

# Pressure-induced superconductivity in non-stoichiometric bismuth telluride $\text{Bi}_{35}\text{Te}_{65}$

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**Abstract.** We performed x-ray diffraction study and electrical resistivity measurement of non-stoichiometric *n*-type  $\text{Bi}_{35}\text{Te}_{65}$  under high pressure to investigate pressure-induced superconductivity and structural phase transition. Stoichiometric bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ), which is a *p*-type semiconductor, has the rhombohedral structure with space group *R*-3*m* at ambient condition. Pressure-induced superconductivity of stoichiometric *p*-type  $\text{Bi}_2\text{Te}_3$  occurs in the high-pressure phases which appear above 8 GPa.  $\text{Bi}_{35}\text{Te}_{65}$  has also the *R*-3*m* structure at ambient condition with electron carriers. X-ray diffraction study shows that the *R*-3*m* structure remains stable up to 8 GPa at room temperature. The superconducting transition in *n*-type  $\text{Bi}_{35}\text{Te}_{65}$  is observed above 6 GPa; the transition temperature is 2.9 K at 6 GPa. The electrical resistivity at room temperature decreases rapidly at pressures from 7 to 8 GPa, indicating the occurrence of structural phase transition. It suggests that the superconducting transition at 6 GPa occurs at the ambient pressure phase with the *R*-3*m* structure.

## 1. Introduction

We have studied structural phase transition and pressure-induced superconductivity (SC) in stoichiometric *p*-type bismuth telluride ( $\text{Bi}_2\text{Te}_3$ ) under hydrostatic condition [1-3].  $\text{Bi}_2\text{Te}_3$  has a rhombohedral structure with space group *R*-3*m* (denoted by phase I) at ambient condition; the lattice parameters in hexagonal axes are  $a = 4.395 \text{ \AA}$  and  $c = 30.44 \text{ \AA}$  [4]. When  $\text{Bi}_2\text{Te}_3$  is compressed at room temperature, the *R*-3*m* structure is stable at pressures up to 8 GPa with the minimum value of the lattice parameter ratio  $c/a$  at around 2 GPa [1]. The high-pressure *C*2/*m* structure (phase II) and the *C*2/*c* one (phase III) appear at 8.0 and 13.4 GPa, respectively. Furthermore, a bcc-like solid solution structure for Bi-Te binary alloy (phase IV) is formed above 14.5 GPa [3, 5] and coexists with phase II and III up to 23.1 GPa. Above 25 GPa, the transformation to phase IV is completed and this phase is stable at least up to 52.1 GPa [5].

In our previous study of *p*-type  $\text{Bi}_2\text{Te}_3$ , a sharp drop of resistivity corresponding to the superconducting transition is observed below 2.2 K at pressure of 6.0 GPa, and zero-resistance states are detected above 8 GPa: onset of superconducting transition temperature  $T_c^{\text{onset}} = 2.8 \text{ K}$  at 8 GPa. The pressure dependence of  $T_c^{\text{onset}}$  shows a maximum value at 9 GPa in the region from 6 to 10 GPa,



and then a sudden increase at 11 GPa. In comparison with sequence of structural transition, we infer that the superconducting transition above 6 GPa and the increase in  $T_c^{\text{onset}}$  at 11 GPa are attributed to the formation of phase II and III, respectively [2]. On the other hand, another high-pressure studies of *p*-type  $\text{Bi}_2\text{Te}_3$  reported that the superconducting transition is observed above 3 GPa in phase I [6, 7], though the pressure dependence of  $T_c$  is similar to that of our results. It is noted that the superconducting transition at 3 GPa in phase I provide the possibility of the existence of a topological superconductor under pressure in *p*-type  $\text{Bi}_2\text{Te}_3$  [7].

Since  $\text{Bi}_2\text{Te}_3$  shows the variations of the carrier types, the carrier density, and the transport properties with the atomic composition, there is a possibility that the difference in the onset temperature of pressure-induced SC depends not only on experimental conditions such as the hydrostaticity but also on the sample measured in each experiment. One of them is the dominant charge carrier which changes from hole to electron above 63 at.% Te [8]. We, therefore, investigate pressure-induced SC in non-stoichiometric *n*-type  $\text{Bi}_2\text{Te}_3$ , which has also crystallizes in the *R*-3*m* structure up to 85 at.% Te [9], under the same experimental conditions as *p*-type  $\text{Bi}_2\text{Te}_3$ . In 1970's, pressure-induced SC in *n*-type  $\text{Bi}_2\text{Te}_3$  had been observed above 6.7 GPa, though no zero-resistance state was observed. The critical pressure where the SC appears ( $P_c$ ) is about 1 GPa higher than that of *p*-type sample in their report [10].

