

High pressure anomalies in exfoliated MoSe₂: Resonance Raman and X-ray diffraction studies

Bishnupada Ghosh*, Pinku Saha and Goutam Dev Mukherjee

National Centre for High Pressure Studies, Department of Physical Sciences, Indian Institute of Science Education and Research Kolkata, Mohanpur Campus, Mohanpur 741246, Nadia, West Bengal, India.

Keywords: high pressure, transition metal dichalcogenides, anisotropic strain.

*e-mail: bishnu2706@gmail.com

Layered transition metal dichalcogenides (TMD's), MX₂ (M: Mo, W, Ti, Re etc.; X: S, Se, Te) have attracted renewed attention due to their interesting mechanical, electronic, and optical properties [1,2]. Layered TMD's crystallize in hexagonal lattice, in which the layers (X-M-X) are held together by a weak van der Waals force and within each layer (X-M-X) atoms have a strong covalent bonding. Exfoliated [3,4] single or multiple two dimensional (2D) layers of these materials show novel opto-electronic properties [4]. Beside hexagonal structure, these materials can adopt octahedral (tetragonal - 1T), and their distorted (1T') crystal structure [1,4]. Electronic properties seem to get modified depending on the type of structure [4] TMD's adopt. Structural and hence electronic properties of these materials are affected either by doping or by the application of pressure. There are several reports suggesting metallization of TMD's under pressure [5,6,7].

In the present work a detailed high pressure Resonance Raman (RR) Spectroscopy and X-ray diffraction (XRD) studies are carried out on exfoliated MoSe₂. Exfoliated MoSe₂ is obtained by liquid exfoliation. The sample is found to consist of three to four layers. The analysis of ambient resonance Raman spectra and XRD pattern reveal that the triclinic phase is embedded with its parent hexagonal phase from the ambient condition. For the generation of high pressure we used piston cylinder type diamond anvil cell (from easy lab, UK). High pressure Raman study reveals emergence of new modes M₁, M₂ at 12.3 GPa and M₃ above 33 GPa. Pressure evolution of Raman modes and their full width at half maximum (FWHM) of prominent modes of the exfoliated sample show slope changes at about 13 GPa and 33 GPa. Pressure evolution of full width at half maximum (FWHM) of prominent modes are shown in Fig.1. Slope change in the linear behavior of reduced pressure (H) with respect to Eulerian strain (f_E) is observed at about 13 GPa in both the phases, which clearly seen from the Fig.2(c & d). A minimum in the FWHM values of E¹_{2g} and A²_{2u} modes as evident from the Fig.1 at the same pressure indicate to an Electronic topological transition (ETT). Above 33 GPa the sample completely gets converted to the triclinic structure, which indicates the importance of strain in structural as well as electronic properties of two dimensional materials.

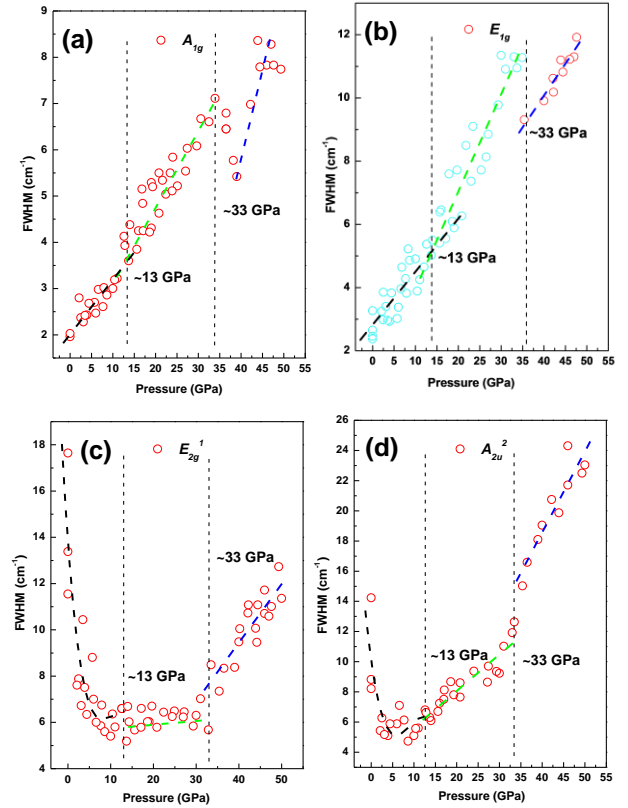


Figure. 1. Pressure evolution of FWHM of A_{1g}, E_{1g}, E¹_{2g}, and A²_{2u} Raman modes are shown in (a), (b), (c), and (d), respectively. FWHM of A_{1g} and E_{1g} show a slope change around 13 GPa followed by a minimum at about 33 GPa. FWHM of E¹_{2g} and A²_{2u} soften with pressure and reach a minimum value around 13 GPa followed by a linear behavior and sudden jump around 33 GPa.

