Optical absorption spectrum of trigonal selenium under high pressure

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Abstract. Optical absorption spectra of trigonal selenium have been measured at pressure up to 5 GPa using a diamond anvil cell with two kinds of pressure-transmitting media, that is, a mixture of methanol, ethanol and water, and a potassium bromide, to confirm no effects of them. With increasing pressure, the absorption edge shifts to a lower energy and the pressure coefficients of the absorption edge at atmospheric pressure obtained by using both pressure-transmitting media agree with each other. At high pressure, as more clearly observed in the spectra obtained by using a potassium bromide, the edge shifts to a lower energy become moderate near 3 GPa, where an abrupt decrease in intramolecular covalent bond length was observed. This result must be related to the transition of the electronic band structure in trigonal selenium at approximately 3 GPa.

1. Introduction
Selenium at ambient condition has trigonal form, which consists of $3_1$ helix chain molecules. With increasing pressure, the selenium changes from the molecular crystal, through several high-pressure phases, to bcc metallic phase [1]. In the process of this pressure-induced molecular dissociation, inter- and intramolecular bonding characters change with pressure.

Recently, a new phase transition of trigonal selenium has been observed at 3 GPa, where an intramolecular covalent bond length decreases abruptly by about 0.8 %, while a volume change is negligible [2]. Since the interatomic distance is related closely to the distribution of the outermost electrons and the ion cores, this isostructural phase transition is expected to cause an anomalous change in the energy band structure of the trigonal selenium at 3 GPa.

In order to obtain the information about the relationship between the interatomic distance and the electronic band structure, we have studied the effect of pressure on the optical absorption spectrum of trigonal selenium by using diamond anvil techniques.

2. Experimental
Two kinds of trigonal selenium were prepared by growing from the vapour phase and by annealing of an amorphous form with 99.999 % purity in high vacuum at 175 °C for two hours. These were then mechanical lapped and polished into the shapes of plane-parallel plates and later broken into small pieces (about $200 \times 170 \times 15 \mu m^3$). A diamond anvil cell was used for high-pressure experiment with a metal gasket, Inconel-750X. The pressure was determined by the ruby fluorescence method.
Two sets of absorption spectra were obtained up to 5 GPa at room temperature. One was measured for the polycrystalline form with a mixture of methanol: ethanol: water in the ratio 16:3:1 (MEW) as pressure-transmitting medium, and another was measured for the single crystalline form with a potassium bromide. Unpolarized white light from a tungsten halogen lamp was used as a light source. Two kinds of spectrometers, C7473-36 (Hamamatsu) and C8147-34 (Hamamatsu) were used in the range from 1.31 to 2.5 eV and in the range from 0.75 to 1.38 eV, respectively. The optical density, –\log(I/I_0), was measured by the sample-in-sample-out method, where I and I_0 are the intensity of transmitted light passing through the sample and that passing through the only pressure-transmitting medium near the sample, respectively.

3. Results and discussion
Figure 1 shows the optical absorption spectra of polycrystalline and single crystalline trigonal selenium measured with MEW (left) and potassium bromide (right), respectively, at various pressures. Although at P < 1.0 GPa and P > 3.0 GPa, one spectrometer could measure the spectra in the absorption edge region, in the middle pressure region 1.0 GPa < P < 3.0 GPa, the spectra with the edges of approximately 1.35 eV were obtained by combining those measured using both spectrometers. The agreement of two spectra measured by using two kinds of spectrometers in the range from 1.31 eV to 1.38 eV is good.

Trigonal selenium has anisotropy in optical absorption. However, significant difference is not observed in the absorption spectra measured for polycrystalline and single crystalline forms at atmospheric pressure using the unpolarized light as the light source. In addition, the effect of pressure on the fundamental absorption edge is not affected by the difference of those crystalline forms in most semiconductors. Therefore, the profiles of the spectra in figure 1 are considered to depend on mainly not the crystalline forms but the pressure transmitting media whose hydrostaticity are different.

