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Pressure induced structural transitions in nanocrystalline grained selenium

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Abstract

Using diamond anvil cell technique, energy-dispersive X-ray diffraction and Raman spectroscopy were employed to study pressure induced phase transitions in nanocrystalline selenium up to 30 GPa. A complex phase transition behavior was observed, with lower transition pressure and more phase transitions than in conventional coarse-grained Se. This is considered a new kind of pressure induced phase transition behavior for a nanocrystalline material. © 2002 Elsevier Science B.V. All rights reserved.

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In recent years, the structural stability of nanocrystalline materials has drawn increasing attention from a fundamental viewpoint. Studies of size dependence of high-pressure phase transitions can improve our understanding of the stable state, and give new insight into the dynamics of solid–solid transformations [1–10]. However, in previous studies only single-phase transitions in those nanocrystalline systems have been investigated. It would be interesting to study systems with more than one phase transition under pressure. In this paper, phase transitions in nanocrystalline selenium (nc-Se) is reported.

The group-VI element Se, whose most stable form under ambient conditions is hexagonal with a spiral chain structure, has a sequence of phase transitions under pressure corresponding to a change towards higher symmetry. Thus, Se transforms from a chainlike structure to a puckered-layered structure, then to a higher-symmetry layered structure, and finally to a cubic structure accompanied by a systematic increase in the coordination number [11–18]. However, the behavior under high pressure for crystalline Se with small grain size down to nanometer is still unknown.

The nc-Se sample with 99.999% purity was synthesized by completely crystallizing a melt-quenched amorphous Se solid [19]. The mean grain size was 13 nm. The sample was placed into a hole of a T301 stainless steel gasket in a Mao–Bell

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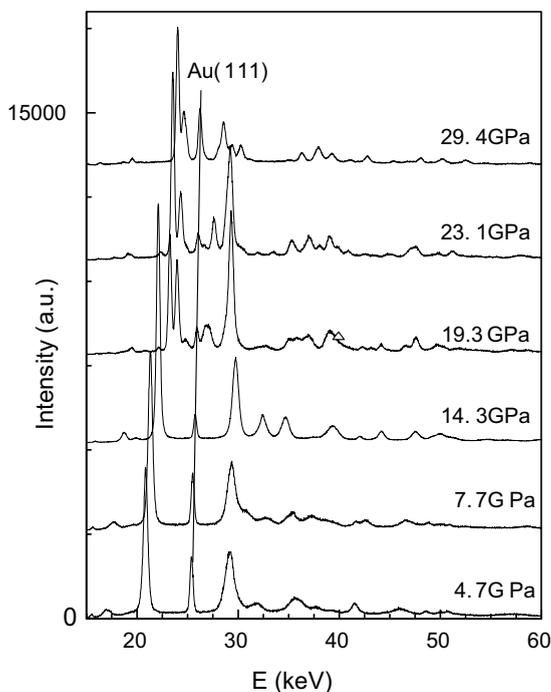


Fig. 1. Typical EDXD patterns of nc-Se at various pressures.

type diamond anvil cell equipment. Energy-dispersive X-ray diffraction (EDXD) spectra of nc-Se were obtained at beamline X17C of the Brookhaven National Synchrotron Source. Au powder was used as a pressure marker, while a Ge solid state detector was fixed at $2\theta = 12^\circ$ to collect the diffraction data. Figs. 1 and 2 show the typical EDXD patterns of nc-Se at various pressures, and the pressure dependence of the d values of the diffraction peaks in EDXD spectra, respectively. It is evident that five high-pressure structural transitions exist. The onset of the first phase transition takes place at a pressure of 5.6 GPa from the hexagonal phase to an unknown structure nc-Se (II). Drastic changes in the d values indicate phase transitions at 14.0, 15.7, 21.3 and 25.7 GPa. Bulk selenium is known to transform to monoclinic (I), monoclinic (II), orthorhombic, rhombohedral, and cubic (BCC) structures at 14, 23, 28, 60, and 140 GPa, respectively [13]. The nc-Se in the present work has more high pressure phases than bulk Se within the 30 GPa range.

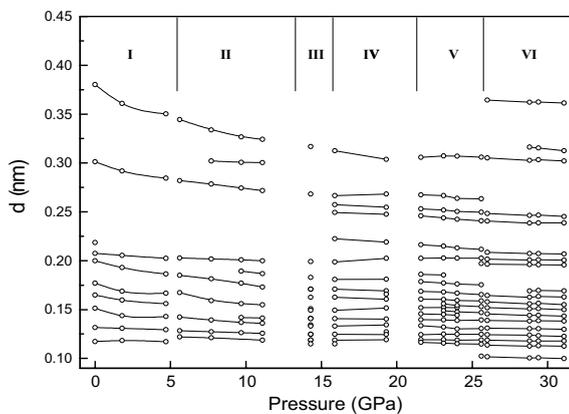


Fig. 2. Pressure dependence of the d values in nc-Se.