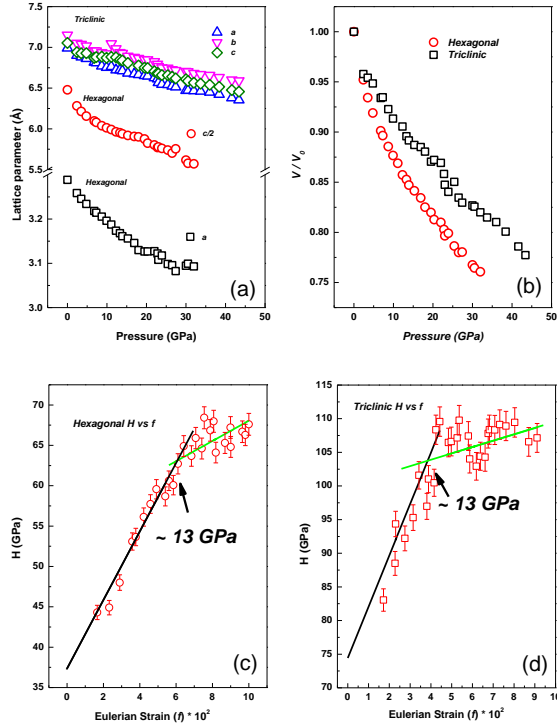


Figure.2. (a) The evolution of lattice parameters with pressure for both the hexagonal and triclinic phases of exfoliated MoSe₂. (b) Pressure dependence of relative volume of both the hexagonal and triclinic phases of exfoliated MoSe₂ with respect to the ambient pressure value. (c) Plot of reduced pressure (H) versus Eulerian strain (f) in the hexagonal phase of exfoliated MoSe₂, showing discontinuous change in their linear behavior around 13 GPa. (d) triclinic phase of exfoliated MoSe₂, showing discontinuous change in their linear behavior around 13 GPa.

Acknowledgments:

This work was supported by Ministry of Earth Sciences, Government of India under the project grant no. MoES/16/25/10-RDEAS. PS and BG wish to thank DST, INSPIRE program by Department of Science and Technology, Government of India for financial support. The authors also gratefully acknowledge the financial support from the Department of Science and Technology, Government of India for carrying out experiments in the XPRESS beam line in the ELETTRA Synchrotron light source under Indo-Italian Executive Programme of Scientific and Technological Cooperation.

References:

- [1] J. Wilson and A. Yoffe, *Adv. Phys.* 1969, **18**, 193.
- [2] K. F. Mak, C. Lee, J. Hone, J. Shan, and T. F. Heinz, *Phys. Rev. Lett.* 2010, **105**, 136805.
- [3] W. Choi, N. Choudhary, G. H. Han, J. Park, D. Akinwande and Y. H. Lee, *Mater. Today*. 2017, **20**, 116.
- [4] Q. H. Wang, K. Kalantar-Zaden, A. Kis, J. N. Coleman, and M. S. Strano, *Nat. Nanotechnol.* 2012, **7**, 699.
- [5] P. Saha, B. Ghosh, R. Jana, and G. D. Mukherjee, *J. Appl. Phys.* 2018, **123**, 204306.
- [6] A. P. Nayak, S. Bhattacharyya, J. Zhu, J. Liu, X. Wu, T. Pandey, C. Jin, A. K. Singh, D. Akinwande, and J. F. Lin, *Nature Communication*. 2014, **5**, 3731.
- [7] D. Zhou, Y. Zhou, C. Pu, X. Chen, P. Lu, X. Wang, C. An, Y. Zhou, F. Miao, C. H. Ho, J. Sun, Z. Yang, and D. Xing, *npj Quantum Materials*. 2017, **2**, 19.