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Intercalation of Lithium and Iodine in the Ferroelectric Layered Compound $Bi_4Ti_3O_{12-x}$

T. Kijima,[1] S. Kimura, Y. Kawahara, K. Ohe, M. Yada, and M. Machida

Department of Materials Science, Faculty of Engineering, Miyazaki University, Miyazaki 889-21, Japan

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The reaction of $Bi_4Ti_3O_{12-x}$ with lithium iodide under an atmosphere of iodine at 350°C was found to afford an intercalation compound $LiI_3Bi_4Ti_3O_{11-x}$ in high yield. The new bismuth titanate is brownish red in color and formed in an orthorhombic cell with the lattice parameters of $a = 5.912\,(1)$, $b = 5.256\,(1)$, and $c = 36.889\,(8)$ Å. The pathway to the new intercalation compound is proposed on the basis of X-ray, XPS, SEM, and compositional observations. © 1999 Academic Press

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INTRODUCTION

The intercalation reaction of iodine with layered metal oxides was first observed for bismuth cuprate high T_c superconductors, for example, $Bi_2Sr_2CaCu_2O_8$ (Bi2212), as the host matrices (1–3). The layered cuprate intercalates iodine to form a modified superconductor $IBi_2Sr_2CaCu_2O_8$ in which the iodine species are located between the double Bi–O sheets. Another example was presented by the recent observation of iodine intercalation in the layered bismuth oxide-ion conductor $BaBi_8O_{13}$ (4). On the other hand, the intercalation of metal iodides or bromides in layered oxides were demonstrated by the formation of Ag–I and Hg–I intercalated $Bi_2Sr_2CaCu_2O_y$ superconductors (5–8). More recently, we have also synthesized a similar but semiconducting layered cuprate $LiI_3Bi_2Sr_2CaCu_2O_8$ with iodine intercalated as I_3 ions (9). No studies, however, have appeared concerning the intercalation of metal iodides into any other class of metal oxides. Here, we report for the first time the intercalation of lithium and iodide ions into the ferroelectric layered bismuth titanate $Bi_4Ti_3O_{12-x}$. In striking contrast to the Bi2212 system, the Li–I intercalation reaction in the titanate system appears much more complicated, probably because the latter bismuth-based compound is largely different from the former in containing an additional oxide anion layer interleaved with any two adjacent BiO sheets (10). The present result would open a route to a large family of metal-iodine intercalated compounds since the titanate is representative of a great number of bismuth-based layered ferroelectrics given by the general formula of $Bi_2M_{n-1}R_nO_{3n+3}$ ($n = 1$–5) with $M = Bi^{3+}$, La^{3+}, Pb^{2+}, Ba^{2+}, K^+, etc. and $R = Fe^{3+}$, Cr^{3+}, Ti^{4+}, Nb^{5+}, Ta^{5+}, etc. (11).

EXPERIMENTAL

The Bi2212 material (**1**) was prepared by the solid state reaction of a stoichiometric mixture of Bi_2O_3 and TiO_2 with twice repeated grinding and firing at 830°C for 12 h in air. To a 1:1 mixed powder of **1** and LiI loaded in a Pyrex tube, iodine was added at various ratios of Bi:Li:I = 1:0.25:y ($y = 0.375$–1.25). After being sealed in air and then preheated at 170°C for 3 h, the mixture was heated at 250, 300, and 350°C for each 10, 50, or 100 h. In several runs, a small amount of water was added to the reaction mixture prior to sealing. Powder X-ray diffraction measurement was made at room temperature on a Shimazu XD-3A diffractometer with Cu$K\alpha$ radiation. Atomic absorption analysis on a Hitachi Spectrophotometer Z-8000 was carried out using 10 mg of the resulting solid dissolved in 5 mL of 1:1 fluoric acid–sulfuric acid mixed solution by sealing the mixture in a stainless steel bomb (fitted with a Teflon liner) and keeping for 24 h at 150°C. Samples mounted on double-sided carbon tape were utilized for XPS measurement at room temperature using a Shimazu ESCA-3300 spectrometer with monochromatized Al$K\alpha_{1,2}$ X rays as the exciting radiation. The spectra were calibrated using pump oil hydrocarbon on the sample surface (C 1s = 284.3 eV). UV-VIS reflectance spectra were measured on a Nippon-Bunko Spectrometer V-550.