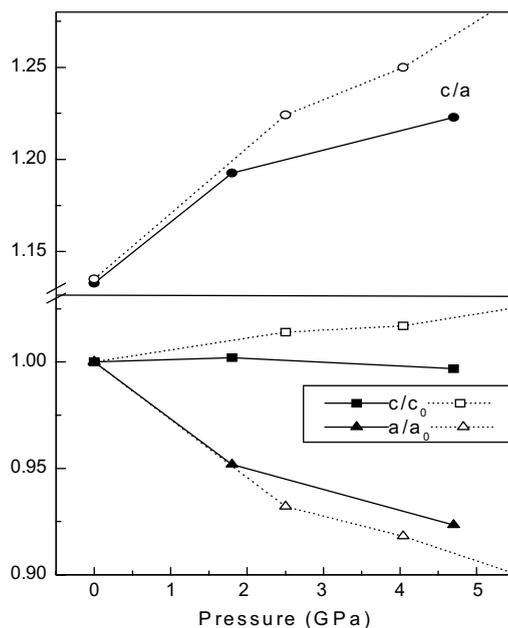


Fig. 3. The changes of lattice parameter a , c and the c/a ratio of nc-Se (I) phase with pressure (solid line). Dashed curves represent the results from Ref. [16] for bulk Se.

Fig. 3 illustrates changes in the lattice parameter a , c as well as the c/a ratio of the nc-Se (I) phase with pressure. The results of bulk Se are also shown as a dashed line [16]. In the latter case, a decreases rapidly while c increases slowly with increasing pressure. The structural transformation in bulk Se occurs as the c/a ratio increases from

1.135 at ambient conditions to 1.417 at 14 GPa, where the helical chains in a hexagonal array transform to a puckered layer structure with a monoclinic unit cell. In the nc-Se case, however, the c/a ratio does not rise like bulk Se, but the phase transition takes place as the c/a ratio increases just beyond 1.223. As a result, nc-Se (II) phase should be different from the puckered layered type of monoclinic structure of bulk Se. The structures of nc-Se (II)–(VI) high pressure phases cannot be indexed as cubic, hexagonal, or tetragonal within reasonable limits of error. They remain unsolved due to their low symmetry and the limited number of diffraction peaks. It is possible that these high-pressure phases in nc-Se are distorted structures.

The fundamental vibration modes in Raman spectra of bulk Se have been identified [20,21]. We have used Raman spectroscopy to investigate the microstructural changes under pressure for nc-Se. The experimental arrangement was the same as in the EDXD experiments except that the pressure was measured by ruby fluorescence. Fig. 4 shows a

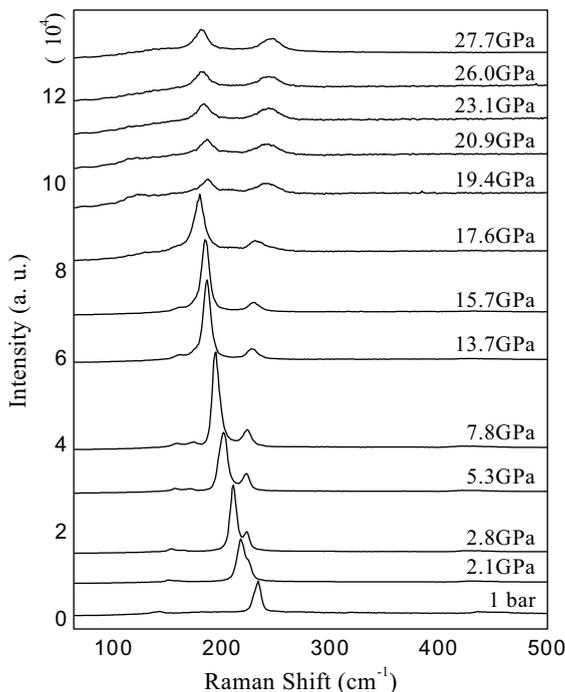


Fig. 4. Raman spectra of nc-Se recorded at room temperature with increasing pressure.