In this study, we prepared a  $\text{Bi}_{35}\text{Te}_{65}$  as the *n*-type  $\text{Bi}_2\text{Te}_3$  sample. In order to search for the pressure-induced SC and investigate the effect of pressure on  $T_c$  and crystal structure, we have performed the x-ray diffraction and the electrical resistivity measurement under hydrostatic pressure.

## 2. Experiments

Polycrystalline *n*-type  $\text{Bi}_{35}\text{Te}_{65}$ , which is equal to  $\text{Bi}_{2-\delta}\text{Te}_{3+\delta}$  ( $\delta = 0.25$ ), was made by melting powders of Bi and Te (99.999 % pure, Kojundo Chemical Lab. Co., Ltd.). A mixture of powders consisting of 35 at.% Bi and 65 at.% Te was ground in an agate mortar, and was sealed under vacuum in quartz tube. The powder mixture in quartz tube was heated to 700 °C for twenty-four hours and slowly cooled to 500 °C taking 100 hours, and then quenched in water. The resulting crystals were easily cleaved along the *a*-*b* plane and have the shining mirror-like surfaces. Electron probe micro analysis (EPMA) and energy dispersive x-ray analysis (EDX) indicated that Bi and Te atoms were distributed homogeneously in the cleaving plane. The Hall coefficients of two samples ( $4.60 \times 3.00 \times 0.88$  and  $7.00 \times 2.50 \times 0.61 \text{ mm}^3$ ) showed negative and the electron carrier density of the resulting crystals was  $1.6 - 4.1 \times 10^{19} \text{ cm}^{-3}$  at ambient condition.

Angle-dispersive powder x-ray diffraction measurements with synchrotron radiation were carried out using diamond anvil cell (DAC) with 0.25 mm culet diameter with increasing pressure up to 13 GPa at room temperature. The samples were ground in an alumina mortar cooled in liquid nitrogen for more than 5 hours in order to obtain fine powders. The powdered sample was placed into a sample chamber, 120  $\mu\text{m}$  in diameter and 50  $\mu\text{m}$  in thickness, made by drilling a small hole in a rhenium gasket. The sample chamber was filled with fluid helium compressed to 180 MPa as a pressure-transmitting medium for hydrostatic condition [11]. Experimental pressure in the sample chamber was measured by ruby fluorescence method [12]. The diffraction patterns were taken using synchrotron radiation beam, which was monochromatized to  $\lambda = 0.41283 \text{ \AA}$  ( $E = 30.036 \text{ keV}$ ), at a beamline Photon Factory Advanced Ring NE1 of High Energy Accelerator Research Organization (KEK), Tsukuba in Japan.

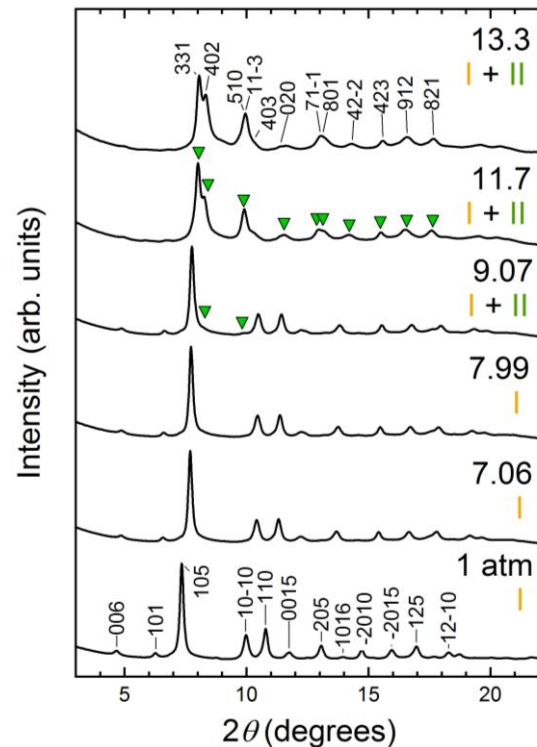
Electrical resistivity measurements by four-probe method were performed on the cleaving plane using a modified Bridgman anvil cell [13, 14] with increasing pressure up to 13 GPa. A small piece of single-crystal with a size of  $1.10 \times 0.38 \times 0.10 \text{ mm}^3$  was set into a Teflon capsule filled with a mixture of Fluorinert FC-77 and FC-70 (1:1 in volume) as a pressure-transmitting medium. The capsule was loaded into the high-pressure cell. The experimental pressure in the sample chamber was calibrated by using the structural phase transitions of Bi at room temperature. The cell under high pressure was clamped at room temperature, and then cooled by  $^3\text{He}$  circulation-type Joule-Thomson 1 K cryogenic refrigerator with the Gifford-McMahon cycle cooler developed by IWATANI INDUSTRIAL GASES

CORP. The temperature dependence of the electrical resistance was measured in the temperature region between 0.8 and 300 K at each pressure.

