

Abstract

Isostructural transitions in layered MX_2 compounds are governed by competing van der Waals (vdW) and Coulomb interactions. While an isostructural transition (at $P \sim 20$ GPa) has been observed before metallization in MoS_2 when subjected to pressure, it is surprisingly missing in layered MoSe_2 and MoTe_2 . Using synchrotron x-ray diffraction and Raman spectroscopic measurements of structural and vibrational properties of layered MoSSe crystals subjected to pressures up to 30 GPa and first-principles density functional theoretical analysis, we demonstrate a layer sliding isostructural transition from its $2H'_c$ structure (space group $P6_3mc$) to a mixed-phase of $2H'_a+2H'_c$ at $P \sim 10.8$ GPa, marked by discontinuity in lattice parameters, pressure coefficients of Raman modes, and accompanying changes in electronic structure. The origin of the unusually lower transition pressure of MoSSe compared with MoS_2 is shown to be linked to chemical ordering of S and Se atoms on the anionic sublattice, possible because of moderate lattice mismatch between the parent compounds MoS_2 and MoSe_2 and large interlayer space in the vdW-bonded structure. Notably, we also report a lower-pressure transition observed at $P \sim 3$ GPa and not reported earlier in the isostructural Mo-based chalcogenides, marked by a discontinuity in the pressure coefficient of the c/a ratio and indirect band gap. The transition observed at $P \sim 10.8$ GPa appears due to the change in the sign of the pressure coefficient of the direct band gap originating from inversion of the lowest-energy conduction bands. Our theoretical analysis shows that the phase transition at $P \sim 18$ GPa marked by sharp changes in pressure coefficients of A_1 Raman modes is associated with the metallization of the $2H'_a$ phase.