Bcc-fcc structure transition of Te

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Abstract. Using the synchrotron radiation x-ray powder diffraction technique, the structure phase transition of Te has been investigated at pressure up to 330 GPa and at 298 K. The phase transition from the bcc (Te-V) to a new high-pressure phase (Te-VI) was found at 100 GPa and the structure of the new phase was suggested to be a superlattice of the fcc structure. The Te-VI phase further transformed to the fcc phase (Te-VII) at 255 GPa with disappearance of satellite peaks. Since for group 16 elements, it has been considered that the structure of the highest pressure phase is bcc, the present results provided new information about the high-pressure behaviour of these elements.

1. Introduction

Group 16 elements of sulfur, selenium and tellurium have an electron configuration of $s^2p^4$ in the ground state and behave as an atom of 2 valences. These elements link covalently and make a cyclic molecule or a spiral chain molecule. These molecules cohere by van der Waals forces and form molecular crystals. At high pressure, it is well known that the crystals undergo the insulator (or semiconductor)-metal transition by way of various phase transitions [1-5]. For tellurium (Te), four phase transitions have been reported up to 36 GPa at room temperature; from the trigonal phase (Te-I) consisting of a spiral chain to the monoclinic phase (Te-II) of a puckered layer at 4 GPa, to the monoclinic phase (Te-III) with an incommensurate modulation at 4.5 GPa, to a $\beta$-Po type phase (Te-IV) at 25 GPa and high temperature, and further to a body centred-cubic (bcc) phase (Te-V) at 27GPa [6-11]. Since the other group 16 elements exhibit similar structure sequence at higher pressures, the sequence of Te is considered to be a prototype of these elements. The successive structural transitions are accompanied by an increase in the coordination number (CN) of Te atoms; 2-4-6-8. Therefore, a transition to the structure with larger coordination number such as the face centred-cubic (fcc) or hexagonal close-packed (hcp) structure with the CN of 12 is expected with further compression. Previous theoretical studies have explained the structural stability of observed high-pressure phases successfully [12-14], however, there is no report of theoretical calculation about the post-bcc phase transition up to now.

In this paper, in order to explore the post-bcc phase, the synchrotron radiation (SR) x-ray powder diffraction experiments of Te at pressure up to 330 GPa have been carried out, and the bcc-fcc structure transition is reported.
2. Experimental
A diamond anvil cell (DAC) was used to generate high pressure. Four compression experiments were performed using different anvil geometries. For ultrahigh-pressure generation, the diameter of the flat face of the diamond anvils was narrowed down to 25 μm. A rhenium (Re) metal sheet of thickness of 250 μm was used as a gasket. The powder sample of Te with 99.9999% purity was loaded in the sample chamber of the gasket without a pressure medium. The lattice constants of the trigonal Te at ambient conditions was \( a = 4.4577(2) \) Å and \( c = 5.9289(1) \) Å. The pressure in the sample chamber was estimated from the equation of state of Pt [15] or the pressure shift of the Raman band edge of the diamond anvils [16], which was calibrated using a Pt scale. Pressure uncertainty was estimated to be within ±3%. Raman spectra were obtained using a micro-optical spectroscopic system. The excitation source was a He–Ne laser of the wavelength 632.8 nm.

X-ray diffraction experiments at high pressure were conducted at room temperature by an angle dispersive method using a monochromatic SR source (\( E = 30 \) keV) on the BL10XU beamline at SPring-8. A compound refractive lens made from glassy carbon and SU8 polymer was used to focus the x-ray on the small sample. Details of the beamline and the x-ray focusing system have been described elsewhere [17]. Diffraction patterns were recorded on an image plate detector and the 2\( \theta \)-intensity patterns were obtained via an integration of the recorded two-dimensional diffraction images [18].

