

Li-Intercalation into the Bi-Based Oxychlorides with Layered Structures

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Li-intercalation into BiOCl and BiMO_2Cl ($M = \text{Pb, Ba, Sr, Ca}$) has been tried using the hexane solution of *n*-butyllithium. In the case of BiOCl and BiPbO_2Cl , the host samples, which had been white and yellow in color, respectively, and insulating, turned black immediately and the electrical resistivity at room temperature decreased. From the x-ray analysis, these changes are guessed to be due to the appearance of Bi metal for BiOCl , while those are guessed to be due to the formation of a new intercalation compound $\text{Li}_x\text{BiPbO}_2\text{Cl}$ for BiPbO_2Cl . In the case of BiMO_2Cl ($M = \text{Ba, Sr, Ca}$), on the other hand, the host samples did not change in color and remained insulating, suggesting that no intercalation compounds were formed.

Key words: BiOCl , BiPbO_2Cl , Li-intercalation, electrical resistivity, powder x-ray diffraction

1. INTRODUCTION

It is well known that layered materials composed of weakly coupled layers, such as graphite and transitional metal dichalcogenides, form intercalation compounds by taking guest atoms or molecules (intercalants) between layers [1 - 3]. In general, electrical properties of host materials change drastically through intercalation due to charge transfer between intercalants and host materials. It is of interest to note that the high- T_c superconductors $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+4}$ ($n = 1, 2, 3$) form intercalation compounds by taking halogen atoms between the BiO - BiO double layers [4, 5]. It had been pointed out that the value of superconducting transition temperature, T_c , is affected by both the structural change and the charge [6].

Recently, there has been growing interest in the superconductivity of Li-intercalation compounds. That is, Takano et al. discovered superconductivity with $T_c \sim 2$ K in the Li-intercalated $\text{KCa}_2\text{Nb}_3\text{O}_{10}$ [7]. Yamanaka et al. also discovered superconductivity of Li-intercalated layered nitrides β - ZrNCl ($T_c = 13$ K) and β - HfNCl ($T_c = 25.5$ K), consisting of Zr(Hf)-N double layers sandwiched between two close-packed chlorine layers [8, 9].

Figure 1(a) shows the schematic diagram of the crystal structure of the Bi-based oxychloride BiOCl , which is the two-dimensional one similar to that of β - Zr(Hf)NCl . It is composed of the two-dimensional $[\text{Bi}_2\text{O}_2]$ layer, instead of the $[\text{Zr(Hf)}_2\text{N}_2]$ in layer in β - Zr(Hf)NCl of the double chlorides layer, $[\text{Cl}_2]$. In addition, it is known that $(\text{Ba, K})\text{BiO}_3$ with the three-dimensional Bi-O network exhibits superconductivity with $T_c \sim 30$ K [10]. Therefore, the Li-intercalated BiOCl is expected as a candidate for a new superconductor with the two-dimensional Bi-O network.

In this paper, we report the trial of Li-intercalation into BiOCl . In addition, we also report the trial of the Li-intercalation into BiMO_2Cl ($M = \text{Pb, Ba, Sr, Ca}$), composed of the $[\text{Bi}_2\text{O}_2]$ layer and the single chloride layer, $[\text{Cl}]$, as shown in Fig. 1(b) [11].

2. EXPERIMENTAL

The commercial powder of BiOCl was used as the host sample of BiOCl . It was pressed into a pellet with the

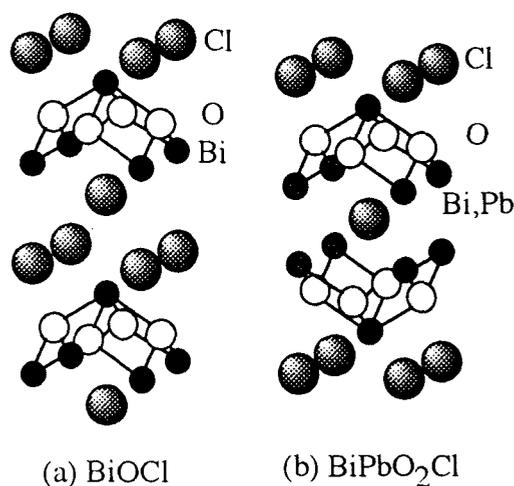


Fig. 1. Schematic diagram of the crystal structure of (a) BiOCl and (b) BiPbO_2Cl .

dimensions of 10 mm in diameter and 1 mm in thickness and sintered in air at 700°C for 24 h. The host samples of BiMO_2Cl ($M = \text{Pb, Ba, Sr, Ca}$) were prepared by the conventional solid-state reaction method, using powders of BiOCl , PbO , BaO_2 , SrO and CaO . The powders weighted stoichiometrically were mixed, pelletized and heated in air at 670°C for 24 h. All products were characterized to be of the single-phase of BiMO_2Cl by the powder x-ray diffraction using $\text{Cu K}\alpha$ radiation.

Li-intercalation was carried out by soaking the pelletized host samples into 20 ml of the hexane solution of 1.6M *n*-butyllithium. The electrical resistivity was measured by the DC four-probe method keeping the samples in the solution. Leads wires of copper had been attached to the host samples with silver paste before the Li-intercalation was carried out.

