Investigation of topological phase transition in BiTeBr under high pressure

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Abstract. The polar semiconductor BiTeBr has the $P\bar{3}m1$ symmetry, similar to that of BiTeI, in which a pressure-induced topological phase transition from a trivial semiconductor to a topological insulator has been theoretically predicted. To investigate the topological phase transition in BiTeBr, we performed X-ray diffraction and electrical resistivity measurement under high pressure, and the band calculation using experimental structural parameters. The $P\bar{3}m1$ structure is stable up to the pressure of $\sim$7 GPa; the ratio of lattice constants ($c/a$) reaches a minimum at around 3 GPa. Furthermore, the following phenomena are observed at around this pressure; 1) the band-gap energy closes and reopens with pressure, 2) the temperature dependence of resistivity changes from metallic to semiconducting. From theoretical prediction in BiTeI, the topological phase transition is accompanied by the band gap closing/reopening. Therefore, the results obtained in BiTeBr suggest that the topological phase transition occurs at around 3 GPa.

1. Introduction
Polar-semiconductors BiTeX ($X = \text{Cl, Br, I}$) are well known as materials exhibiting the giant bulk Rashba spin-split, which is caused by the combination of non-centrosymmetric structure and strong spin-orbit interaction (SOI) [1-4]. Recently, Bahramy et al. theoretically predicted the occurrence of pressure-induced topological phase transition in BiTeI [5]. Their report concludes that the bulk electronic states of BiTeI change from a trivial semiconductor to a topological insulator at a few gigapascals under hydrostatic condition. The valence and conduction bands near Fermi energy are mainly composed of Bi-6p and Te, I-5p orbitals, respectively. The transition is accompanied by the band-gap closing and re-opening, and the band inversion between the bands mentioned above occurs at higher pressures. Since the publication of Bahramy et al., the X-ray diffraction, the spectroscopy, and the band calculation were performed on BiTeI to investigate the topological phase transition [6-8].
These experiments suggested that a minimum ratio of lattice constants, $c/a$, makes a significant contribution to the topological transition; the free-carrier spectral weight shows a maximum and the band-gap closes when the $c/a$ has a minimum.

BiTeBr has a non-centrosymmetric layered structure with space group $P3m1$ (space group No.156), which is the same structure as BiTeI. The Bi-Te and Bi-Br bonds in each layer have covalent and ionic properties, respectively, and a unit of Te-Bi-Br three layers is weakly bonded by van der Waals forces along the $c$-axis. Since the crystal structure and the electronic state of BiTeBr are similar to those of BiTeI, the topological phase transition is also expected to occur in BiTeBr.

Therefore, we have performed synchrotron radiation X-ray diffraction and electrical resistivity measurement of BiTeBr under high pressure, and then the first-principles calculations in the framework of density functional theory using the experimental structural parameters to obtain the pressure variation of bulk electronic structures.

2. Experiments

Single crystals of BiTeBr were grown utilizing the vapor transport technique [3]. We used the modified Bridgman anvil cell for electrical resistivity measurement under high pressure. A fragment of BiTeBr with a size of $0.30 \times 0.75 \times 0.07 \text{ mm}^3$ was placed into a Teflon capsule filled with a mixture of Fluorinert (FC70 : FC77 = 1:1) as the pressure-transmitting medium for quasi-hydrostatic compression. The pressure scale in the sample chamber was calibrated in advance by transition pressures of structural phase transition in bismuth. The high-pressure cell was cooled down to the temperature of $\sim 3 \text{ K}$ by the Gifford-McMahon 4K cryogenic refrigerator developed by Iwatani Industrial Gases Corporation.

The powder sample for X-ray diffraction was prepared by grinding fragments of single crystals in an alumina mortar that is cooled by liquid nitrogen in a glove-bag. We used a diamond anvil cell and loaded the sample into a hole drilled in the SUS301 gasket. For hydrostatic compression, the sample hole was filled with fluid helium (He), which was compressed to $\sim 180 \text{ MPa}$ by the gas-loading system [8]. Synchrotron radiation X-ray diffraction at room temperature was carried out at the beamline of AR-NE1 of Photon Factory in High-Energy Accelerator Research Organization (KEK) in Japan. The incident beam was tuned to the energy of $29.723 \text{ keV}$ ($\lambda = 0.41718(9) \text{ Å}$). The imaging plate was used as a detector. The experimental pressure was determined using the ruby fluorescence method [9].