RESULTS AND DISCUSSION

The lattice parameters of the host titanate with an orthorhombic structure, **1**, were $a = 5.417\,(2)$, $b = 5.456\,(2)$, and $c = 32.861\,(2)$ Å, obtained from the X-ray diffraction (XRD) pattern shown in Fig. 1. The TG curve for the titanate

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[1] To whom correspondence should be addressed.

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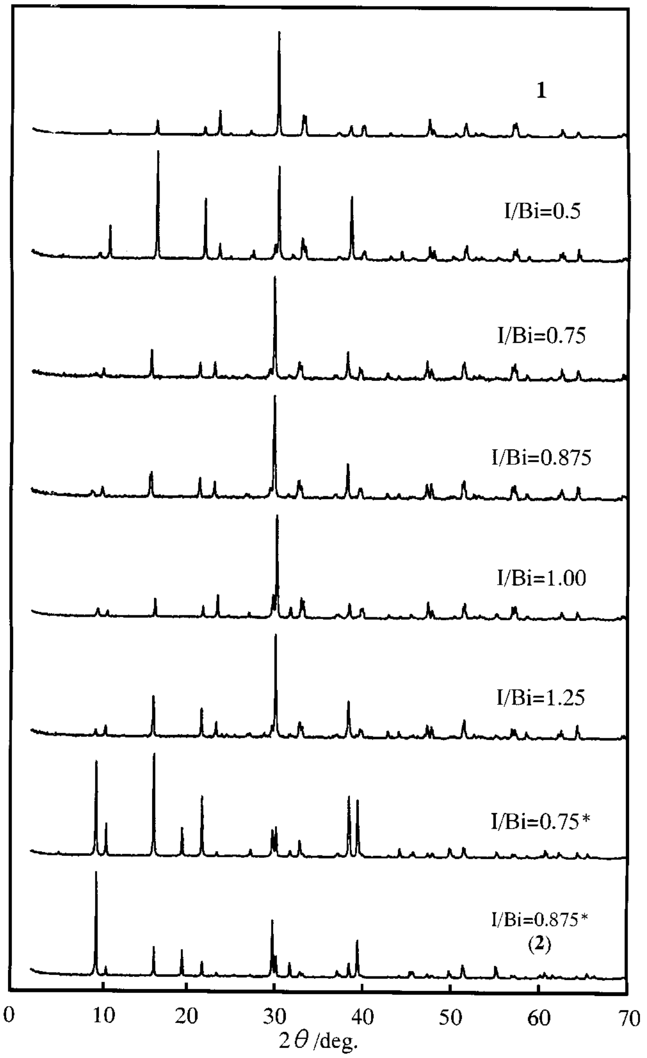


FIG. 1. X-ray diffraction patterns of the host compound $Bi_4Ti_3O_{12-x}$ (**1**) and **1** reacted at 350°C for 10 h with different I/Bi molar ratios (Cu*K*α). The superscript (*) indicates the reaction system containing water added at a water/Bi ratio of 0.005.