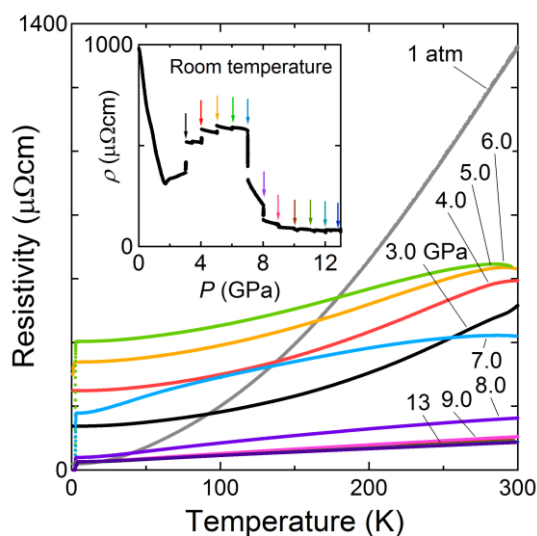
### 3. Result and discussion

Figure 1 shows pressure variation of x-ray diffraction patterns up to 13 GPa at room temperature. All reflections observed at 1 atm are indexed by space group  $R\bar{3}m$  (the ambient phase I) with lattice parameters,  $a = 4.3892(6)$  Å and  $c = 30.352(6)$  Å, which are determined by the Rietveld refinement [15, 16]. The ambient phase I remains stable up to  $\sim 8$  GPa. As shown in figure 1, new reflections marked with triangles appear above 9.07 GPa. These reflections are indexed with space group  $C2/m$  (the high-pressure phase II), which is the same monoclinic structure as phase II in stoichiometric  $p$ -type  $\text{Bi}_2\text{Te}_3$ . The high-pressure phase II coexists with the ambient phase I in the pressure range from 9.07 to 13.3 GPa.

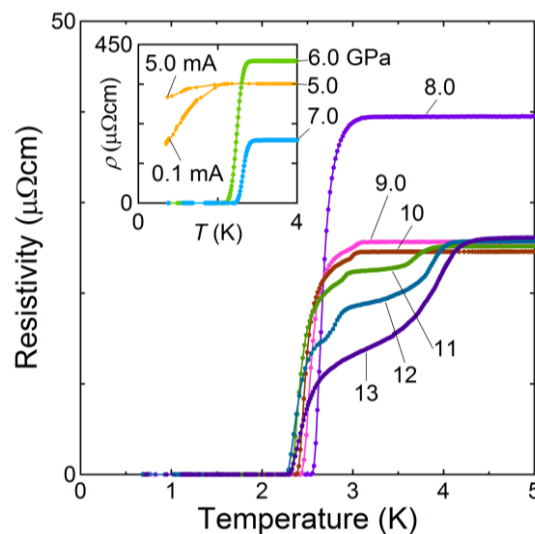
The inset of figure 2 shows pressure dependence of the electrical resistivity  $\rho$  at room temperature on compression up to 13 GPa. The pressure derivative of  $\rho$  changes from negative to positive at around 2 GPa.  $\rho$  has the local maximum value at around 5 - 6 GPa. And then  $\rho$  rapidly decreases above 7 GPa with increasing pressure. It indicates the structural phase transition from the ambient phase I to the high-pressure phase II, above mentioned, although the transition pressure is about 2 GPa lower than that in x-ray diffraction study. The lower transition-pressure determined by resistivity measurement is probably due to the pressurizing single crystal sample under quasi-



**Figure 1.** Pressure variation of the x-ray diffraction patterns at room temperature. Triangles indicate the reflections from phase II.



**Figure 2.** Temperature and pressure dependence of the electrical resistivity. Arrows shown in inset indicate the clamping-pressure at which  $\rho$  vs.  $T$  curves were measured.



**Figure 3.** Temperature dependence of the electrical resistivity near the superconducting transition. Inset shows  $\rho$  vs.  $T$  curve from 5 to 7 GPa and the current dependence of that at 5 GPa.

hydrostatic condition. As shown in the main panel of figure 2, the temperature dependence of  $\rho$  has the positive temperature coefficient at each pressure. However,  $\rho$  vs.  $T$  curve gradually changes as a function of pressure up to 7 GPa and then exhibits metallic linear behavior above 8 GPa after the structural phase transition to the high-pressure phase II. As shown in the main panel, the values of  $\rho$  near room temperature at 7 and 8 GPa are lower than that where arrows pointing in the inset because of the phase transition to phase II during the clamping process.

