Intercalation in thermoelectric layered cobaltites

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$Bi_2(Sr, Ca)_2Co_2O_9$ (BC-222) single crystalline whiskers intercalated I_2 and $HgBr_2$ have been prepared. The *c*-cell parameter of the single crystals are elongated 3.6Å and 6.2Å by the I_2 and $HgBr_2$ intercalation, respectively. The I_2 and $HgBr_2$ present between two Bi-O layers. While Seebeck coefficient of the intercalated samples is lower than no-intercalated ones because of increase in hole concentration, electrical resistivity is increased by the intercalation. Moreover, the I_2 intercalation reduces thermal conductivity.

Key words: Thermoelectric material, Oxide, Intercalation, 2D structure

1. INTRODUCTION

One form of energy expected to develop in the next few decades is thermoelectric power generated from vast amounts of waste heat emitted by automobiles, factories, and similar sources. Thermoelectric generation systems can convert heat energy into electric energy directly without using moving parts such as turbines and without producing carbon dioxide gas, radioactive substances, or other emissions. To realize thermoelectric power generation, not only higher thermoelectric figure of merit ($ZT = S^2T/\rho\kappa$, S: Seebeck coefficient, T: temperature, ρ: electric resistivity, and κ: thermal conductivity) than 1.0, but also high chemical stability and no content of harmful elements are indispensable to thermoelectric materials. For this purpose, oxide materials are the one of the strongest candidates. Especially, layered CoO_2-based single crystals indicating p-type properties have enough thermoelectric figure of merit (ZT) at high temperature in air [1, 2].

Recently, improvement of thermoelectric properties has been reported by controlling nano-structure. In this strategy, it is possible only phonons are scattered but no electrons. Usually, mean free path of electrons is longer than that of electrons. In fact, huge high ZT has been obtained in Bi_2Te_3/Sb_2Te_3 superlattice thin films [3]. In this film, electrons can flow as ballistic current. On the other hand phonons are scattered at the interface between Bi_2Te_3 and Sb_2Te_3 sublattices. Although CoO_2-based materials mentioned above has a superlattice structure, they shows no effect caused by the two dimensional (2D) structure obviously. It is expected to cause the 2D effect if the thickness of the rock-salt sublattice can be controlled.

In this paper, I_2 and $HgBr_2$ intercalation into the rock-salt sublattices and thermoelectric properties in intercalated $Bi_2(Sr, Ca)_2Co_2O_9$ (BC-222) single crystals are discussed.

2. EXPERIMENTAL

The BC-222 single crystalline whiskers were grown by annealing glassy precursor plates possessing a cationic composition of Bi:Sr:Ca:Co = 1:1:1:2, which were obtained by quenching melt of Bi_2O_3, $SrCo_3$, $CaCo_3$ and Co_3O_4 from 1300°C in air [4]. The precursor plates were annealed at 880°C for 50h in O_2 gas flow. The whiskers were grown from the surface of the plates and reaped using a tweezers.

The whiskers and I_2 or $HgBr_2$ were put into a glass tube and sealed in vacuum. Intercalation of I_2 and $HgBr_2$ was carried out at 150°C and 400°C for 20-500h using electrical furnaces, resistively. After the heat treatment the whiskers were washed using ethanol. The c-cell parameter of the whiskers was measured by X-ray diffraction (XRD). Element ratio was evaluated using energy dispersive X-ray (EDX) analysis.

Seebeck coefficient (S) was measured from 90-400K using a measurement system made by MMR Technologies Inc. Electrical resistivity (ρ) measurement was performed at 4-300K by a DC four terminals method. Thermal conductivity (κ) was calculated by thermal diffusibility and specific heat measured using an AC calorimetric method and a differential scanning calorimetric method, respectively. Transmitting electron microscopic observation was carried out for the cross sections of the whiskers.

3. RESULT AND DISCUSSION

Figure 1 shows XRD patterns for both no-intercalated and intercalated whiskers. In the case of I_2 intercalation, diffraction peaks of both original no-intercalate BC-222 and I_2 intercalated BC-222 (IBC-222) phases are observed after the heat treatment for 20h at 150°C. The diffraction angles of the IBC-222 phase are lower than the BC-222 phase for the same indexed peaks. This is due to elongation of the c-cell