showed a weight increase of 2.2% during heating from room temperature to 1000°C in air (Fig. 2a), yielding a nonstoichiometric composition of $Bi_4Ti_3O_{12-x}$ with $x \sim 1.6$. Although the host titanate **1** remained unreacted on heating with I_2 alone, it changed in color from yellowish gray to brownish red or dark brown on heating with both LiI and I_2 at the prescribed temperatures. All the reacted samples, brownish red or dark brown, gave a XRD pattern characterized by two main peaks at $2\theta = 9.6$ and 29.6° ($d = 9.22$ and 3.02 Å) and indicative of the formation of an intercalated phase, as exemplified for the solids produced by the reaction at 350°C for 10 h in Fig. 1. As a result of the reaction the thickness of the macrolayer ($= c/2$) increased by ca. 2.0 Å relative to that for the host phase. The extent of conversion into an intercalated phase exhibited a tendency to decrease with an increase of either reaction temperature or time, as in the order of $250 > 300 > 350$°C or $10 > 50 > 100$ h. The reaction time dependences are likely because the intercalation reaction occurs in competition with the conversion of the starting oxygen-deficient titanate into its stoichiometric form less reactive with Li–I species. The intercalation reaction at 300°C or below was little affected or rather depressed by the addition of a slight amount of water, whereas the reaction at 350°C was remarkably accelerated by the water addition (Fig. 1). This is probably due to such a micro-hydrothermal effect that water molecules are thermally activated to catalytically induce the lithium and iodine species into the oxide-ion deficient layer.

The Li–I intercalation thus developed to its highest level by the intercalation reaction at 350°C for 10 h at the Bi:I:water ratio of 1:0.875:0.005, leading to the formation of an intercalated phase in its high yield. Except for those for the remaining host oxide, all the observed X-ray diffraction peaks in the 2θ range of 3–60° for the 350°C product (**2**) could be indexed by the least square fitting method on the basis of an orthorhombic unit cell with the lattice parameters $a = 5.912(1)$, $b = 5.256(1)$, and $c = 36.889(8)$ Å (Fig. 3 and Table 1). The SEM image of the intercalated product showed that the major solid is lamellar in shape. EDX microanalysis data for Bi, Ti, and I, coupled with atomic absorption analysis data for Li and Bi, led to an overall composition of $Li_{0.92}I_{2.63}Bi_{4.00}Ti_{3.12}O_{11-x}$ for **2**.

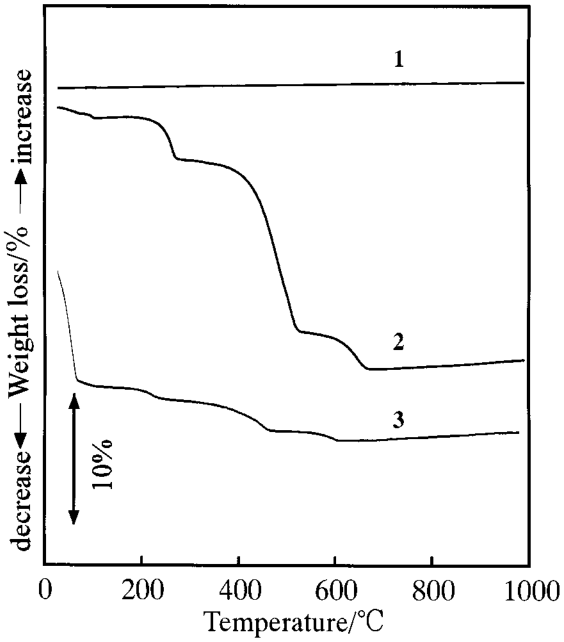


FIG. 2. TG curves for **1** and **2** and **3**, measured with a heating rate of 10°C min^{-1} in air.

