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Pressure-induced crystallization and phase transformation of amorphous selenium: Raman spectroscopy and x-ray diffraction studies

Kaifeng Yang¹, Qiliang Cui¹, Yuanyuan Hou¹, Bingbing Liu¹,
Qiang Zhou^{1,3}, Jingzhu Hu², Ho-Kwang Mao² and Guangtian Zou^{1,3}

¹ National Laboratory of Superhard Materials, Jilin University, Changchun 130012, People's Republic of China

² Geophysical Laboratory, Carnegie Institution of Washington, Washington, DC 20015, USA

E-mail: Zhouqiang@jlu.edu.cn and gtzou@jlu.edu.cn

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Abstract

High-pressure Raman spectroscopy studies have been carried out on amorphous Se (a-Se) at room temperature in a diamond anvil cell with an 830 nm exciting line. Raman evidence for the pressure-induced crystallization of a-Se and the coexistence of the unknown high-pressure phase with the hexagonal phase is presented for the first time. Further experimental proof of high-pressure angle-dispersive x-ray diffraction studies for a-Se indicates that the unknown high-pressure phase is also a mixture phase of the tetragonal $I4_1/acd$ and Se IV structure. Our Raman and x-ray diffraction results suggest that hexagonal Se I undergoes a direct transition to triclinic Se III at about 19 GPa, which is in good agreement with the theoretical prediction.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The group VIA element Se has several allotropic modifications under ambient conditions. These modifications are essentially molecular solids. Among them, hexagonal Se (h-Se) is the most stable variety; it consists of trigonal spiral chain molecules. Amorphous Se (a-Se) is also a stable modification with chain structures and/or Se₈ rings under ambient conditions [1]. So far, a-Se has attracted special attention in view of its unique pressure-induced phase transitions [2, 3], complex crystal structures under high pressure [4], phenomenon of photo-crystallization [5] and photo-induced volume change [6]. Although the pressure-induced crystallization of a-Se has been observed at around 11 GPa, the crystal structure of

³ Authors to whom any correspondence should be addressed.

the high-pressure phase is still a matter of great controversy [4, 7]. In the case of h-Se, many high-pressure x-ray diffraction (XRD) experiments have been performed [8–11]. Five phase transitions have been reported when the pressure is increased up to 150 GPa [11]: from hexagonal (Se I) to an intermediate (Se II) phase at 14 GPa, to a base-centered monoclinic (Se III) phase at 23 GPa, to a base-centered orthorhombic (Se IV) phase at 28 GPa, to a primitive rhombohedral (Se V) phase at 60 GPa, and to a body-centered cubic (Se VI) phase at 140 GPa. In recent years, with the development of high-pressure techniques, many new polymorphs of both Se and Te have been obtained under high pressure, such as the complex incommensurate monoclinic Se IV (Te III) [12], the body-centered triclinic Se III (Te II) [13] and the square chain structure Se VII (Se II') [14, 15]. The phase transition from Se IV to Se V has been predicted to occur at 82 GPa [16] and then it was confirmed to be true in a subsequent investigation [17]. These new phenomena make the studies of the high-pressure behavior of Se and Te more interesting. Many theoretical studies have also been done on the high-pressure behavior of Se [18, 19]. A total energy calculation for high-pressure selenium has shown the instability of the proposed Se II [19]. The authors [19] predicted a direct phase transition from hexagonal Se I to triclinic Se III at 21.5 GPa. Up to now there is still not sufficient experimental evidence which is in good agreement with the reported sequence of transitions because of the complexity of the high-pressure polymorphism of Se. Much work still needs to be done to resolve the controversies between experimental and theoretical results.