![Figure 1. The representative 2\( \theta \)-intensity patterns of the high-pressure phases; Te-V of bcc at 85 GPa, Te-VI of a superlattice of fcc at 117 GPa and Te-VII of fcc at 255 GPa. The pattern at 85 GPa was assigned to bcc with a lattice constant \( a = 3.2756(4) \) Å. Since for the pattern at 117 GPa, main peaks marked by open circles, which are listed in table I, were well explained as fcc, sub-peaks marked by stars were considered to be superlattice reflections of the fcc. Te-VI was assigned to the superlattice of fcc. For the pattern of Te-VII at 255 GPa, sub-peaks disappear completely and observed peaks were well assigned as fcc with a lattice constant \( a = 3.7573(8) \) Å. Asterisks show diffraction peaks from the Re gasket.](image)
3. Results and Discussion
Above 30 GPa and below 97 GPa the $2\theta$-intensity patterns agreed with the pattern expected for the bcc phase. A pattern measured at 85 GPa is shown in figure 1. All reflections allowed within the cubic space group $Im3m$ were observed to a maximum diffraction angle of $2\theta = 32^\circ$. The $d$-spacing of the pattern was well explained with the lattice constant of $a = 3.2756(4)$ Å, while the relative intensity of the 110 diffraction peak suggests strong preferred orientation of the sample.

With increasing pressure, new diffraction peaks appeared at 99 GPa. The intensity of these peaks increased with increasing pressure and diffraction peaks from the bcc phase disappeared completely near 116 GPa. This change of the pattern suggested a structural transition from the bcc (Te-V) to a new high-pressure phase (Te-VI) between 99 and 116 GPa. The diffraction pattern of new high-pressure phase at 117 GPa is also shown in figure 1. The main peaks with relatively strong intensity labeled by the open circle are well indexed to an fcc lattice with the lattice constant $a = 4.0058(5)$ Å. Observed and calculated $d$-values are listed in table 1. The structure phase transition reproduced other three different experimental runs.

Table 1. The list of observed and calculated $d$-values of main peaks of Te-VI phase at 117 GPa. The observed main peaks are well assigned to the fcc lattice with $a = 4.0058(5)$ Å.

| $h$ | $k$ | $l$ | $d$(obs), (Å) | $d$(cal), (Å) | $d$(obs)-$d$(cal), (Å) |
|-----|-----|-----|---------------|---------------|------------------------|
| 1   | 1   | 1   | 2.3122        | 2.31274       | -0.00054               |
| 2   | 0   | 0   | 2.0063        | 2.00341       | 0.00341                |
| 2   | 2   | 0   | 1.4159        | 1.41626       | -0.00036               |
| 3   | 1   | 1   | 1.2089        | 1.20779       | 0.00111                |
| 2   | 2   | 2   | 1.1557        | 1.15637       | -0.00067               |
| 4   | 0   | 0   | 1.0012        | 1.00145       | -0.00025               |
| 3   | 3   | 1   | 0.9188        | 0.91899       | -0.00019               |
| 4   | 2   | 0   | 0.8956        | 0.89572       | -0.00012               |
| 4   | 2   | 2   | 0.8179        | 0.81768       | 0.00022                |

Figure 2. The pressure evolution of the relative intensity of main peaks and sub-peaks in the $2\theta$ region between 9º and 14º for Te-VI. The $2\theta$-values of the x axis were arbitrarily shifted so that the main fcc-111 peaks were centered on $2\theta = 0^\circ$. With increasing pressure, the intensity of sub-peaks labelled by the star (+) decreases rapidly.
Figure 3. (a) The pressure dependence of the ratio \( \frac{I_{\text{sub}}}{I_{\text{main}}} \) of integrated intensities between main peak assigned to the fcc-111 reflection and each sub-peak assigned by +1, +2 and +3 in figure 2. The intensity of sub-peaks decays with a similar tendency with pressure. The dependence suggests that the sub-peaks disappear at pressure about 250 GPa. The broken lines are guide for eyes. (b) The d-value ratios \( \frac{d_{\text{sub}}}{d_{\text{main}}} \) between the main peak assigned to the fcc-111 and sub-peaks. The relative position of the sub-peaks does not show remarkable change.