3. RESULTS

In the case of BiOCl , the host sample, which had been white in color and insulating, turned black 2 h after that had been put into the solution. As shown in Fig. 2, the electrical resistivity at room temperature decreased with increasing the Li-intercalation time, which showed the value of $10^3 \Omega\text{cm}$ order after 50 h. In the powder x-ray diffraction pattern, however, the peaks of Bi metal appeared for the sample which had been soaked for 10 h, and the intensity of the peaks of Bi metal increased with the increase of the Li-intercalation time, as shown in Fig. 3. Thus, both the change in color and the decrease in the electrical resistivity at room temperature are guessed to be due to the appearance of Bi metal, which was extracted through the reduction of BiOCl during the Li-intercalation process. However, there remains a possibility that a new intercalation compound Li_xBiOCl was formed in the beginnings of the Li-intercalation process, because the host sample turned black and the electrical resistivity decreased in spite of no observation of the peaks of Bi metal in the x-ray diffraction pattern within 8 h.

In the case of BiMO_2Cl , the host sample also turned black and the electrical resistivity at room temperature decreased with increasing the Li-intercalation time, which showed the value of $10 \Omega\text{cm}$ order after 300 h, for $M = \text{Pb}$, as shown in Fig. 2. From the powder x-ray diffraction analysis, it was found that Bi metal did not appear within 50 h and that the structure of BiPbO_2Cl was almost retained during the Li-intercalation process even after 300 h, as shown in Fig. 4. These results suggest that a new intercalation compound $\text{Li}_x\text{BiPbO}_2\text{Cl}$ has been formed. However, the Li content is not determined and the site of intercalated Li atoms is also not identified. For BiMO_2Cl ($M = \text{Ba}, \text{Sr}, \text{Ca}$), on the other hand, the host samples did not change in color and remained insulating, suggesting that Li-intercalation compounds were not formed.

In summary, we have succeeded in the synthesis of a new Li-intercalated compound $\text{Li}_x\text{BiPbO}_2\text{Cl}$.

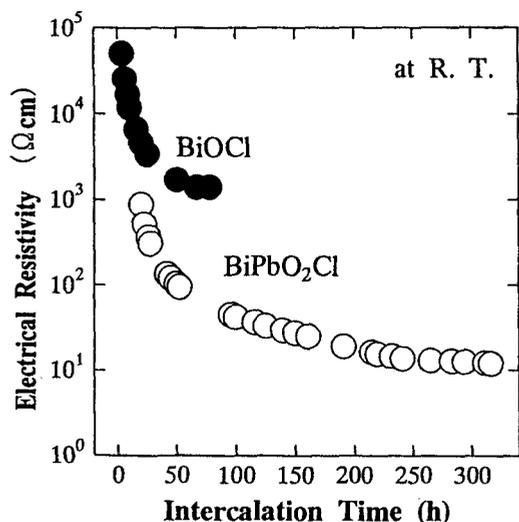


Fig. 2. Dependence of the electrical resistivity at room temperature on the Li-intercalation time for BiOCl and BiPbO_2Cl .

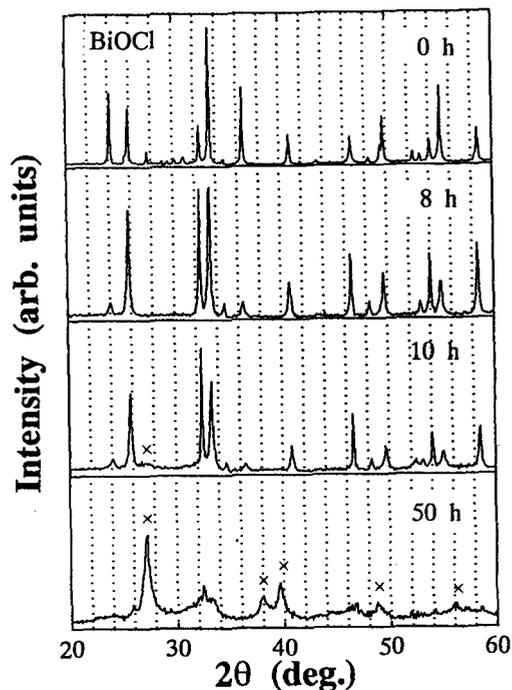


Fig. 3. Variation of the x-ray diffraction patterns with the Li-intercalation time for BiOCl . Symbol \times indicates peak due to Bi.

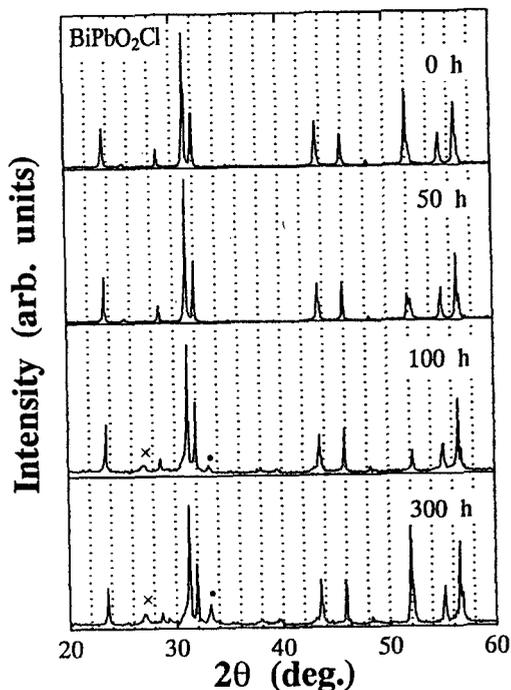


Fig. 4. Variation of the x-ray diffraction patterns with the Li-intercalation time for BiPbO_2Cl . Symbols \times and \bullet indicate peaks due to Bi and Pb_7Bi_3 , respectively.

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