Raman spectroscopy permits the identification of a substance from the characteristic wavelengths of the spectral patterns, and it provides useful information about the structural and thermodynamic properties of materials. Development of high-resolution and sensitive spectroscopic techniques makes it possible to perform high-pressure Raman spectroscopy in a diamond anvil cell [20, 21]. So far there has only been one *in situ* high-pressure Raman experiment that has been done on a-Se [7] to our knowledge. In that study, the 488 nm exciting line was used, but the effect of photo-crystallization was not taken into account, so we cannot obtain more high-pressure Raman information about a-Se from their Raman data, such as the differences between the Raman pattern before and after crystallization. The effect of photo-crystallization can be avoided successfully by using a near-infrared exciting laser (830 nm), so here we present Raman evidence for the pressure-induced crystallization of a-Se and the coexistence of the unknown high-pressure phase with the hexagonal phase by high-pressure Raman studies for the first time. High-pressure angle-dispersive XRD studies have also been carried out on a-Se to determine its complex polymorphism under high pressure. Many other important and interesting results are also reported in this paper.

2. Experimental details

High-purity (99.999%) a-Se was obtained from the Aldrich Chemical Company. Samples were loaded into diamond anvil cells using 16:3:1 methanol:ethanol:water as a pressure-transmitting medium and a small ruby sphere for pressure measurement.

In situ high-pressure Raman spectra of a-Se were measured on a Renishaw inVia Raman microscope in the back-scattering geometry mode with a resolution of 2 cm^{-1} , using a CCD detector to collect the Raman scattered light. Data were acquired using computerized data-acquisition systems. To produce the Raman spectrum in high-pressure experiments the 830 nm line of a semiconductor laser was used at low incident power levels of 1 mW; the actual power on the sample should be much lower than this. The spectra were recorded at room temperature. In order to confirm the phenomenon of photo-crystallization of a-Se, the 514 nm exciting line of an argon-ion laser was also used to obtain the room-temperature Raman spectra of a-Se.

Powder x-ray-diffraction experiments at high pressure and room temperature were carried out using the angle-dispersive method with a diamond anvil cell and an image-plate detector.

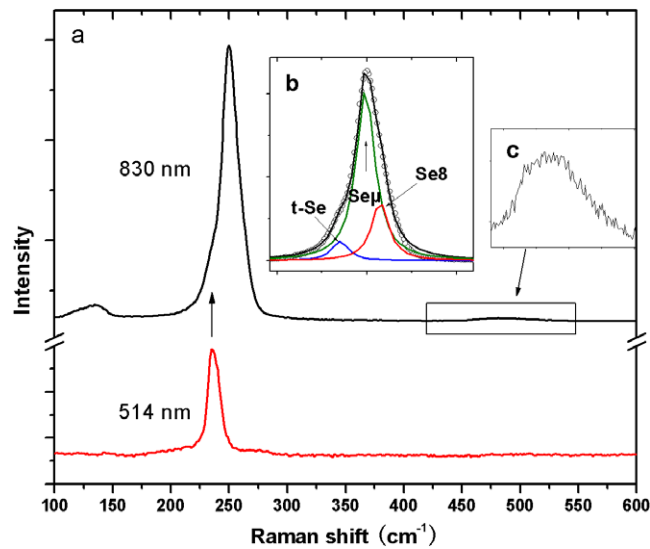


Figure 1. Raman spectra of a-Se measured at ambient conditions. The upper and lower Raman patterns shown in (a) were recorded with 830 and 514 nm lasers, respectively. The inset pattern (b) shows enlarged views of the broad band of a-Se, and an example for the peak fit for the broad band using three Lorentz peaks is shown. The inset pattern (c) shows enlarged views of the second-order Raman scattering of a-Se.

Powder-diffraction data were collected on beam line x17c at the National Synchrotron Light Source (NSLS), Brookhaven Laboratory. The x-ray beam was monochromatized to a wavelength of 0.4066 Å and was collimated to a 20 μm square. The two-dimensional diffraction images were integrated using FIT2D to give standard diffraction profiles.

