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X-ray structural analysis of the high-pressure phase III of tellurium

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Abstract

A structure of a high-pressure phase of tellurium (Te-III) has been re-examined by an x-ray diffraction method. This phase appears at a pressure between 7 and 27 GPa, where a second-order phase transition to Te-IV occurs. The newly obtained crystal lattice of Te-III at 8 GPa is monoclinic with $a = 8.4682(14)$ Å, $b = 4.7424(8)$ Å, $c = 3.9595(7)$ Å, $\beta = 88.112(11)°$. The space group is $C2/m$, with six atoms in the unit cell, two in positions 2a at (0, 0, 0) and four in positions 4i at $(x, 0, z)$ with $x = 0.324(11)$, $z = 0.675(3)$.

1. Introduction

It is known that the Te-I phase which has a trigonal lattice at ambient pressure transforms to a monoclinic phase (Te-II) at 4 GPa, to an orthorhombic phase (Te-III) at 7 GPa, to a rhombohedral phase (Te-IV) at 11 GPa, and to a bcc phase (Te-V) at 27 GPa [1, 2]. Recently, however, Akahama and Kawamura [3] have reported that the phase transition from Te-III to Te-IV occurs at about 23 GPa and is of second order. If this is true, the well-known structural model of Te-III should be changed, because a second-order phase transition from Te-III whose space group is $P2_1$ to Te-IV whose space group is $R\bar{3}m$ is impossible. In order to clarify whether or not the phase transition from Te-III to Te-IV is of second order, x-ray diffraction patterns of tellurium have been measured at pressures up to 33 GPa with good signal-to-noise ratio and high resolution using synchrotron radiation, and to re-examine the structure of Te-III, Rietveld analysis has been performed.

2. Experimental details

A diamond anvil cell was used for the high-pressure experiment. A commercial 99.999% purity tellurium sample was powdered and put into a hole in a metal gasket, Inconel-750X, with a methanol:ethanol:water mixture in a 16:3:1 ratio as the pressure-transmitting medium.

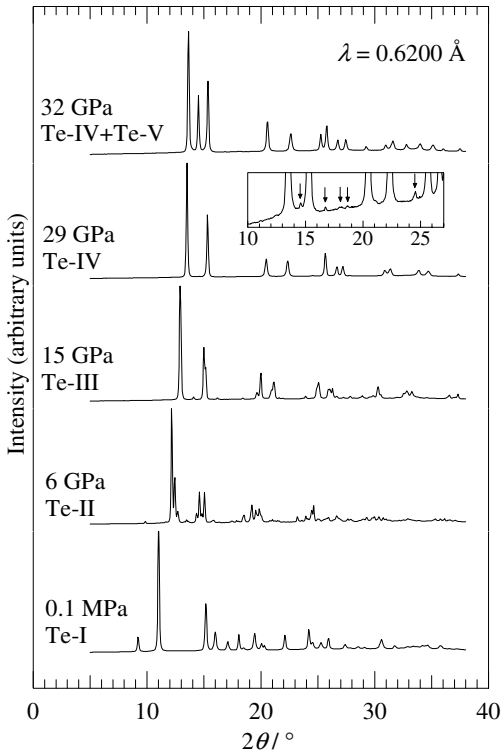

Figure 1. The x-ray diffraction patterns of tellurium under various pressures.

The pressure was determined by ruby fluorescence measurement. An angle-dispersive x-ray powder diffraction experiment was carried out using synchrotron radiation on beamline BL-18C at the Photon Factory. An incident x-ray beam was monochromatized to a wavelength of 0.6200 Å and collimated to 80 μm diameter. All diffraction data were collected with an imaging plate detector at room temperature. The Rietveld analysis was performed using the computer program RIETAN-94 [4].

3. Results and discussion

X-ray diffraction patterns of tellurium at various pressures are shown in figure 1. Previously reported phase transitions from Te-I to Te-II, and from Te-II to Te-III are observed at 4 and 7 GPa, respectively. On pressure increase, the diffraction pattern of Te-III changes continuously to that of Te-IV and at 27 GPa, the diffraction pattern agrees with that of Te-IV. This shows that the phase transition from Te-III to Te-IV occurs at 27 GPa and is a second-order transition, as is reported by Akahama and Kawamura [3] who also report that a similar phase transition is observed in selenium [5].

The structure of Te-IV is rhombohedral and the unit cell contains one atom. However, some very weak reflections which cannot be explained by this rhombohedral structure appear in the diffraction profile of Te-IV (as shown in the inset of figure 1). Moreover, these very weak reflections also appear in the diffraction profile of Te-III. Therefore, a very small amount of unknown phase exists possibly at a pressure between 7 and 32 GPa, where the Te-IV phase changes to the Te-V phase. The phase diagram is summarized in figure 2.