parameter from 14.8Å to 18.4Å by I_2 intercalation. This value is similar to that in $Bi_2Sr_2CaCu_2O_x$ superconducting phase intercalated I_2 [5]. I_2 penetrates between BiO-BiO double layers, which are weakly bonded by Van der Waals force (Fig. 2). Intercalation time longer than 50h, the diffraction peaks of the original BC-222 phase disappear.
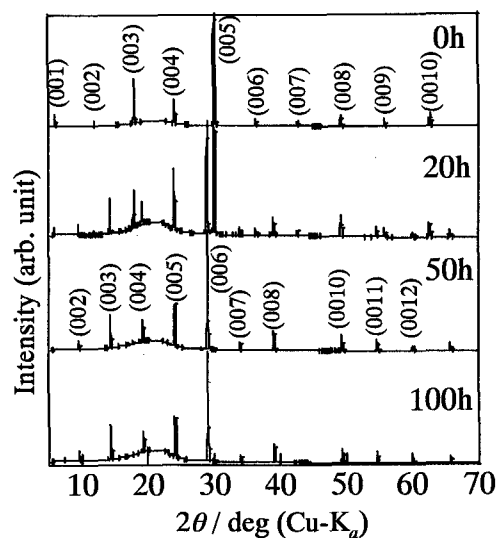

Fig. 1   X-ray diffraction patterns for no-intercalated (0h) and I_2 intercalated whiskers for 20-100h at 150°C.
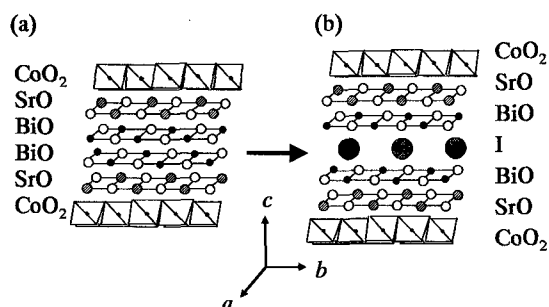

Fig. 2   Schematic crystallographic structures for no-intercalated (a) and I_2 intercalated (b) BC-222 phase.

Figure 3 shows XRD patterns for the $HgBr_2$ intercalated (HBBC-222) whiskers. The c-cell parameter is increased by $HgBr_2$ intercalation from 14.8Å to 21.0Å. No diffraction peaks for the original BC-222 phase is observed in the whiskers intercalated

for 100h. In the case of HBBC-222 phase, $HgBr_2$ seems to be also present between the double BiO-BiO layers.

It is clear from EDX measurement that contents of all intercalating elements increase with intercalation time. The content of I saturates at 50h, while those of Hg and Br increases up to 100h and decreases at 200h (Fig. 4).
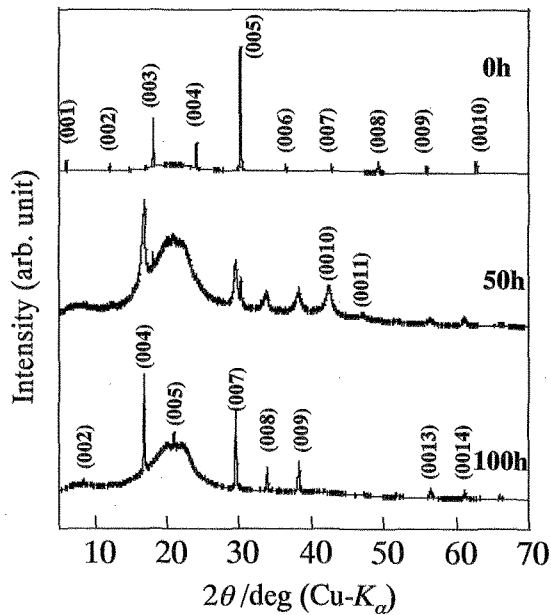

Fig. 3   X-ray diffraction patterns for no-intercalated (0h) and $HgBr_2$ intercalated whiskers for 50 and 100h at 400℃
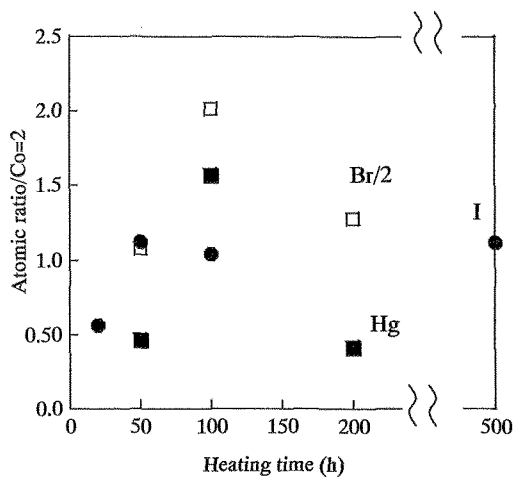

Fig. 4   I, Hg, and Br contents in intercalated whiskers to Co content of 2.0.