3. Results and discussion

3.1. Resonance Raman scattering of a-Se before crystallization

The upper and lower Raman patterns shown in figure 1(a) were recorded with 830 nm and 514 nm lasers, respectively. The spectra were recorded with a very low laser power to avoid sample heating. In the upper pattern we can see a broad band component with a dominant peak at ~ 250 cm^{-1} and two shoulders at ~ 235 and ~ 258 cm^{-1} (shown in figure 1(b)). It was suggested that the dominant peak at ~ 250 cm^{-1} could be attributed to the intrachain bond-stretching vibrational mode of the disordered Se_μ chains, while the low-intensity shoulder located at ~ 258 cm^{-1} is attributed to the intraring bond-stretching vibrational mode of Se_8 species, and the 235 cm^{-1} mode is assigned to the intrachain bond-stretching vibrational mode of the chains disposed at a t-Se-like conformation [22]. In the lower pattern, it can be seen that there is only one peak centered at ~ 237 cm^{-1} (A_1 mode of h-Se), but not the characteristic peak of a-Se at ~ 250 cm^{-1} , although the lowest laser power was used. This behavior is due to the effect of photo-induced crystallization [5]. We noticed that the crystallization also occurred when the high incident laser power of a 830 nm laser was used, and this is due to the temperature-induced crystallization effect [2]. So we must use low incident laser power to avoid both sample heating and crystallization. As a result, the effect of photo-crystallization can be avoided successfully by using the 830 nm exciting line with very low incident laser power.

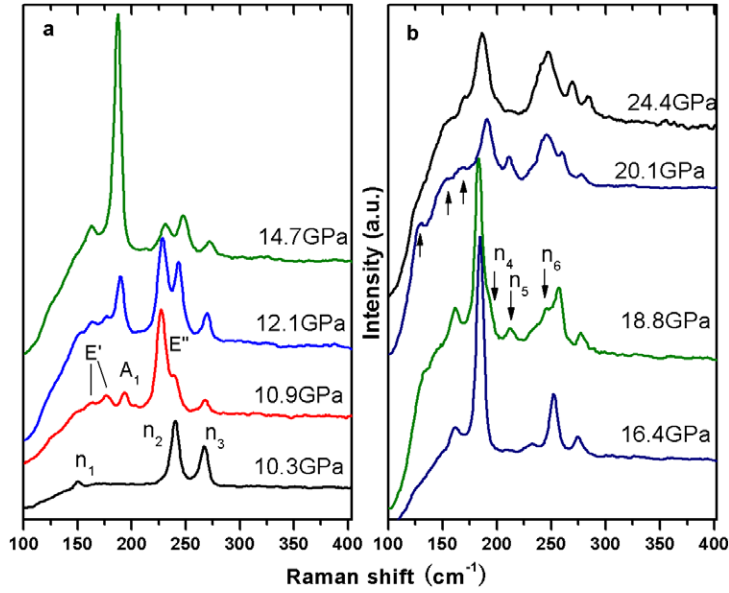


Figure 2. Representative Raman spectra of a-Se at different pressures up to 24.4 GPa: (a) in a lower-pressure region and (b) in a higher-pressure region. New features observed at 10.3 GPa and after 18.8 GPa which are attributed to the new phases are indicated by n_1 – n_6 . The pressure is shown above each trace.

Generally, the intensity of a Raman peak I_R and the wavelength of the exciting laser λ satisfy the relationship

$$I_R \propto \frac{1}{\lambda^4}.$$

That is, the Raman intensity I_R will decrease with the increase of λ . In contrast, we notice that the intensity of the Raman spectrum recorded with the 830 nm line is much stronger than that with the 514 nm line. To explain this abnormal change, we take into account the resonant Raman scattering effect, which is associated with the absorption band around 1.5 eV reported by Benkhedir *et al* [23]. With increasing pressure, the broad band is still the main component of the whole Raman spectra of a-Se before crystallization. It is interesting that the intensity of the broad band increases at first and then decreases steeply with increasing pressure, although all the spectra were taken under identical conditions. We consider that the abnormal behavior of the Raman intensity for the broad band is due to the pressure-induced resonance Raman scattering effect. Detailed discussions will be published elsewhere.