![Figure 1](image)

**Figure 1.** Optical absorption spectrum of trigonal selenium at various pressures. A mixture of methanol: ethanol: water in the ratio 16:3:1 (left) and potassium bromide (right) were used as pressure-transmitting medium, respectively.
At atmospheric pressure, a large increase is observed between 1.8 and 1.9 eV in the absorption spectrum. Trigonal selenium is known to be indirect transition semiconductor at atmospheric pressure, because phonon-assisted absorption of the indirect transitions was resolved clearly at low temperature [3]. However, as it is difficult to observe this phonon structure at room temperature, the fundamental absorption edge of trigonal selenium is estimated from the onset energy of the large absorption. Obtained band-gap energy of 1.8 eV at atmospheric pressure agrees well with previously reported value [3, 4].

With increasing pressure, the absorption spectrum becomes broad and continuously shifts to the lower energy region. This shows that the energy band gap becomes narrow with pressure. Figure 2 shows the shift of absorption edges with pressure. Filled circles and squares denote the absorption edges obtained from the absorption spectra measured with the MEW and the potassium bromide as pressure-transmitting medium, respectively. Open marks denote the data reported by Suchan et al. [5]. As is mentioned above, the different behavior of the absorption edge shift with pressure comes from not the difference in crystalline form but that in pressure transmitting medium. The pressure coefficients of the absorption edge at atmospheric pressure obtained from the spectra measured with MEW and potassium bromide are −0.25 eV/GPa and −0.22 eV/GPa, respectively. These coefficients agree well with each other despite of differences in pressure-transmitting media and crystalline forms. However, these values are larger than the values of −0.13 eV/GPa estimated from Suchan et al.’s data which were obtained by using Drickamer anvil type high pressure cell with sodium chloride as a pressure-transmitting medium [6]. The difference in the pressure coefficients of the absorption edge may be attributed to not only the difference in pressure-transmitting medium but also that in high pressure cell.

![Figure 2](image_url)

**Figure 2.** Shift of absorption edges with pressure. The solid lines represent the results of linear least-squares fits to the obtained data.

The pressure coefficients of the absorption edge obtained from the spectra measured with MEW and potassium bromide changes from −0.25 eV/GPa to −0.17 eV/GPa at 2.8 GPa, and from −0.22 eV/GPa to −0.05 eV/GPa at 3.5 GPa, respectively. Although the pressure coefficients of the
absorption edge and the pressures where the pressure coefficients change are different a little in two measurements with different crystalline forms and pressure-transmitting media, the absorption edge shift to low energy with pressure becomes moderate obviously near 3 GPa. This phenomenon is observed clearly in the absorption spectrum measured with potassium bromide and is observed near 4.5 GPa in the data of Suchan et al. Though the phase transition from sodium chloride structure to cesium chloride structure occurs at 1.7 GPa in potassium bromide, no change is observed in the shift of absorption edge around 1.7 GPa, showing that the potassium bromide as pressure-transmitting medium does not affect the change in pressure coefficients of absorption edge at 3.5 GPa.

The pressure where the pressure coefficient of absorption edge changes is in agreement with the phase transition pressure where the intramolecular covalent bond length decreases abruptly. In the band structure of selenium, valence and conduction bands are formed by lone-pair electron and antibonding states, respectively. With decreasing the covalent bond length, the splitting of these states increases, resulting in the band gap broadening. Therefore, the decreasing in covalent bond length near 3 GPa is consistent with that the absorption edge shift to a lower energy becomes moderate near 3 GPa. Moreover, previously calculated energy band structure of trigonal selenium at high pressure has predicted that the trigonal selenium changes near 3 GPa from indirect semiconductor to direct one such as tellurium, which has the same trigonal form at atmospheric pressure [7, 8]. The most recent energy band calculation [9] by using newly obtained structural parameter of trigonal selenium under high pressure [2] also shows that indirect semiconductor to direct one occurs at 2.3 GPa. Therefore, it is suggested that the change of pressure coefficient near 3 GPa is attributed to the change from selenium-like band structure to tellurium-like one and that the newly found isostructural phase transition in trigonal selenium near 3 GPa is related to this change in band structure. This shows that with increasing pressure, the selenium does not change continuously but changes discontinuously from selenium-like structure to tellurium-like one in the first place in the process from molecular crystal, through several high-pressure phases, to bcc metallic phase.

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