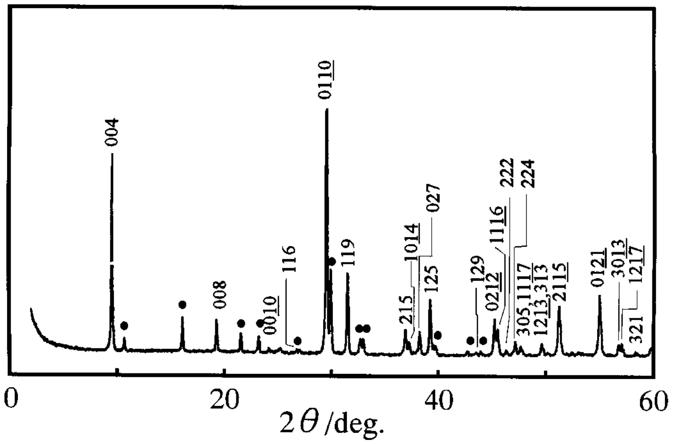


FIG. 3. Indexing of the X-ray diffraction peaks of the Li–I intercalated phase for **2** (Cu$K\alpha$). Unindexed diffraction peaks (●) are due to the host phase.

The I3$d_{5/2}$ XPS spectrum of the intercalated product showed a single peak centered at the binding energy of 618.0 eV close to 618.6 eV for the standard sample of KI, as shown in Fig. 4. This indicates that the iodine species is intercalated as the monoiodide ion I^-, in contrast to the intercalation of triiodide ions I_3^- in the Bi2212–LiI–I_2 system (9).

TABLE 1
X-Ray Diffraction Patterns of the Li–I Intercalated Phase in 2

Index	d_{cal}/Å	d_{obs}/Å
004	9.222	9.222
008	4.611	4.594
$00\underline{10}$	3.689	
116	3.310	3.314
$01\underline{10}$	3.019	3.018
119	2.836	2.833
215	2.433	2.429
$10\underline{14}$	2.407	2.409
027	2.352	2.350
125	2.284	2.292
129	2.072	
$02\underline{12}$	1.998	2.001
$11\underline{16}$	1.988	1.988
222	1.953	1.954
224	1.921	1.922
305	1.904	1.904
$11\underline{17}$	1.899	1.900
$12\underline{13}$	1.833	1.833
313	1.825	1.825
$21\underline{15}$	1.779	1.780
$12\underline{14}$	1.775	1.774
$01\underline{21}$	1.666	1.667
$30\underline{13}$	1.619	1.618
$12\underline{17}$	1.610	1.610
321	1.575	1.575

Note. The calculated d values were obtained on the basis of an orthorhombic cell with the lattice parameters of $a = 5.912(1)$, $b = 5.256(1)$, and $c = 36.889(8)$ Å.

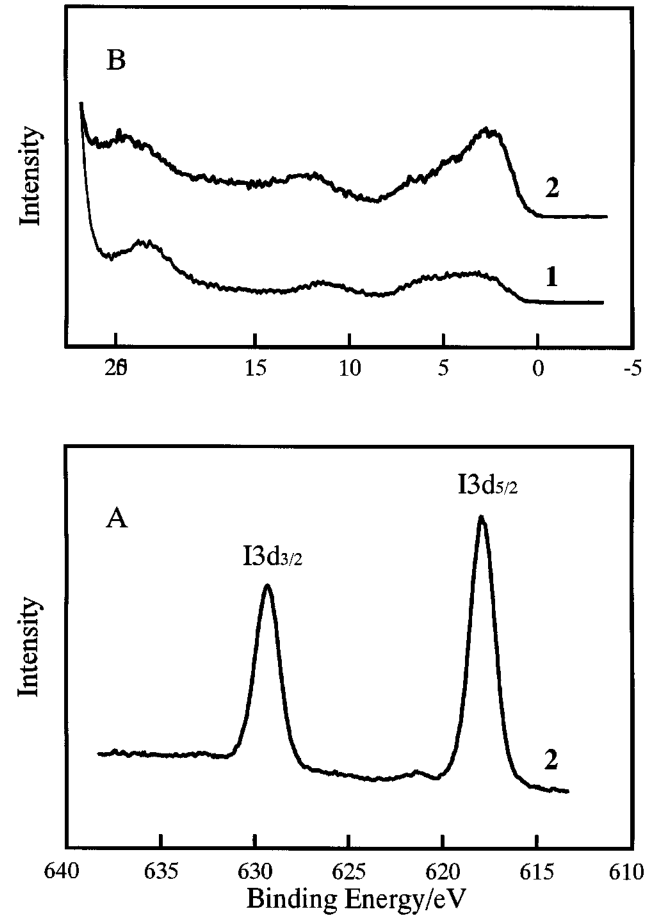


FIG. 4. X-ray photoelectron spectra of **1** and **2** at room temperature: (A) iodine 3$d_{5/2}$ and 3$d_{3/2}$ bands and (B) low energy bands including their valence bands.