3.2. Raman evidence for pressure-induced crystallization and phase transition in a-Se

The use of the 830 nm line makes it possible to avoid the photo-crystallization of a-Se, so we can verify the pressure-induced crystallization effect by the Raman scattering method for the first time. No such investigations have yet been performed to our knowledge. The pressure-induced crystallization occurs following with the disappearance of the broad band of a-Se and the appearance of several new Raman modes at pressures between 10 and 11 GPa, as shown in figure 2. When the pressure increases to 10.3 GPa, three new peaks, centered at about 150, 240 and 267 cm^{-1} , appear (n_1 – n_3). At 10.9 GPa, another three new peaks, at about 176, 193, and 228 cm^{-1} , which correspond to the E' , A_1 and E'' modes of the hexagonal phase, are clearly observable. Meanwhile, peaks n_2 and n_3 are still observable at 10.9 GPa, whereas peak

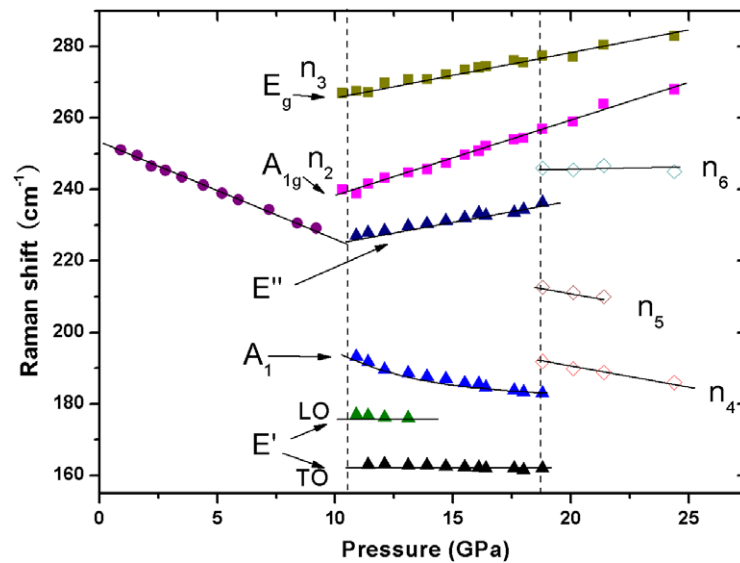


Figure 3. Pressure dependence of Raman peaks of a-Se to 24.4 GPa. The dashed lines mark the phase transition pressures at ~ 10.3 and ~ 19 GPa. Solid lines are guides for the eye. Some peaks that we have observed in the Raman pattern are not included in the figure because of their weakness.

n_1 is undetectable because of its weakness. We believe that the peaks n_1 – n_3 are attributed to an unknown high-pressure phase of a-Se. So the crystal structure after pressure-induced crystallization is not a single hexagonal phase: it should be a mixture of both the hexagonal phase and the unknown high-pressure phase. This assumption is consistent with the results of Akahama *et al* [4], but different from the results of Bandyopadhyay *et al* [7], in which a pure hexagonal phase was obtained. The wavenumber of peaks n_2 and n_3 increased linearly with increasing pressure, as shown in figure 3. This indicates that the unknown high-pressure phase is stable up to at least 24.4 GPa.

With further compression, there are only a few changes in the overall Raman pattern, and no phase transition was observed around 14 GPa, which has been widely reported in a-Se and h-Se [7, 8, 10, 11]. The pressure evolution for the Raman modes in h-Se is similar to that found in other Raman experiments on h-Se [24–26]. However, there are large differences between our results and others in the relative intensity of the A_1 and E'' modes. We attribute the differences to the different exciting lines that we used. Also, the resonance effect should be taken into account. Remarkable changes are observed at pressures between 18.8 and 20.1 GPa. At 18.8 GPa, we observe three new peaks (n_4 – n_6) coexisting with the original peaks. At 20.1 GPa, another three new weak peaks appeared, followed by the sudden disappearance of the strongest A_1 peak and other peaks due to the hexagonal phase. These are all strong Raman evidence for a phase transition that occurs at about 19 GPa. The coexistence of both phases indicates that the phase transition is of first order. Similar behavior in this pressure region has also been observed in high-pressure Raman studies on h-Se and nanocrystalline Se [26, 27]. However, they [26, 27] did not observe peak n_5 and coexistence of both phases, which can be clearly seen in our Raman pattern. There are still no authentic explanations for the appearance of these new peaks. We attribute them to a phase transition from a spiral chain structure to a puckered structure. That so many new peaks have appeared in the pattern indicates that the new phase should have a lower symmetry than hexagonal Se I. High-pressure XRD studies have been performed to help us determine the crystal structure of a-Se at high pressures (see section 3.3).