series of Raman spectra recorded at room temperature from ambient pressure to 27.7 GPa. The Raman modes of nc-Se differ very much from those of bulk Se [11]. Fig. 5 demonstrates the shifts of these Raman modes with pressure. The strong peak at 234 cm^{-1} which can be seen at 1 bar is the A1 mode produced by the helical chain-expansion type lattice vibration. With increasing pressure, the A1 mode shifts to lower frequency, indicating a pressure induced strengthening of the interchain bonds and a weakening of the intrachain bonds. This trend is in agreement with previous reports for bulk Se [11,16]. The strange change of the A1 mode around 15.7 GPa suggests a phase transition, which corresponds to an intermediate phase as nc-Se(III) in Fig. 2. The A1 mode keeps the softening trend, and disappears at 17.6 GPa, indicating a structural distortion of the helical chain. Finally, the chainlike microstructure in nc-Se entirely disjoins.

The E' mode is attributed to rotational motion about axes perpendicular to the helical axis, whereas the E'' mode is due to asymmetric breathing motions. The peaks of the E'' and A1 modes overlap at 1 bar, and then split with increasing pressure. A phase transition is clearly indicated around 5.4 GPa where the E'' mode has a minimum as a function of pressure while a weak

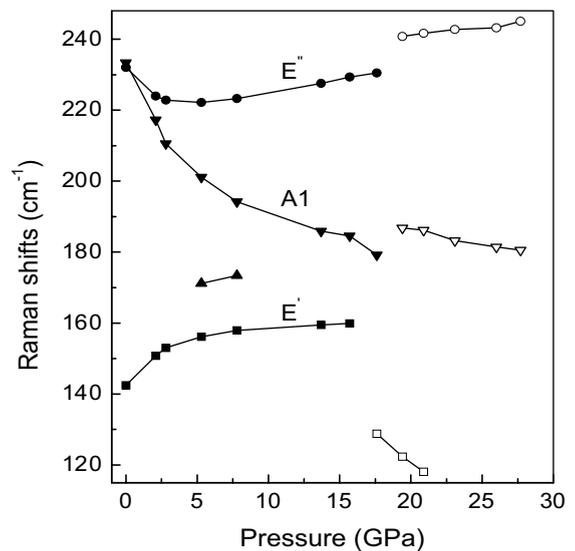


Fig. 5. Raman shifts as a function of pressure for nc-Se.

peak appears around 171 cm^{-1} (Fig. 5). Above 19.4 GPa, a new weak peak moves from 241 cm^{-1} to 245 cm^{-1} . This peak may be identified as the A1 mode of the Se_8 ring type microstructure [20], implying a structural change from the helical chain microstructure to a denser packed layer type microstructure. Another new weak peak, which appears in the range $187\text{--}180\text{ cm}^{-1}$ in the 19.4–27.7 GPa pressure range, cannot be explained by any known modes for Se. These new Raman peaks with a soft mode trend with pressure reveal that nc-Se undergoes a complicated structural evolution above 19.4 GPa, suggesting the possibility of an intermediate, lower-symmetry high pressure phase nc-Se (VI). In summary, the Raman shifts support the phase transitions shown in Fig. 2.

Previous studies of nanocrystals under high pressure show that the grain size effect on the structural stability can be of either sign with respect to the change of the transition pressure depending on the material system. Nanocrystals of CdSe, Si, PbS, CdS, ZnS and ZnO are stable at pressures higher than in bulk [1–8]. The increase in the transition pressure with decreasing grain size is interpreted in terms of higher surface energy of nanocrystals which impedes the formation of the high pressure phase, and therefore elevates the phase transition pressure. On the contrary, nanometer size materials of $\gamma\text{-Fe}_2\text{O}_3$ and TiO demonstrate lower phase transition pressure than for bulk materials [9,10]. This is explained by the larger volume change upon transition in the nanocrystals as compared with bulk materials.

It has been shown that nc-Se has a more complicated sequence of phase transitions than bulk Se up to 30 GPa. The pressure behavior of nc-Se is remarkably different from previous studies on nanocrystalline materials which change their phase transition pressures but keep the same transition sequence as the corresponding bulk materials. The nc-Se is grained while other studies in CdSe, Si, etc. are discrete. This difference may be one possible origin of the different behavior observed. However, quantitative X-ray diffraction and extended X-ray absorption fine structure (EXAFS) reveal that nc-Se has significant lattice distortion with a dilated unit-cell volume [19,22,23], implying that it exists in a metastable

structure. The intrinsic structural instability of nc-Se may be the main factor for the reduction in transition pressure, and the appearance of lower-symmetry high-pressure phases as compared to bulk Se. This is a new kind of high-pressure behavior in nanocrystalline materials, and it can give us new insight into the complicated stability of nanostructured materials under pressure.

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