The thermogravimetric (TG) curves for the resulting samples showed three or four weight losses in the temperature range up to 680°C, as exemplified in Fig. 2. Here the dark brown product **3** was obtained by the reaction at 300°C for 10 h at the I/Bi ratio of 0.75 without water. On heating at 100°C under an open atmosphere of air dark brown samples turned brownish red while their XRD patterns remained unchanged. Brownish red samples, as grown or 100°C-pyrolyzed, were characterized primarily by the same XRD pattern as that observed for **2**. The first weight loss at temperatures below 100°C is therefore attributable to desorption of surface-adsorbed iodine species. The second and third weight losses at temperatures of 200–540°C are assignable to desorption of intercalated iodine species since the solids are converted into a white color solid on heating at 550°C for 0.5 h in air. The fourth weight loss at temperatures of 580–680°C is probably due to desorption of the remaining iodine and lithium species. For **2**, the surface iodine species amounted to as little as 0.8% and the total weight loss of 20.2% in the temperature range below 680°C was in close agreement with 21.6% expected from the analytical composition. At temperatures above 680°C, a slight weight increase was observed for all samples, due to the uptake of oxygen to oxidize titanium species.

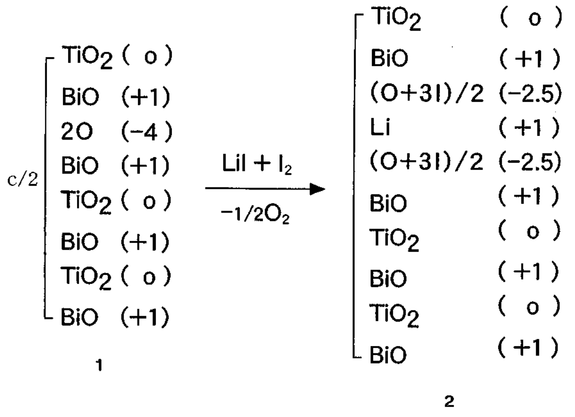
On the basis of the above compositional and XPS observations, the experimental molar ratio of Li to I for the intercalated phase was estimated to be $(2.63 \times 19.4/20.2)/0.92(=2.74)$ or approximately 3. Thus the overall reaction leading to the intercalated phase would be stoichiometrically represented by

$$\mathrm{Bi_4Ti_3O_{12-x} + LiI + I_2 \rightarrow LiI_3Bi_4Ti_3O_{11-x} + (1/2)O_2}. \qquad [1]$$

Taking into further consideration the X-ray and SEM observations as well as the structure of the host titanate (10), a reaction pathway for the Li–I intercalation could be proposed, as illustrated in Scheme 1. The oxide anion layer with a layer charge of -4 between any two BiO sheets would be rearranged into the same-charged layer composed of two 1:3 oxy iodide sheets incorporated with lithium cations through the interlayer redox reaction given by