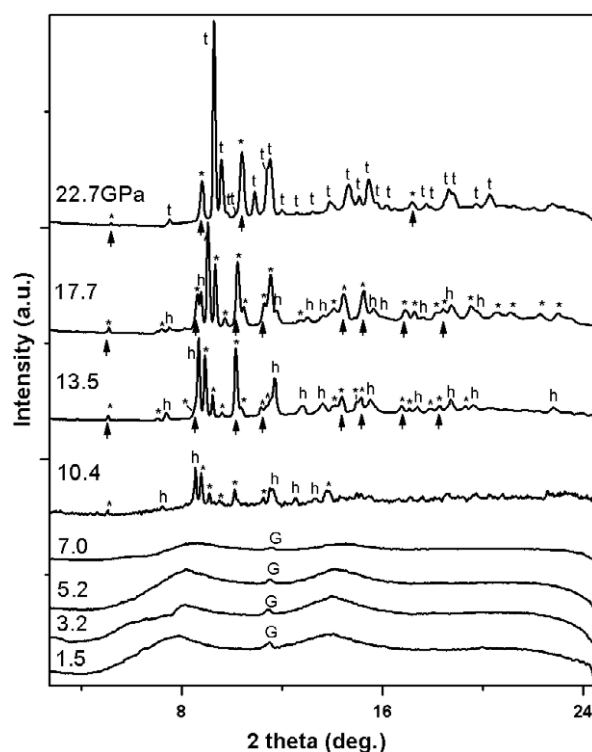


Figure 4. Pressure change in the diffraction pattern starting with a-Se obtained with x-rays with $\lambda = 0.4066 \text{ \AA}$. The peaks labeled (*), (h), and (t) correspond to the unknown high-pressure phase [4], hexagonal Se I, and the triclinic phase [13], respectively. Peaks labeled (G) come from a metal gasket. The arrows indicate peaks due to the tetragonal $I4_1/acd$ structure. The pressure is shown above each trace.

In figure 3 the pressure dependence of the Raman shifts is shown. Changes and abrupt shifts in the Raman peaks occur in two places due to pressure-induced crystallization and the phase transition, respectively. These are marked by dashed lines in the figures. The corresponding transition pressures are ~ 10.3 and ~ 19 GPa. There is a significant mode softening of the broad band, the A_1 peak, the n_4 and n_5 peaks with pressure. The mode softening of the A_1 mode is consistent with other experimental results for h-Se in the same pressure region [24–26]. The softening of the A_1 mode is mainly due to the strengthening interchain bonds and weakened bonds within the chains. We think that this explanation is also appropriate for the softening of the broad band, because their vibration behaviors are very similar. We do not understand the softening behavior of peaks n_4 and n_5 at the moment. The fact that all of these modes soften reveals that the high-pressure behavior of a-Se is very complicated. To further understand this behavior, it is necessary to perform high-pressure Raman calculations for the complex high-pressure phases of Se.

3.3. The determination of the high-pressure polymorphism of a-Se by XRD studies

Figure 4 shows a series of diffraction patterns of a-Se at different pressures. a-Se exhibits a typical halo pattern at pressures lower than 10 GPa. All halos move to high angles with increasing pressure. At 10.4 GPa, many diffraction peaks suddenly appeared in the pattern:

Table 1. *In situ* x-ray diffraction data of hexagonal Se I at 13.5 GPa, hexagonal Se I at 17.7 GPa, and triclinic Se III at 22.7 GPa and at room temperature.