Figure 4. The pressure dependence of the atomic volume, together with previous data (solid lines) [9]. Vertical broken lines show transition pressures. The volume of Te-VI was calculated by assuming a superlattice of fcc. The bcc phase coexists with the new phase up to 110 GPa. From the dependence, the volume reduction (-\( \Delta V \)) at the transition pressure around 100 GPa was estimated to be 0.15 Å\(^3\) which corresponds to 0.9% of the volume at the transition pressure. At the transition from Te-VI to Te-VII the volume change was not detected.
On the other hand, sub-peaks labelled by the star exhibit remarkable decrease in the relative intensity. Figure 2 illustrates the pressure evolution of the relative intensity of main peaks and sub-peaks in the 2θ region between 9° and 14°. The 2θ-values of the x axis were arbitrarily shifted so that the main fcc-111 peaks were centered on 2θ = 0°. The intensity of sub-peaks decreases with increasing pressure. Figure 3(a) shows the pressure dependence of the ratio I(sub)/I(main) of integrated intensities between main peak assigned to the fcc-111 reflection and each sub-peak assigned by symbols +1, +2 and +3 in figure 2. The intensity of sub-peaks decays with a similar tendency with pressure and these peaks seem to disappear at pressure about 250 GPa. From the results we propose that the structure of the new phase is a superlattice of fcc. The d-value ratios d(sub)/d(main) between the main peak assigned to the fcc-111 and sub-peaks are shown in figure 3(b). The relative position of the sub-peaks does not show remarkable change. Namely, the period of modulation of the fcc-superlattice is considered to be constant.

The pressure dependence of the atomic volume is depicted in figure 4, together with previous data [9]. The volume of Te-VI was calculated by assuming a superlattice of fcc. The bcc phase coexists with the new phase up to 110 GPa. From the dependence, the volume reduction (-ΔV) at the transition pressure around 100 GPa was estimated to be 0.15 Å³ which corresponds to 0.9% of the volume at the transition pressure. The result satisfies the pressure-volume relationship at a phase transition and supports our proposition, that is, the structure of Te-VI is a superlattice of fcc.

The dependence in figure 3 predicts that the sub-peaks disappear at pressure about 250 GPa. Namely, the new high-pressure phase (Te-VI) may transform to a complete fcc phase (Te-VII) of a cubic close-packed structure. In order to examine the prediction, x-ray diffraction experiments using diamond anvils with the culet diameter of 25 mm were carried out at pressure up to 330 GPa. As the result, the sub-peaks were gradually merged in the background with pressure and at 255 GPa disappeared completely. The representative diffraction pattern of the fcc phase (Te-VII) is shown in figure 1, compared with that of Te-VI. The pattern at 255 GPa was well indexed as the fcc lattice with a lattice parameter of a = 3.7573(8) Å though the Γ-plot of observed d-values indicated a tendency of slight uniaxial stress effect [19].

Upon further compression, the diffraction patterns did not show any sign of the phase transition up to the present maximum pressure of 330 GPa. Obtained pressure-volume data are also plotted in figure 4. From the compression curve, the volume change at the transition from Te-VI to Te-VII was not detected. Therefore, the transition would be of the second order. At 330 GPa, the volume contracts to 12.46 Å³ which corresponds to 36.5% of V₀ =34.01(1) Å³ at ambient pressure. From these pressure-volume data, estimated bulk modulus K₀ and its pressure derivative K₀' for Te-VI and Te-VII by a least square fitting to the Vinet formula [20] with V₀* = 23.95(14) Å³ of the virtual volume at 0 GPa were 121(3) GPa and 4.54(8), respectively. The K₀, K₀' and V₀* for Te-V were also estimated to be 38.8(4) GPa, 6.01(6) and 28.95(7) Å³, respectively.

4. Conclusion
In this study, we searched for the structure phase transition of Te in the ultra-high pressure range up to 330 GPa. As the result, the phase transition from the bcc (Te-V) to a new high-pressure phase (Te-VI) was found at 100 GPa. The structure of the new phase was suggested to be a superlattice of the fcc structure. And further, Te-VI transformed to the fcc phase (Te-VII) at 250 GPa completely with disappearance of satellite peaks. Since for group 16 elements, it has been considered that the structure of the highest pressure phase is bcc, the present results provided new information about the high-pressure behaviour of these elements. However, there is no study on theoretical calculation about the post-bcc phase transition up to now. On the elucidation of the superlattice structure of Te-VI, theoretical study on the structural stability of tellurium in the range of ultra-high pressure up to 300GPa is required. At present, the structure analysis of Te-VI is in progress.
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