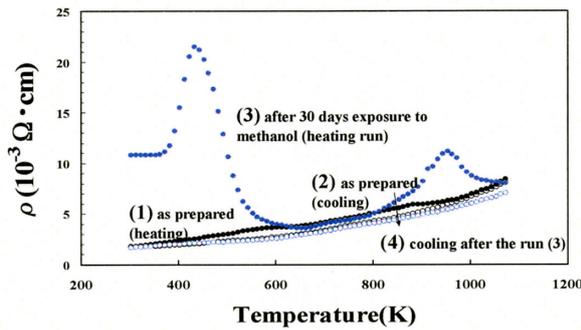


Figure 14. Electrical resistivity  $\rho$  for Bi2212 as a function of temperature: (1) heating run for as-prepared sample, (2) subsequent cooling run after the *run*-(1), (3) heating run for the sample after 30 days of exposure to methanol, and (4) subsequent cooling run after the *run*-(3).

Figure 14 shows  $\rho$ - $T$  curves for Bi2212 at high temperatures: (1) heating run for as-prepared sample, (2) subsequent cooling run after the *run*-(1), (3) heating run for the sample after 30 days of exposure to methanol, (4) subsequent cooling run after the *run*-(3). No apparent anomaly was observed in the as-prepared sample (*run*-(1) and *run*-(2)). After exposure to methanol, the sample showed two large peaks of  $\rho$  at  $\sim 450$  K and  $\sim 950$  K (*run*-(3)). It is supposed that the anomaly at  $\sim 450$  K would originate from the release of possibly adsorbed methanol molecules on the surfaces, and the anomaly at  $\sim 950$  K the release of intercalated methanol molecules. These two anomalies were not observed in the subsequent cooling run (*run*-(4)). These anomalies were detected again in the sample re-exposed to methanol after the *run*-(4), while the peak height is smaller than those in the *run*-(3). No apparent anomaly, however, was observed in DTA (differential thermal analysis), TG (thermogravimetric) analysis, and DSC (differential scanning calorimetry) measurements.

Figure 15 exhibits temperature variations of mag-

netic susceptibility  $\chi$  for the samples of Bi2212; (1) as-prepared, (2) after exposing as-prepared sample to methanol for 30 days, (3) after re-annealing the *sample*-(2) at 1027 K, and (4) after re-exposing the *sample*-(3) to methanol for 30 days.  $T_c$  (onset) of the sample after exposure to methanol was observed to be 92 K, which is higher than that of other observations. When the sample after exposure to methanol was heated again at 1027 K,  $T_c$  was returned to the initial value of 80 K. When the initialized sample was exposed to methanol again, the  $T_c$  increased to 92 K. These results can be interpreted that the intercalated methanol molecules were completely removed from the samples by heating at 1027 K.

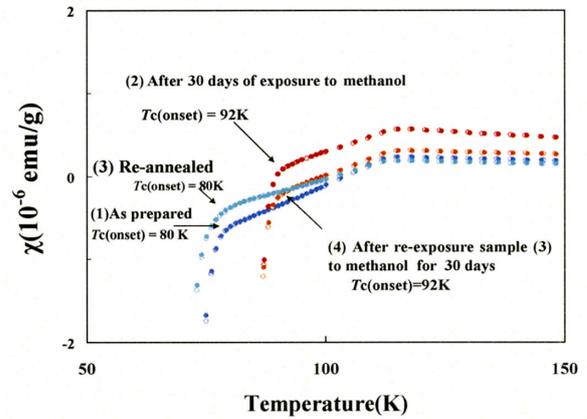


Figure 15. Magnetic susceptibility  $\chi$  of Bi2212 as a function of temperature: (1) as-prepared, (2) after exposing as-prepared sample in methanol for 30 days, (3) after re-annealing the *sample*-(2) at 1027 K, (4) after re-exposing the *sample*-(3) to methanol for 30 days.

The  $T_c$  change of Bi2212 was investigated by successively exposing the samples to different organic liquids: methanol  $\rightarrow$  benzene or acetone. Once  $T_c$  was increased up to 89 K by being exposed to methanol,  $T_c$  did not show any increase by the subsequent exposure to benzene and/or acetone. These results show that the methanol molecules intercalated once were not exchanged by the subsequent exposure to benzene or acetone. The molecular dipole moment of methanol, which is higher than that of benzene or acetone, would be responsible for it. On the other hand, when the sample was exposed to methanol after the exposure to benzene,  $T_c$  increased up to 86 K. These results can be explained by that the intercalated benzene molecules were exchanged by methanol mole-

cules, while a small amount of benzene molecules remained.