13.5 GPa			17.7 GPa			22.7 GPa						
d (obs)	(hkl)	d (cal) ^a	d (obs) ^d	d (obs)	(hkl)	(cal) ^b	d (obs)	(hkl)	d (cal) ^c	d (obs)	(hkl)	d (cal) ^c
3.156	(100)	3.154	3.175	3.097	(100)	3.097	3.101	(110)	3.095	1.594	(200)	1.606
2.690	(101)	2.689	2.686	2.659	(101)	2.652	2.509	($\bar{1}\bar{3}0$)	2.513	1.550	($2\bar{3}\bar{1}$)	1.553
1.996	(102)	1.994	1.993	1.980	(102)	1.976	2.432	($10\bar{1}$)	2.438	1.511	($23\bar{1}$)	1.513
1.824	(110)	1.821	1.822	1.792	(110)	1.788	2.374	(011)	2.379	1.480	(141)	1.482
1.714	(003)	1.715	1.714	1.711	(003)	1.711	2.301	($1\bar{2}\bar{1}$)	2.303	1.445	(071)	1.445
1.504	(201)	1.507	1.505	1.493	(103)	1.497	2.138	(031)	2.142	1.318	($1\bar{1}\bar{2}$)	1.322
1.344	(202)	1.344	1.350	1.456	(112)	1.467	2.046	($03\bar{1}$)	2.048	1.306	(161)	1.306
1.249	(113)	1.248	1.247	1.328	(202)	1.326	2.025	(060)	2.011	1.255	($2\bar{6}0$)	1.256
1.191	(210)	1.191	1.187	1.247	(113)	1.236	1.944	(041)	1.951	1.243	($1\bar{9}0$)	1.238
1.027	($30\bar{1}$)	1.030		1.184	(104)	1.185	1.851	($04\bar{1}$)	1.857	1.185	($22\bar{2}$)	1.183
							1.764	(051)	1.765	1.154	($30\bar{1}$)	1.152
							1.674	(101)	1.670			

^a Calculated on the basis of a hexagonal unit cell with $a = 3.642 \text{ \AA}$, $c = 5.147 \text{ \AA}$.

^b Calculated on the basis of a hexagonal unit cell with $a = 3.576 \text{ \AA}$, $c = 5.133 \text{ \AA}$.

^c Calculated on the basis of a triclinic unit cell with $a = 3.4648 \text{ \AA}$, $b = 12.0875 \text{ \AA}$, $c = 2.6481 \text{ \AA}$, $\alpha = 86.805^\circ$, $\beta = 112.021^\circ$ and $\gamma = 91.344^\circ$.

^d Data from reference [8].

this is evidence of pressure-induced crystallization. The crystal structure is determined to be a mixture phase of the hexagonal phase and the unknown high-pressure phase mentioned above. A similar result has also been reported by Akahama *et al* [4], but the crystallization pressure is 12 GPa, which is higher than ours which is about 10.4 GPa. The coexistence was still maintained at 22.7 GPa. The observed diffraction peaks of the hexagonal phase at 13.5 and 17.7 GPa were consistent with our calculation results and the results of McCann and Cartz [8] (shown in table 1). With increasing pressure, at 22.7 GPa, hexagonal Se transformed to a body-centered triclinic phase. This triclinic structure has a nonstandard $I\bar{1}$ space group, with lattice parameters $a = 3.4648(1) \text{ \AA}$, $b = 12.0875(5) \text{ \AA}$, $c = 2.6481(1) \text{ \AA}$, $\alpha = 86.805(5)^\circ$, $\beta = 112.021(5)^\circ$ and $\gamma = 91.344(8)^\circ$ at 25.6 GPa [13]. The observed diffraction peaks of the triclinic phase were well assigned by the lattice they proposed (shown in table 1). In summary, we have determined the high-pressure structure of a-Se to be triclinic for the first time.

The diffraction peaks of the unknown high-pressure phase at 13.5 and 17.7 GPa are in good agreement with the high-pressure diffraction patterns of α -monoclinic Se₈ at 13.5 and 18.4 GPa, respectively [4]. The crystal structure of the high-pressure phase of α -monoclinic Se₈ was not determined at that time. Recent studies have indicated that all these patterns could be fitted by the tetragonal $I4_1/acd$ and Se IV structures [14]. A special feature of this tetragonal $I4_1/acd$ structure is the coexistence of both the 4₁-screw and the 4₃-screw chains, unlike hexagonal Se, which only has a 3₁-screw or 3₂-screw chain. A similar square chain structure was also found for a high-pressure and high-temperature phase of hexagonal Se (for example, at 20 GPa and 450 K) [15]. Some of the unassigned peaks can be well fitted by this tetragonal $I4_1/acd$ structure (shown in table 2). At pressures of 13.5 and 17.7 GPa, the whole pattern can be fitted by the hexagonal Se I, the tetragonal $I4_1/acd$ and Se IV structures. However, at 22.7 GPa, the whole pattern can only be fitted by the triclinic Se III and the tetragonal $I4_1/acd$ structures. In view of our Raman results, we suggest that the three new peaks we have found in the unknown high-pressure phase are due to the tetragonal $I4_1/acd$ structure of Se. Since the mode assignment for this structure has been reported by Degtyareva *et al* [26], we can assign

Table 2. *In situ* x-ray diffraction data of tetragonal Se II' at 13.5 GPa, 17.7 GPa and 22.7 GPa.

