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Study of $CuInTe_2$ Quantum Dots under Extreme Conditions

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Introduction

In recent years, Quantum Dot (QD) materials have attracted considerable interest due to their versatile properties and potential applications in electronics, biology, and optoelectronics, i.e. photovoltaic solar cell materials [1-2].

In 2000, Rincón *et al.* reported an extensive study of the bulk material of $CuInTe_2$ along with its comparison to its ordered defect compounds [3]. The chalcopyrite structure consists of eight atoms per unit cell. This means there are 24 vibrational modes expected for the tetragonal structure. Out of the 24 modes, 21 vibrational modes belong to optical modes, and the other 3 modes are acoustical modes. The irreducible representation of the optical modes at Γ point is given as,

$$\Gamma = 1A_1 + 2A_2 + 3B_1 + 3B_2 + 6E,$$

where *E* modes are twofold degenerate vibrations. Theoretically, other than A_2 modes, the optical modes at Γ point should be Raman-active [3].

At ambient conditions, both bulk and nanoparticle of $CuInTe_2$ exhibit chalcopyrite structure [3-5]. In bulk, the $CuInTe_2$ chalcopyrite structure is reported to undergo a pressure-induced phase transition to an orthorhombic (d-Cmcm) structure around 3.6 GPa (see Fig. 1) [5]. In QDs, Kosuga *et al* reported I-42d as the space group of $CuInTe_2$ [6]. The I-42d space group is translated to D_{2d} or V_d point group. At ambient conditions, the Raman peaks of $CuInTe_2$ nanocubes were observed at 121 cm^{-1} and 174 cm^{-1}. The 121 cm^{-1} and 174 cm^{-1} have been assigned as A_1 and E or B_2 (LO) modes, respectively. The A_1 mode of $CuInTe_2$ is due to of the motion of tellurium atoms with the idle Copper and Indium atoms [7].

This present project aims on investigation the phase transition properties of $CuInTe_2$ QDs under high pressure. We have used high pressure Raman Spectroscopy to map the variation of vibrational modes up to 7.7 GPa. A pressure-induced phase transition is observed around 2.9 GPa for the QDs in our experiment.

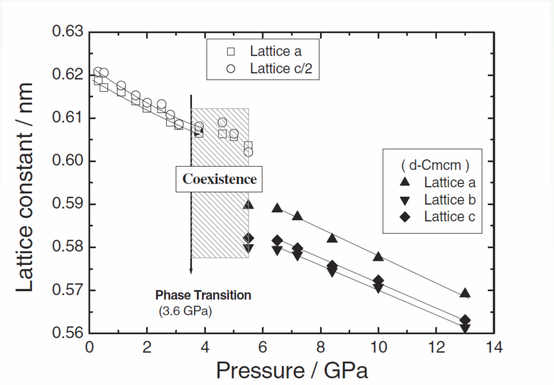

Figure 1. Pressure dependent of the lattice parameters of bulk $CuInTe_2$ materials [5].

Experimental Method

The experiment was accomplished using the optical facility of High Pressure Science and Engineering Center (HiPSEC), the Department of Physics and Astronomy at University of Las Vegas Nevada (UNLV) [8]. High purity (>99.0%) $CuInTe_2$ QDs in powder form was purchased from NNCrystal US Corporation and used without further purification. The sizes of the $CuInTe_2$ QDs are 3-8 nm. Powder X-Ray diffraction performed using Cu-Kα radiation from a Bruker D8 Discover XRD® equipment showed tetragonal structure for QDs which is in good agreement with literature.

A Symmetric-type Diamond Anvil Cell (DAC) with ~300 μm diamond culet diameter was used to confine the high purity $CuInTe_2$ QDs powder. The diamonds used were low fluorescence type II (preferable for Raman experiment usage) quality. A 250 μm thick stainless steel gasket was used as the container of $CuInTe_2$ QDs. The stainless steel gasket was pre-indented to ~60 μm in thickness, and a hole is drilled with ~100 μm in diameter using electric discharge machine (EDM). Then, the $CuInTe_2$ QDs along with a 10 μm ruby sphere were loaded to the DAC without any pressure-transmitting medium.

The Raman spectra from the DAC were obtained for $CuInTe_2$ QDs using a Spectra Physics® Ar Ion laser. The laser was tuned to 514.5 nm. During the experiment, the power of the laser is between 60 – 120 mW, and the acquisitions was 600 seconds/scan. After the laser interacted with the sample, the backscattered light was dispersed by a Jobin Yvon U1000® spectrometer (~1 cm^{-1} of resolution) and stored with an ISA Instruments Spectrum One® detector. With a Kaiser optics® 514.5 nm holographic notch filter, the Rayleigh scattered light was filtered. The high pressure Raman experiment was carried out from ambient to 7.7 GPa.