### 3-6 Increase of $T_c$ induced by photocatalysis

Charge transfer processes play a vital role in photocatalytic reactions<sup>11</sup>). In the preset study we have investigated photocatalytic effects on the  $T_c$  in the system of Bi2212 +  $\text{TiO}_2/\text{Pt}$ . The experiments were performed by following ways. The powdered samples of Bi2212,  $\text{TiO}_2$  (rutile or anatase) and Pt were mixed together, followed by irradiating the ultraviolet (UV) light (254 nm) to the mixture. The weight ratio of Bi2212 :  $\text{TiO}_2$  was 10 : 1.

Figure 16 shows temperature variations of magnetic susceptibility for as-prepared sample and for the samples obtained by irradiating ultraviolet (UV) rays to the mixture of (Bi2212 +  $\text{TiO}_2$  (rutile or anatase)/Pt) for 3 weeks at room temperature.  $T_c$  increased up to 83 K and 85 K from 80 K for the mixtures of (Bi2212 + rutile/Pt) and for (Bi2212 + anatase/Pt), respectively.  $T_c$  did not change in the absence of Pt. The present study showed the activity of anatase is higher than the rutile. It is generally accepted that the anatase exhibits higher photocatalytic activities compared to the rutile<sup>12,13</sup>). These observations prove that the photocatalysis induces the increase of  $T_c$  of Bi2212.

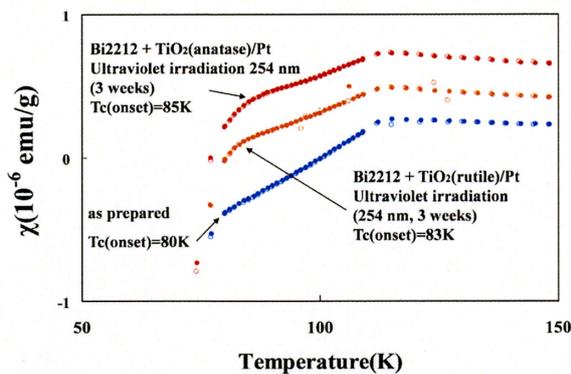


Figure 16. Temperature variations of  $\chi$  for the mixture of Bi2212 and  $\text{TiO}_2$  (rutile or anatase)/Pt after irradiation of UV light (254 nm) for 3 weeks at room temperature.

Figure 17 gives temperature dependences of  $\chi$  for the mixture of Bi2212 and  $\text{TiO}_2$  (rutile or anatase) after UV ray (254 nm) irradiation in methanol for 2 weeks.  $T_c$  was observed at 91 K and 93 K for rutile and anatase, respectively. The  $\Delta T_c$  is higher than that

in the case of methanol alone or  $\text{TiO}_2$  alone, indicating that the exposure to methanol and UV irradiation were both responsible for the increase of  $T_c$ . The higher activity of anatase was also observed in this case.

$T_c$  of Bi2223 phase was scarcely changed by the photocatalysis as similarly observed in the cases of exposure to organic liquids.

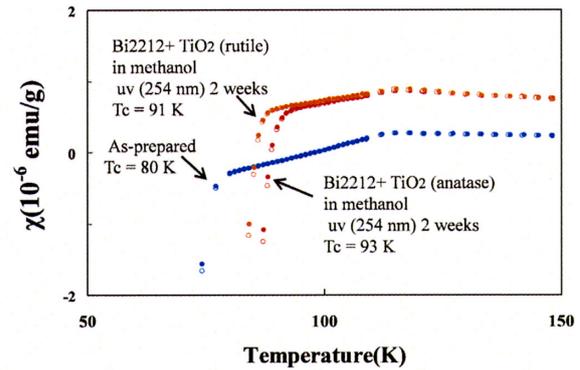


Figure 17. Temperature variations of  $\chi$  for the samples of Bi2212: as-prepared sample, Bi2212 + rutile after UV irradiation in methanol for 2 weeks, Bi2212 + anatase after UV irradiation in methanol for 2 weeks.

