

Theoretical study of phase transitions in Sb_2S_3 , Bi_2S_3 and Sb_2Se_3 under compression

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We have carried out a comprehensive set of calculations based on Density Functional Theory to investigate the pressure stability of five possible phases in sesquichalcogenides Sb_2S_3 , Bi_2S_3 and Sb_2Se_3 under hydrostatic pressures up to 60 GPa, viz. *Pnma*, *R-3m*, *C2/m*, *C2/c* and *Im-3m*.

For Bi_2S_3 and Sb_2S_3 , we find that the orthorhombic *Pnma* phase is the most stable phase at ambient pressure, while the *R-3m*, *C2/m* and *C2/c* phases are not energetically competitive over the range of pressures examined. These results are contrary to recent experimental results [1][2][3] suggesting several phase transitions in Sb_2S_3 between 10 and 25 GPa. Therefore, we suggest that the observation of the multiple high-pressure phases may be due to the non-hydrostatic behavior of the pressure-transmitting medium. The disordered bcc-like *Im-3m* phase (which can be understood as a disordered solid solution of atoms) is predicted to be the most energetically stable phase of the two compounds above 30 and 35 GPa, respectively. However the calculated phonon dispersion curves indicate that the *Im-3m* phase remains dynamically unstable up to at least 60 GPa. We therefore do not anticipate that a disordered bcc-like structure will be observed for Bi_2S_3 and Sb_2S_3 under hydrostatic conditions. This conclusion agrees with the non-observation of a *Im-3m* phase in Bi_2S_3 [4][5] under pressure up to 65 GPa.

For Sb_2Se_3 , we again find that the *C2/m* and *C2/c* phases are not energetically competitive over the range of pressures examined. As regards to the *Im-3m* phase, our calculations predict a transition to above 21 GPa, in good agreement with experimental observations [6]. In fact, unlike the other two compounds, our lattice-dynamics calculations indicate this phase is dynamically stable at high pressures in Sb_2Se_3 . Moreover, and unexpectedly, calculations at ambient pressure suggest that the trigonal *R-3m* phase is the most energetically favorable - competitive with the *Pnma* phase - and that a transition to the *Pnma* phase should occur at a moderate pressure (5 GPa). Since the *Pnma* phase is invariably obtained in experiments, we suggest that the *Pnma* phase is stabilized by the thermal energy at room temperature, allowing for the possibility of synthesizing the *R-3m*

phase under optimized conditions. Moreover, the inconsistency found between the theoretical and experimental data can be explained on kinetic reasons; i.e. that the *Pnma* phase forms faster than the *R-3m* phase, under the usual synthesis conditions. We would expect this phase to show topological insulating properties under ambient conditions, which would likely make the synthesis of the *R-3m* phase in Sb_2Se_3 an undertaking highly worthwhile.

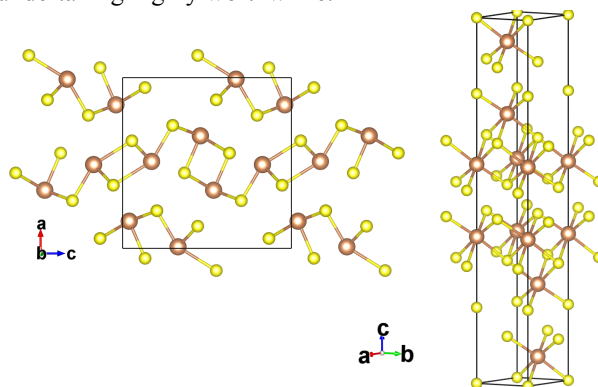


Figure 1. Representations of the unit-cell of the *Pnma* (left) and *R-3m* (right) phases of Sb_2Se_3 . The A cations and X anions are shown as brown and yellow spheres respectively.

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