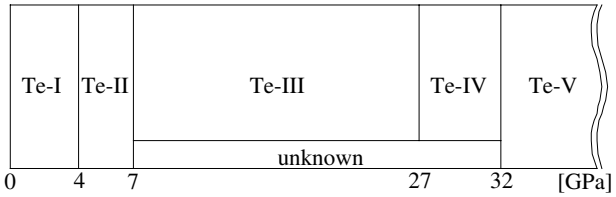

Figure 2. The phase diagram of tellurium.

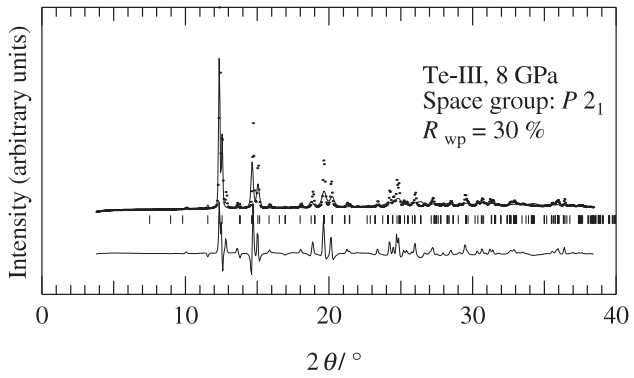

Figure 3. The Rietveld refinement fit of the $P2_1$ structure to the Te-III profile at 8 GPa. The observed data are indicated by dots, and the calculated pattern is the solid curve superimposed on them. The difference between the observed and calculated data is represented in the lower portion.

Figure 3 shows the results of the Rietveld analysis performed for Te-III at 8 GPa using the space group $P2_1$ which was reported as the space group of Te-III previously [1]. The final R_{wp}-factor is 30%. Agreement between the observation and the calculation is not so good. The final R_{wp}-factors of Rietveld analyses for other data in the pressure range from 7 to 11 GPa are more than 27%. This suggests that the space group of Te-III is different from $P2_1$.

In order to find the structure of Te-III, Rietveld analyses were performed using many kinds of unit cell and space group which were derived from the rhombohedral lattice of Te-IV. The minimum reliability factor is obtained for a monoclinic lattice whose space group is $C2/m$, and $Z = 6$. This unit cell contains six atoms located on Wyckoff 2a sites at (0, 0, 0) and 4i sites at $(x, 0, z)$.

Figure 4 shows the results of the Rietveld analysis performed for Te-III at 8 GPa using the space group $C2/m$. Agreement between the observed and the calculated diffraction patterns is good except for the very weak reflections which are due to an unknown phase. The final R_{wp} is less than 15% for all Rietveld analyses of the high-pressure phase at pressures between 7 and 27 GPa. The structure parameters obtained at 8 GPa are given in tables 1 and 2.

The relation between the lattice vectors of $C2/m$ and those of $R\bar{3}m$ is shown in figure 5. The open and closed circles, squares and triangles denote the atomic positions of tellurium. The symbols $\boldsymbol{a}_m$, $\boldsymbol{b}_m$ and $\boldsymbol{c}_m$ represent the lattice vectors of the Te-III monoclinic phase. The symbol $\boldsymbol{a}_r$ represents the lattice vector of the Te-IV rhombohedral phase. This figure shows that the structure of $C2/m$ is identical to that of $R\bar{3}m$ when the lattice parameter β of $C2/m$ is equal to 90° and the atomic position parameters x_2 and z_2 are equal to 1/3 and 2/3, respectively. Therefore, the second-order phase transition from this structure to rhombohedral Te-IV is possible. Interatomic distances at 8 GPa are given in table 3. The coordination number of each

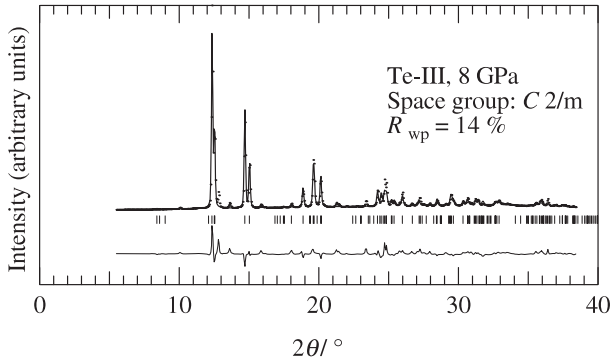

Figure 4. The Rietveld refinement fit of the $C2/m$ structure to the Te-III profile at 8 GPa. The observed data are indicated by dots, and the calculated pattern is the solid curve superimposed on them. The difference between the observed and calculated data is represented in the lower portion.

Table 1. Lattice parameters of tellurium at 8 GPa.

a/Å	b/Å	c/Å	β/°
8.4682(14)	4.7424(8)	3.9595(7)	88.112(11)
	$V = 158.92(8)$ Å^3		

Table 2. Parameters of atoms in Te-III at 8 GPa.