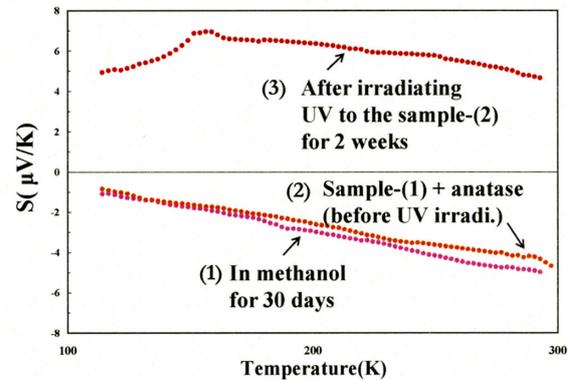


Figure 18. Temperature variations of Seebeck coefficients ( $S$ ) of Bi2212: (1) The sample exposed to methanol liquid for 30 days, (2) The mixture of the *sample*-(1) and anatase (before UV irradiation), (3) The sample after irradiating UV light to the mixture of *sample*-(2) for 2 weeks.

Figure 18 shows the temperature dependences of Seebeck coefficients ( $S$ ) for the samples obtained by various treatments: (1) sample after exposure to methanol liquid for 30 days, (2) Mixture of *sample*-(1) and anatase (before UV irradiation), (3) Sample after irradiating UV light to the mixture of *sample*-(2) for

2 weeks. As-prepared sample showed the negative values of  $S$ . Simply considering, the negative  $S$  indicates that the dominant carriers are electrons, which is contrary to the well accepted conception that hole conduction is dominant in Bi2212. We have previously observed that many cuprate superconductors show the negative  $S$  in the wide temperature range<sup>14)</sup>, which may be due to two carrier conduction in these oxides. The sample obtained by being exposed to methanol for 2 weeks showed the similar temperature dependence as that of as-prepared sample. It should be notable in Fig. 18 that the  $S$  showed the positive values for the sample after the UV irradiation. This shows that the conduction mechanism was changed by the UV irradiation. This result, however, does not imply the increase of hole concentration, because the  $T_c$  increase by UV irradiation definitely shows the decrease of hole concentration. The detailed mechanism is not clear yet. Another notable result is that a kink was observed in the  $S$ - $T$  curve at about 150 K, indicating an unknown phase transition.

### 3-7 $T_c$ decrease due to mixing with $\text{KNbO}_3$

If the hole concentration of Bi2212 increases from that of as-prepared samples,  $T_c$  would be lowered. During this study we have accidentally found that the  $T_c$  was lowered by mixing Bi2212 with  $\text{KNbO}_3$ .

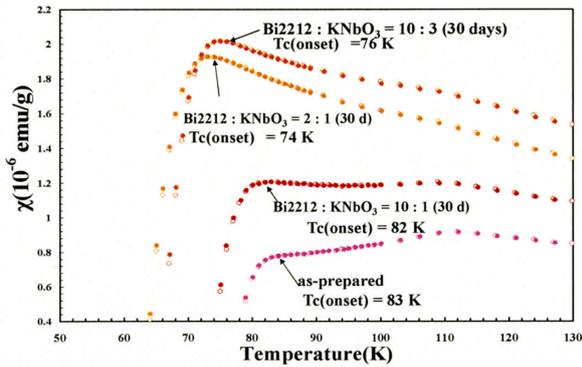


Figure 19. Temperature dependences of  $\chi$  for the mixtures of Bi2212 and  $\text{KNbO}_3$  with various weight ratios (Bi2212 :  $\text{KNbO}_3 = 10 : 1, 10 : 3, 2 : 1$ ) after being kept at room temperature for 30 days.

Figure 19 shows temperature dependences of  $\chi$  for the mixtures of Bi2212 and  $\text{KNbO}_3$  with various weight ratios (Bi2212 :  $\text{KNbO}_3 = 10 : 1, 10 : 3, 2 : 1$ ) after being kept at room temperature for 30 days.  $T_c$

was observed to decrease by 1 K, 7 K, and 9 K for the mixture of Bi2212 :  $\text{KNbO}_3 = 10 : 1, 10 : 3, 2 : 1$ , respectively. XRD measurements showed that the unit cell volume of Bi2212 was expanded after 30 days of keeping for all cases, e.g. the unit cell volume was  $0.4500 \text{ nm}^3$  and  $0.4508 \text{ nm}^3$  for as-prepared sample and for sample obtained by keeping the mixture (Bi2212 :  $\text{KNbO}_3 = 2 : 1$ ) for 30 days, respectively. The lattice expansion would be due to that a small amount of  $\text{K}^+$  ions are substituted for  $\text{Ca}^{2+}$  ions. The decrease of  $T_c$ , thus, would be caused by the increase of hole concentration.