Results and Discussion

The stack plot of the high pressure Raman spectroscopy results for $CuInTe_2$ QDs is depicted in Fig. 2. At the ambient conditions, the Raman peaks are observed at 125.1 cm^{-1} and 142.8 cm^{-1}. The 125.1 cm^{-1} is labeled as the A_1 mode and the 142.8 cm^{-1} is the E mode. This A_1 mode is due to the complete symmetry and is the strongest Raman peaks in chalcopyrite structure. Typical Raman modes usually shift toward higher frequencies as the pressure increases. Nevertheless, as seen in Fig. 2, the A_1 mode is found to shift toward lower frequency as pressure increases.

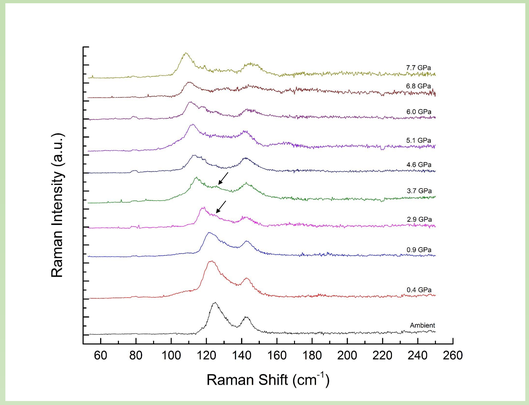

Figure 2. High pressure Raman spectra of $CuInTe_2$ OD from ambient up to 7.7 GPa. The arrows indicate the splitting of the A_1 peak.

Comparing the spectra at 2.9 and 3.7 GPa, the A_1 mode drops by approximately 5 wavenumbers (shown in Fig. 4), and a new Raman peak, 124.5 cm^{-1}, is noticed at 2.9 GPa (shown in Fig. 3). Based on these results, a pressure-induced phase transition starts to occur at 2.9 GPa. At 3.7 GPa, the new peak shifts to 125.6 cm^{-1}. The B_2 or E mode is consistently shifting toward higher frequency. Later at ~6 GPa, another Raman peak shows up. These two new peaks are also consistently shifting toward higher frequencies as pressure increases indicating pressure-induced phase transition.

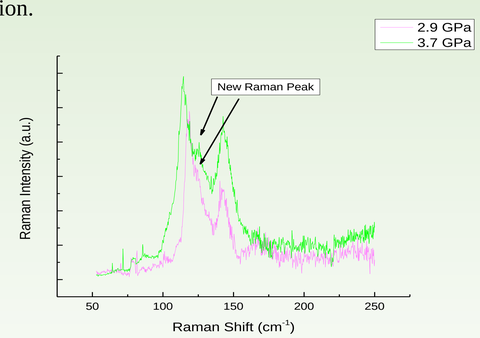

Figure 3. Raman spectra at 2.9 and 3.7 GPa.

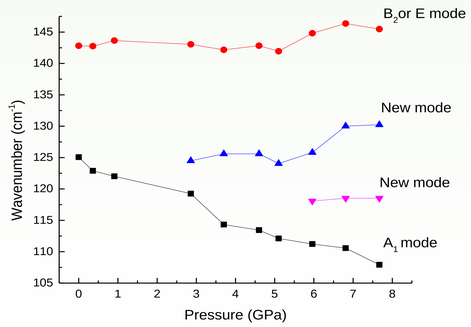

Figure 4. Pressure-dependency of the Raman modes for $CuInTe_2$ QDs.

Conclusions

High pressure Raman spectroscopy study of $CuInTe_2$ QDs was carried out up to 7.7 GPa. At ambient conditions, the Raman modes from the DAC were observed at 125.1 cm^{-1} (A_1 mode) and 142.8 cm^{-1} (B_2 or E mode). From the variation of the Raman modes and splitting of the peaks, we have found a phase transition of $CuInTe_2$ QDs occurring at 2.9 GPa. The transition pressure mainly depends on the particle size and is lower for $CuInTe_2$ QDs in comparison with the bulk.

To supplement our results, we would like to further extend our experiment using Infrared Spectroscopy to study the optical and vibrational modes of $CuInTe_2$ QDs and high-pressure X-Ray diffraction experiments to obtain the crystal structure of $CuInTe_2$ QDs at extreme conditions.

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