Atom	x	y	z	B/Å^2
Te(1)	0 (fixed)	0 (fixed)	0 (fixed)	2.6(15)
Te(2)	0.324(11)	0 (fixed)	0.675(3)	2.2(8)

Table 3. Interatomic distances of tellurium at 8 GPa.

Te–Te distances/Å					
1–2	3.0	3′–6	3.0	1–3	3.1
1–6	3.0	4′–6	3.0	1–4	3.1
2′–5	3.0	1–5	3.1	3′–5	3.2
2′–7	3.0	1–7	3.1	4′–7	3.2

atom is almost six even at 8 GPa. This shows that the structure of Te-III is similar to that of Te-IV, though the space group of Te-III is different from that of Te-IV. In order to emphasize the anisotropy in the structure of Te-III, the shortest bonds of 3.0 Å are shown in figure 5 by solid lines. These bonds may tightly bind each atom and constitute a puckered layer structure stacked along the [102] direction as shown in figure 5(b). This layer structure is different from those obtained for tellurium and selenium previously [1, 6].

With increasing pressure, the lattice parameters, a, b, c decrease and β increases up to the transition pressure. The compression behaviours along the a-, b- and c-axes are slightly different from each other. When pressure is applied from 7 to 27 GPa, the a- and c-axes decrease by 5 and 10%, respectively, while the b-axis decreases by only 2%. These results are consistent with the puckered layer being parallel to the b-axis.

With increasing pressure, the second- and third-shortest bond distances of 3.1 and 3.2 Å, respectively, decrease, while the very shortest bonds of 3.0 Å gradually increase. Consequently,

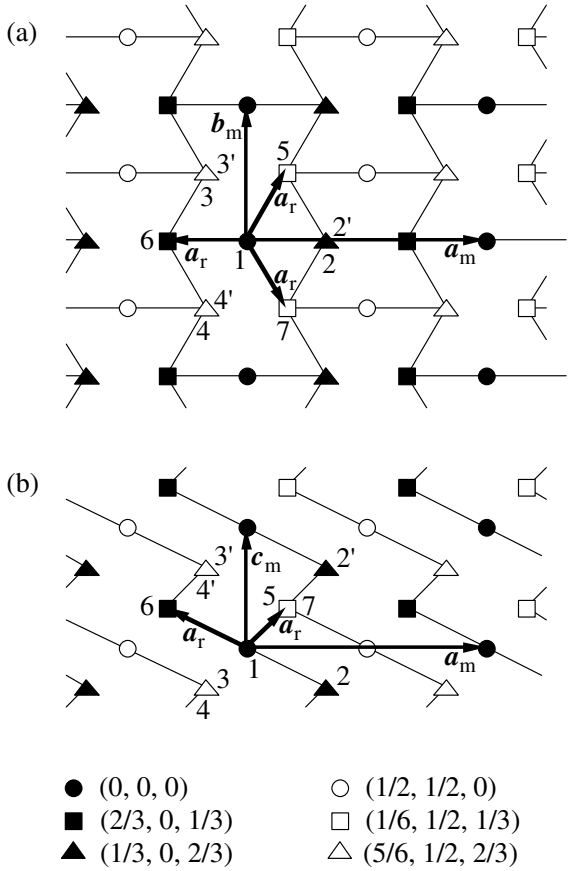

Figure 5. The structure of the Te-III phase viewed along the *c*-axis (a), and the *b*-axis (b). Solid lines show the short bonds of 3.0 Å. The symbols $\boldsymbol{a}_m$, $\boldsymbol{b}_m$ and $\boldsymbol{c}_m$ represent the lattice vectors of Te-III, monoclinic phase. The symbol $\boldsymbol{a}_r$ represents the lattice vector of Te-IV, rhombohedral phase.

these bond lengths become continuously the same, 3 Å at 11 GPa. However, since the lattice parameter β is still less than 90° at this pressure, the transition to Te-IV is not yet accomplished at 11 GPa.

References

[1] Aoki K, Shimomura O and Minomura S 1980 *J. Phys. Soc. Japan* **48** 551
[2] Parthasarathy G and Holzapfel W B 1988 *Phys. Rev.* B **37** 8499
[3] Akahama Y and Kawamura H 1996 *Rev. High Pressure Sci. Technol.* **5** 143 (in Japanese)
[4] Kim Y-I and Izumi F 1994 *J. Ceram. Soc. Japan* **102** 401
[5] Akahama Y, Kobayashi M and Kawamura H 1993 *Phys. Rev.* B **47** 20
[6] Ohmasa Y, Yamamoto I, Yao M and Endo H 1995 *J. Phys. Soc. Japan* **64** 4766