Figure 3 shows the magnified view of  $\rho$  vs.  $T$  near the superconducting transition at the pressures from 5.0 to 13 GPa. A small drop is observed around 2.1 K at 5.0 GPa, and suppressed with increasing current as shown in inset of figure 3. Further compression causes the pressure-induced superconducting transition with zero-resistance state above 6 GPa. Therefore, a small decrease in  $\rho$  observed at 5 GPa is due to the superconducting transition. There is a possibility that the drops show superconducting transition arising from the ambient phase I. Other small drops are observed at higher temperature above 9 and 11 GPa, respectively. But such stepwise decreases were not observed in the previous report [2]. The highest one of the temperatures where  $\rho$ -drop appears,  $T_c^{\text{onset}}$ , specifically increases with increasing pressure above 11 GPa. The sudden increase of  $T_c^{\text{onset}}$  above 11 GPa suggests the appearance of phase III [2].

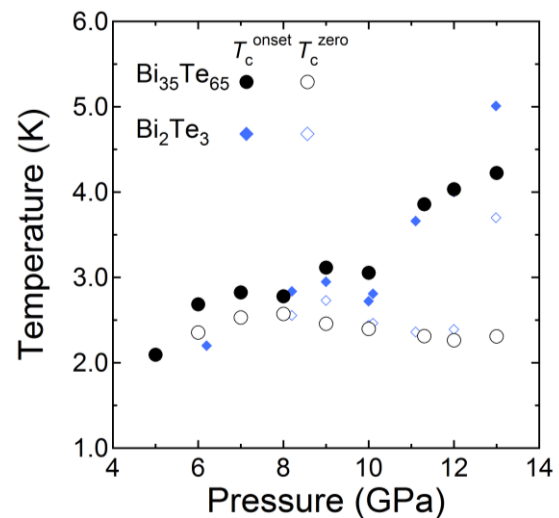
Pressure variations of  $T_c^{\text{onset}}$  and the zero-resistance temperature  $T_c^{\text{zero}}$  of  $\text{Bi}_{35}\text{Te}_{65}$  and  $\text{Bi}_2\text{Te}_3$  are shown in figure 4. Pressure dependence of  $T_c^{\text{onset}}$  has a maximum at 7 GPa in the pressure range of 5 - 8 GPa and discontinuously changes at around 9 and 11 GPa. After a sudden increase at 11 GPa,  $T_c^{\text{onset}}$  gradually increases up to 13 GPa. On the other hand, pressure dependence of  $T_c^{\text{zero}}$  shows maximum at 8 GPa, and decreases up to 12 GPa, and a slight increase at 13 GPa. The pressure dependences of  $T_c^{\text{onset}}$  and  $T_c^{\text{zero}}$  above 8 GPa is similar to those of  $p$ -type  $\text{Bi}_2\text{Te}_3$  [2]. In both samples, the effect of pressure on  $T_c^{\text{onset}}$  and  $T_c^{\text{zero}}$  changes from negative to positive at 10 and 13 GPa, respectively.

The superconducting transition is observed below 7 GPa, at which the high pressure phase II appears. Because there is no remarkable change indicating structural phase transition in  $\rho$  vs.  $T$  curve at 5 and 6 GPa. In [10], the critical-pressure  $P_c$  at which the SC appears in  $n$ -type  $\text{Bi}_2\text{Te}_3$  is higher than that in  $p$ -type one, if the carrier density of both samples is of the same order of magnitude. But in our results which have been carried out under same experimental condition, the  $P_c$  in  $n$ -type  $\text{Bi}_{35}\text{Te}_{65}$  sample is lower than  $p$ -type  $\text{Bi}_2\text{Te}_3$  (carrier densities  $2.7 - 7.0 \times 10^{-19} \text{ cm}^{-3}$  at ambient condition) which has never shown the  $T_c^{\text{zero}}$  in less than 7 GPa. Therefore, it is inferred that the  $\text{Bi}_2\text{Te}_3$  has an optimal carrier type and concentration for lowest  $P_c$  and highest  $T_c$ .

In summary, by performing x-ray diffraction and electrical resistivity measurement of non-stoichiometric  $n$ -type  $\text{Bi}_{35}\text{Te}_{65}$  under high pressure, the pressure-induced superconductivity occurs below 7 GPa in ambient phase where the crystal structure preserves the rhombohedral symmetry.

### Acknowledgment

The present work was performed under proposal No. 2012G162 of Photon Factory, KEK. This work was supported by Grant-in-Aid for JSPS fellows and Young Scientists (B) (No. 24740229), and the "Topological Quantum Phenomena" (No. 25103710) Grant-in Aid for Scientific Research on



**Figure 4.** Pressure dependence of the superconducting transition temperature:  $T_c^{\text{onset}}$  (●) and  $T_c^{\text{zero}}$  (○) in  $n$ -type  $\text{Bi}_{35}\text{Te}_{65}$  and  $T_c^{\text{onset}}$  (◆) and  $T_c^{\text{zero}}$  (◇) in  $p$ -type  $\text{Bi}_2\text{Te}_3$ .

Innovative Areas from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

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