$$\mathrm{LiI + I_2 + O^{2-} \rightarrow Li^+ + 3I^- + (1/2)O_2}. \qquad [2]$$

Since the long period of Bi2212 is 30.6 Å (9), the average thickness per oxide layer, estimated by assuming the thickness of Ca layer to be 2.0 Å, is $(30.6/2 - 1.0 \times 2)/6$ or 2.27 Å. In contrast, the appreciably high layer charge (-4) of the oxide anion layer in $\mathrm{Bi_4Ti_3O_{12-x}}$ may induce a considerable contraction of the stacking period resulting in the average thickness per oxide layer of as little as $(32.76/2)/8$ or 2.05 Å. If we assume a similar lattice contraction effect for the intercalated solid as well as a small contribution of lithium cations to interlayer expansion, the substitution of a 1:3 oxy iodide bilayer for the oxide layer would lead to a value of 2.05×9 or 18.45 Å for the thickness of the macrolayer, being in good agreement with the observed value of 36.89/2 or 18.45 Å. No intercalation occurred when the reaction mixture was sealed together with oxygen in place of air, whereas the reaction in a tube filled with nitrogen proceeded similarly as in air. This atmospheric effect is also in keeping with a presumption from Eqs. [1] or [2] that the reaction will be depressed by an increase of the partial pressure of oxygen. Based on the above reaction scheme, the analytical data for **2** also indicate that $\mathrm{LiI_3Bi_4Ti_3O_{11-x}}$ is formed in a yield of as high as 88%.



SCHEME 1. Schematic representation of a probable pathway for the lithium and iodine intercalation into $\mathrm{Bi_4Ti_3O_{12}}$. The average charge of each atomic layer is given in parentheses.

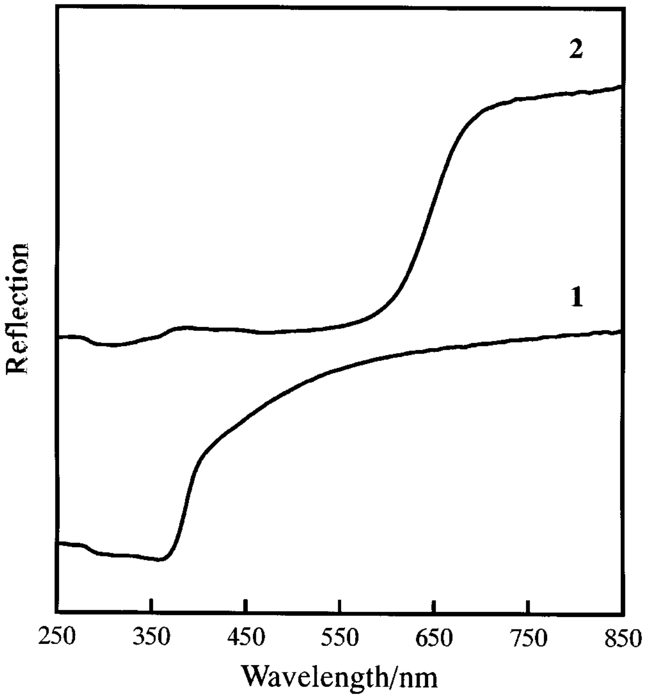


FIG. 5. Optical UV-VIS reflectance spectra of **1** and **2** at room temperature.

In harmony with the observed color change, the optical absorption region of the titanate was largely extended to the longer wavelength on the Li–I intercalation, resulting in a decrease of band gap from 3.0 to 1.7 eV (Fig. 5). The decrease of 1.3 eV in the band gap was in good agreement with the shift of the top of the valence band from 1.2 eV for the host titanate to 0.0 eV observed for the Li–I intercalated solid, as suggested from Fig. 4B. Furthermore, during the XPS measurement without any charge neutralization, on exposure to X-ray radiation the ferroelectric host material was observed to be so extremely electrified as to shift all the peaks greatly to apparently higher binding energy, whereas such an extreme electrification seldom occurred for the intercalated samples. This fact suggests that the ferroelectricity of the host oxide might be highly weakened or completely degraded on Li–I intercalation. A more complete study of the ferroelectric properties of the Li–I intercalated product will be presented in a succeeding paper. That the present Li–I intercalated solid is also likely nonstoichiometric similar to the host oxide would arouse our interest in studying lithium and/or oxide ionic conductivities of the intercalated phase, as well as its gas adsorption properties.

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