We remind now that  $\text{KNbO}_3$  is a typical ferroelectric material with strong spontaneous polarization. If the ferroelectricity is responsible for the decrease of  $T_c$ , other ferroelectric compounds would give similar results. We performed, thus, the similar experiments using  $\text{PbTiO}_3$ ,  $\text{BaTiO}_3$ , and  $\text{PbZr}_{0.5}\text{Ti}_{0.5}\text{O}_3$  with various weight ratios to Bi2212. In these cases, however,  $T_c$  was not changed. Therefore, the substitution of K for Ca would be the most plausible reason for the decrease of  $T_c$ .

## 4. Discussion

Now, we will discuss on the origin of decrease of the hole concentration in the samples of Bi2212 by being exposed to organic liquids. The most possible origin for it is the charge transfer from the intercalated organic molecules to  $\text{CuO}_2$  planes. The plausible situation of intercalated organic molecules is shown in Fig. 20. Organic molecules are situated between SrO and  $\text{CuO}_2$  layers. The ellipsoids represent the molecular dipoles of organic molecules. Since the  $\text{CuO}_2$  layers have  $p$ -type conduction, the negative side of molecular dipoles is attached to the  $\text{CuO}_2$  planes. In such a situation the electrons are donated to  $\text{CuO}_2$  planes from organic molecules, which causes the decrease of hole concentration in Bi2212 phase. Accordingly,  $T_c$  would be raised because as-prepared samples are in the overdoping state. This mechanism is also the cases when the molecules are adsorbed on the surfaces. Similar type of charge transfer was discussed in the previous papers on the gas detection of Se nanowires<sup>15,16)</sup>.

It was reported that  $\text{I}_2$ ,  $\text{Br}_2$ , and  $\text{AgI}$  can be intercalated between BiO-BiO layers<sup>17)</sup>, suggesting that organic molecules would be easily intercalated between BiO-BiO layers. In this case, however, organic mol-

olecules are not situated near the  $\text{CuO}_2$  planes, and thus electron donation to  $\text{CuO}_2$  planes would be not so easy compared to the intercalation between SrO and  $\text{CuO}_2$ . Another possibility is that the organic molecules are intercalated between Ca and  $\text{CuO}_2$  layers. In such a case the positive side of organic molecules may attach to  $\text{CuO}_2$  planes, and thus the electrons are hardly donated to  $\text{CuO}_2$  planes.

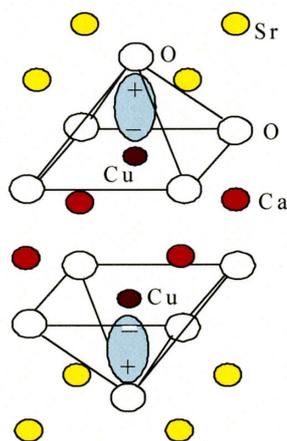


Figure 20. Schematic illustration of intercalated organic molecules between SrO and  $\text{CuO}_2$  layers. The ellipsoids represent the dipoles of organic molecules.

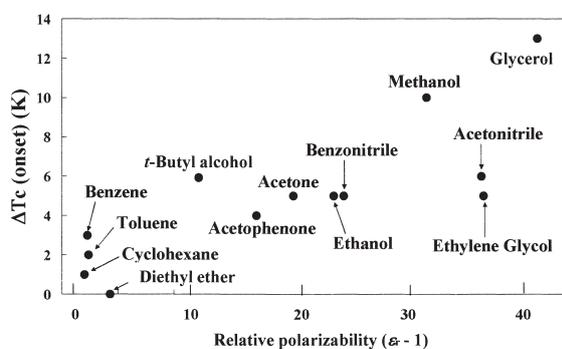


Figure 21.  $\Delta T_c$  of Bi2212 as a function of relative polarizability  $\alpha_s (= \epsilon_r - 1)$  of the organic liquids, where  $\epsilon_r$  is relative dielectric constant.

Figure 21 gives  $\Delta T_c$  as a function of relative polarizability  $\alpha_s (= \epsilon_r - 1)$  of various organic liquids ( $\alpha_s$  is proportional to the dipole moment  $P$ ). The  $\Delta T_c$  has a tendency to increase with increasing  $\alpha_s$ , indicating that the higher  $\alpha_s$  of organic molecules induces the larger  $\Delta T_c$ . This tendency can be well explained by that the organic molecules having the larger  $\alpha_s$  would

donate larger number of electrons to the samples, resulting in the decrease of hole concentration leading to the increase of  $\Delta T_c$ .