S values are decreased by both I_2 and $HgBr_2$ intercalation (Fig. 5). In the case of the IBC-222 phase, this would be due to the increase in the hole concentration. It is an open question in the HBBC-222 phase. Although the hole concentration would be increased in the IBC-222 whiskers, ρ values are increased. From TEM observation, many stacking faults are formed by the I_2 intercalation (Fig. 6). Electrical carriers seem to be scattered at the stacking faults. If such the stacking faults were removed, ρ could be reduced because of the increase in the hole concentration.
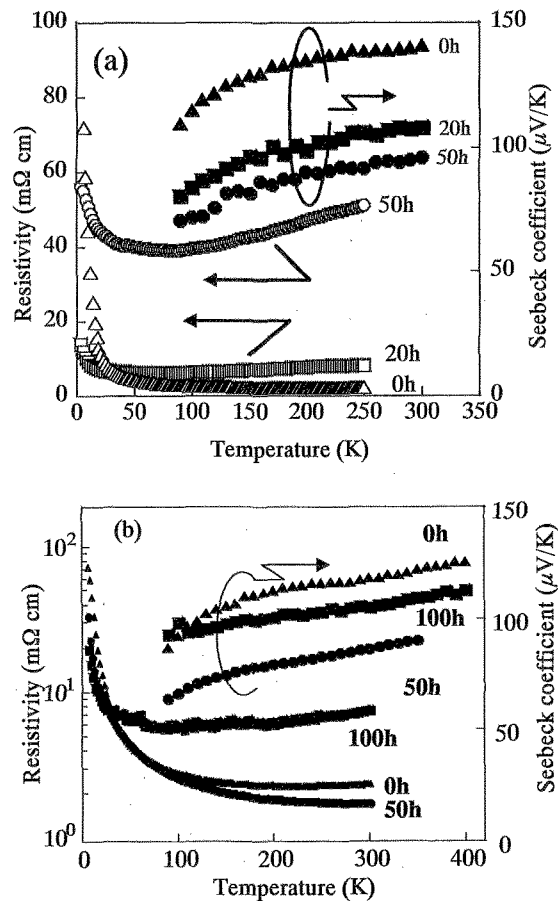

Fig. 5 ρ and S of no-intercalated (0h) and I_2 intercalated (a) and $HgBr_2$ intercalated whiskers (b).
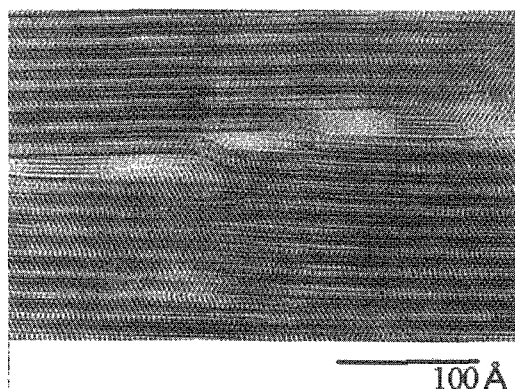
Fig. 6   A TEM image of I_2 intercalated whisker for 50h.

Temperature dependence of κ is indicated in Fig. 7. It is clear that I_2 intercalation is effective to decrease κ. The reduction in κ must be caused by the stacking faults. It also might be, however, due to elongation of the rock-salt sublattice in the c-axis direction. Z values can not be improved by I_2 intercalation because of the decrease in S and increase in ρ. If I_2 or $HgBr_2$ are intercalated completely and the stacking faults are removed, Z values of the intercalated samples should become higher than the no-intercalated ones.
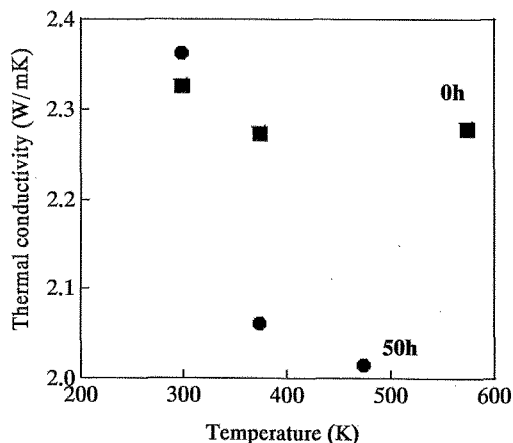

Fig. 7   Temperature dependence of κ for no-intercalated (0h) and I_2 intercalated whisker for 50h.

4. CONCLUSION

$Bi_2(Sr, Ca)_2Co_2O_9$ (BC-222) single crystals intercalated I_2 and $HgBr_2$ have been prepared. The c-cell parameter of the single crystals is elongated 3.6Å and 6.2Å by the I_2 and $HgBr_2$ intercalation, respectively. Because the intercalation has been incompletely, the effect of the elongation in the c-axis on thermoelectric properties can not be clear. If the proper elements are intercalated without stacking faults, the enhancement of thermoelectric properties is expected by controlling nano-structure.

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