First-principles calculations in the framework of density functional theory (DFT) were performed within the generalized gradient approximation (GGA), using the pseudopotential plane-wave method as implemented in the ABINIT code [10]. Electronic structures were calculated using structural parameters, which were experimentally obtained at each pressure in this study. Within the experimental unit cell, atomic coordinates were optimized based on the minimum of force on each atom. The effect of SOI on the band structure was examined by tuning the SOI parameters for the pseudopotential.

3. Results and Discussion

Figure 1 shows the X-ray diffraction patterns with increasing pressure at room temperature. The DAC, after being filled with He, was sealed at the pressure of 0.31 GPa. The $P3m1$ symmetry of BiTeBr indexes most reflections at this pressure. The remaining peaks indicated with an asterisk are reflections from BiBrO (bismuth oxybromide). We think that
BiBrO results from the reaction of BiTeBr with atmospheric moisture during the handling of fine powder. The $P3m1$ structure is stable at the pressure of 7.55 GPa since the pattern’s characteristics do not change with pressure.

We applied the Rietveld analysis on the coexistent pattern of BiTeBr and BiBrO using the program of Rietan-FP [11], and refined only lattice parameters of the $P3m1$ structure, $a$ and $c$, due to the quality of diffraction patterns. Figure 2 (a) and (b) show pressure variations of $a$, $c$, and the ratio of them, $c/a$, respectively. Lattice constants monotonically decrease as a function of pressure. The $c$-axis largely decreases at lower pressures, reflecting the layered structure, while the $a$-axis linearly decreases. The linear compressibility of the $c$-axis is about twice as large as that of the $a$-axis. The $c/a$ reaches a minimum between 2 and 3 GPa similar to the behavior of BiTeI.

Pressure variation of the band-gap energy, $E_g$, obtained from the DFT calculations in this study, is shown as solid circles in Fig. 3(a). As pressure increases, the $E_g$ first decreases and then increases again beyond ~3 GPa. To estimate a critical pressure, $P_c$, at which the band-gap closes, we inverted the values along the zero-gap point, creating a mirror-like effect. Both variations, namely the actual data (positive) and the mirrored data (negative), smoothly relate to each other. Consequently, we can estimate the $P_c$ of 3 GPa from the position of an intersection point on the zero-gap line.

This result suggests the topological phase transition in BiTeBr occurs at the pressure of 3 GPa, since the band-gap closing is necessary for the phase transition from a trivial state to a topological one. Hence, we examined the effect of SOI on the bulk electronic states at $P = 1$ atm and 7.55 GPa to judge whether or not the quantum states at lower and higher pressures of $P_c$ are topologically different. The results are shown in Fig. 3 (b) and (c), respectively. The electronic states at 1 atm vary monotonically.

Figure 2. Pressure variation of (a) lattice constants $a$ (closed circle), $c$ (open circle) and (b) their ratio, $c/a$. Dashed lines are the guides for the eye.

Figure 3. (a) $E_g$ calculated at each pressure (closed circles) and its mirror image (open circles) and the effect of spin-orbit interaction on bulk band structures at (b) 1 atm and (c) 7.55 GPa.
with the decreasing effect of SOI; the Rashba-type spin-split becomes smaller, and the magnitude of $E_g$ increases. In contrast, those at 7.55 GPa show the band-gap closing at the SOI-strength of ~ 90% and reopening at ~80 %, indicating that the quantum state returns from topological to trivial.

Finally, we show the temperature dependences of electrical resistivity of BiTeBr below 3 GPa in Fig. 4. The resistivity has the value of ~2.4 m$\Omega$·cm at ambient conditions and shows metallic-like behavior up to pressures of 2 GPa. Applying pressure causes a change in the temperature derivative of resistivity from positive to negative. Considering the $E_g$ closes/reopens at around 3 GPa, the semiconducting behavior suggests that the bulk carriers localizes with the opening of $E_g$. Furthermore, the temperature dependence of resistivity at 3 GPa has a plateau region between 50 and 150 K. We consider that this is proof of the topological phase because the plateau region suggests the dominance of surface conduction at low temperatures, and it is observed in the topological insulators [12].

4. Summary
We investigated pressure-induced topological phase transition in BiTeBr by combining theoretical and experimental studies. When the ratio of lattice constants in the $P3m1$ structure reaches a minimum at around 3 GPa, the closing/reopening of band-gap occurs and the transport property changes from metallic to semiconducting behavior. Furthermore, the effect of SOI on the electronic structure is clearly different above and below $P_c$. At 7.55 GPa above $P_c$, a decrease in the SOI-strength causes the reverse transition from a topological to a trivial state. From these results, we concluded that the topological phase transition in BiTeBr occurs at 3 GPa.

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