There remain some unsolved problems on the intercalation of organic molecules: (a) If the organic molecules are intercalated into Bi2212, the lattice constants would be more expanded than the observed ones. In addition, it has not been directly observed yet that the organic molecules are intercalated in the samples. (b) The other copper oxide superconductors have all similar layered structure. Nevertheless, it was revealed in the present work that  $\text{La}_{1-x}\text{Sr}_x\text{CuO}_4$ ,  $\text{YBa}_2\text{Cu}_3\text{O}_7$ , and Bi2223 showed no increase of  $T_c$  when exposed to organic liquids. The more detailed investigations on the intercalation of organic molecules into Bi2212 phase should be needed.

The observed increase of  $T_c$  induced by UV irradiation can be explained by the charge transfer from  $\text{TiO}_2$  to Bi2212, as schematically shown in Fig. 22. When the UV light is irradiated to  $\text{TiO}_2$  powder, the side where the UV light irradiates is charged positively, and the opposite side contacting with Bi2212 particles is charged negatively, due to the interfacial charge polarization. The negative charge, thus, would transfer to Bi2212 to decrease the hole concentration in Bi2212, leading to the increase of  $T_c$ . The use of cocatalyst promotes electron-hole separation. Pt has been demonstrated to be a highly active cocatalyst<sup>18)</sup>.

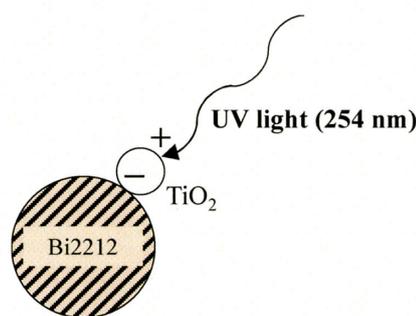


Figure 22. Schematic illustration of irradiation of UV light to the mixture of Bi2212 +  $\text{TiO}_2$ .

The present study showed that the Bi2212 phase is a very flexible oxide compared with other cuprate superconductors; the structure and properties are easily modified by various treatments. The complex modulated structure observed in the Bi2212 phase would be a typical example for the flexible nature<sup>19)</sup>.

## 5. Summary

Superconducting transition temperature  $T_c$  of Bi2212 phase was increased when the samples were exposed to organic liquids at room temperature. No structure change was observed after the treatments.  $T_c$  increased gradually with an exposure time, and was saturated about 30 days later. Examined organic liquids are cyclohexane, benzene, toluene, diethyl ether, acetophenone, acetone, ethanol, benzonitrile, methanol, *t*-butyl alcohol, acetonitrile, ethylene glycol, and glycerol. The increase of  $T_c$  ( $\Delta T_c$ ) was observed to be at most 13 K for glycerol.

The lattice expansion after the exposure to organic liquids indicates that the organic molecules are intercalated in Bi2212. Electrical resistivity measurements showed the anomalies at  $\sim 450$  K and  $\sim 950$  K, which could be associated with the release of adsorbed organic molecules and of intercalated molecules, respectively. Intercalation of organic molecules was supported by the observation that the  $T_c$  increased by the exposure to methanol returned to the initial  $T_c$ , when the samples were heated again at 1027 K.

As-prepared samples of Bi2212 were observed to be in the overdoping state in the study of Y-substituted Bi2212. The increase of  $T_c$  was interpreted to be owing to the decrease of hole concentration caused by the transfer of electrons from intercalated and adsorbed organic molecules to  $\text{CuO}_2$  layers.  $\Delta T_c$  showed a tendency of increasing with increasing the relative polarizability  $\alpha_s$  ( $= \epsilon_r - 1$ ) of the organic liquids. This tendency was interpreted by that the molecules with the higher  $\alpha_s$  would transfer the larger number of electrons to the  $\text{CuO}_2$  layers, which results in the decrease of hole concentration leading to the increase of  $T_c$ .

The  $T_c$  increased by 2-3 K when the mixture of Bi2212 and  $\text{TiO}_2/\text{Pt}$  was irradiated with UV light (254 nm). This observation can be explained by the transfer of negative charge from  $\text{TiO}_2$  to Bi2212.

$T_c$  was observed to be lowered when the samples were mixed with  $\text{KNbO}_3$  powder. This was interpreted by that  $\text{K}^+$  ions were substituted for  $\text{Ca}^{2+}$  ions, giving rise to the increase of hole concentration, leading to the decrease of  $T_c$ .

Finally, the present study showed that the  $T_c$  of Bi2212 phase was increased when the samples were

exposed to organic liquids or the mixture with  $\text{TiO}_2/\text{Pt}$  was irradiated with UV light. The increase of  $T_c$  is owing to the decrease of hole concentration for both cases.

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