13.5 GPa			17.7 GPa			22.7 GPa		
<i>d</i> (obs)	(<i>hkl</i>)	<i>d</i> (cal) ^a	<i>d</i> (obs)	(<i>hkl</i>)	<i>d</i> (cal) ^b	<i>d</i> (obs)	(<i>hkl</i>)	<i>d</i> (cal) ^c
4.597	(200)	4.592	4.565	(200)	4.558	4.508	(200)	4.486
2.731	(211)	2.732	2.705	(211)	2.705	2.648	(211)	2.648
2.296	(400)	2.296	2.279	(400)	2.279	2.243	(400)	2.243
2.089	(321)	2.090	2.066	(321)	2.072	1.360	(611)	1.361
1.625	(440)	1.623	1.615	(440)	1.623			
1.543	(521)	1.546	1.533	(521)	1.533			
1.394	(611)	1.396	1.382	(611)	1.384			
1.281	(631)	1.282	1.269	(631)	1.272			
			1.138	(800)	1.139			
			1.109	(651)	1.111			
			1.052	(712)	1.050			
			1.019	(840)	1.019			

^a Calculated on the basis of a tetragonal unit cell with $a = 9.184 \text{ \AA}$, $c = 3.658 \text{ \AA}$.

^b Calculated on the basis of a tetragonal unit cell with $a = 9.116 \text{ \AA}$, $c = 3.616 \text{ \AA}$.

^c Calculated on the basis of a tetragonal unit cell with $a = 8.972 \text{ \AA}$, $c = 3.524 \text{ \AA}$.

these peaks (n_1, n_2, n_3) to E_g , A_{1g} and E_g modes, respectively. The pressure evolution of these peaks is also consistent with their results.

A total-energy calculation for high-pressure selenium reported the instability of the proposed Se II and predicted that there would be a direct phase transition from hexagonal Se I to triclinic Se III at 21.5 GPa [19]. Our high-pressure Raman study on a-Se indeed indicates that the first phase transition would occur at 19 GPa rather than 14 GPa. Considering the coexistence for both the new and old peaks at 18.8 GPa, the phase transition should be of first order. We think that the huge changes in the Raman pattern are simply related to the transition from the spiral chain structure to a puckered structure. So the reported first phase transition that should occur at 14 GPa may not be correct, according to our Raman results. The high-pressure phase of a-Se is determined to be body-centered triclinic according to our XRD results. So for a-Se, the phase transition at about 19 GPa may simply be related to the direct transition from hexagonal Se I to triclinic Se III.

4. Conclusions

To summarize, high-pressure Raman spectroscopy and angle-dispersive x-ray diffraction studies on a-Se are reported. We have avoided the effect of photo-crystallization of a-Se successfully by using the 830 nm line with very low incident laser power. The use of this near-infrared laser is very important in understanding the complex high-pressure behavior of a-Se. Furthermore, the pressure-induced crystallization of a-Se and the coexistence of the unknown high-pressure phase with the hexagonal phase are shown for the first time by means of Raman spectroscopy. Then the unknown high-pressure phase is confirmed to be a mixture phase of tetragonal $I4_1/acd$ and Se IV structures, according to our XRD results. The complex triclinic structure Se III is also determined to be the high-pressure phase of a-Se for the first time. We suggest that there may be a direct transition from hexagonal Se I to triclinic Se III that should occur at ~ 19 GPa, which is consistent with the theoretical prediction [19]. Further experimental and theoretical investigations need to be done to give us a deeper understanding of the disagreements between the results of high-pressure Raman and XRD studies on h-Se.

Acknowledgments

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