Unraveling structural and bonding nature of Sb-based chalcogenide glass for electronic and photonic applications

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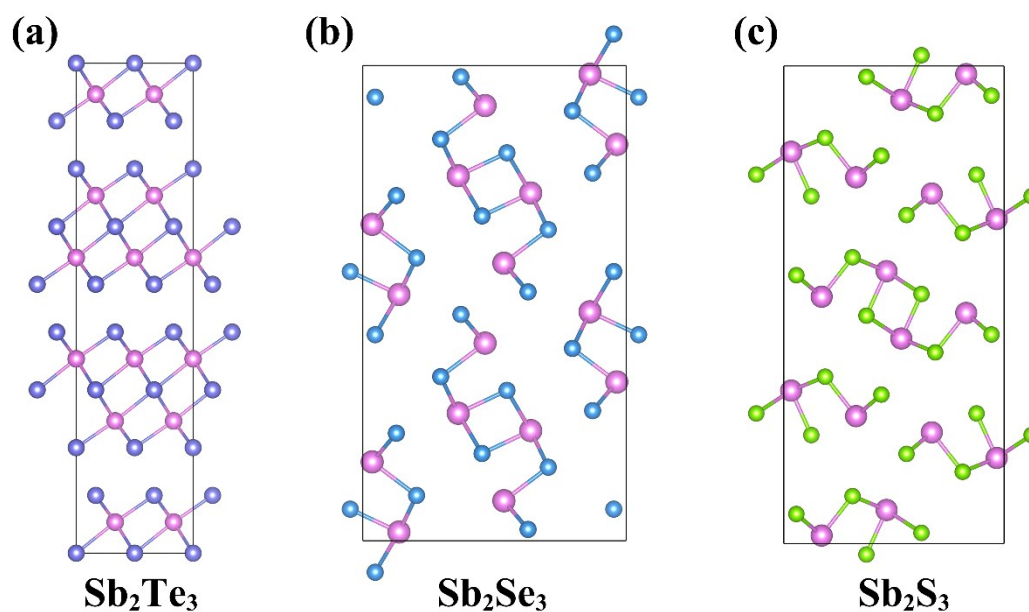
Figure S1. Crystal structures of Sb_2Te_3, Sb_2Se_3 and Sb_2S_3, in whichSb_2Te_3 is a rhombohedral crystal structure with octahedral atomic cluster, while both Sb_2Se_3 and

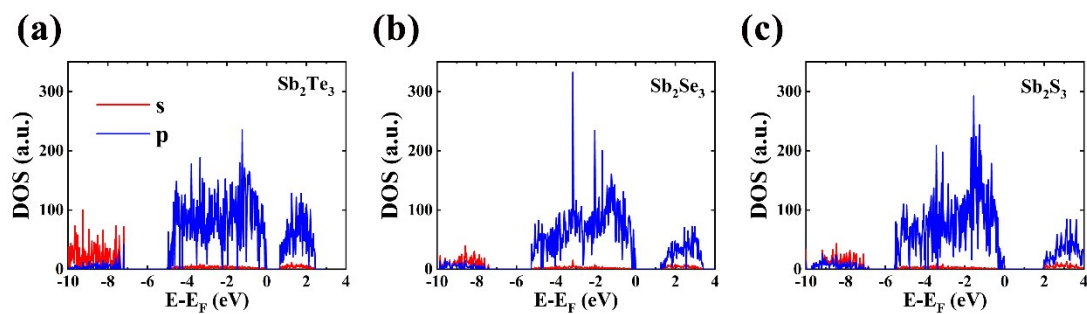Sb_2S_3 are orthorhombic structures with chain-like atomic arrangement and strong anisotropy.

Figure S2. Partial density of states (PDOS) of amorphous Sb_2Te_3, Sb_2Se_3 and Sb_2S_3. All of them mainly show p orbital contribution, explaining their dominant 90° bonding angle.
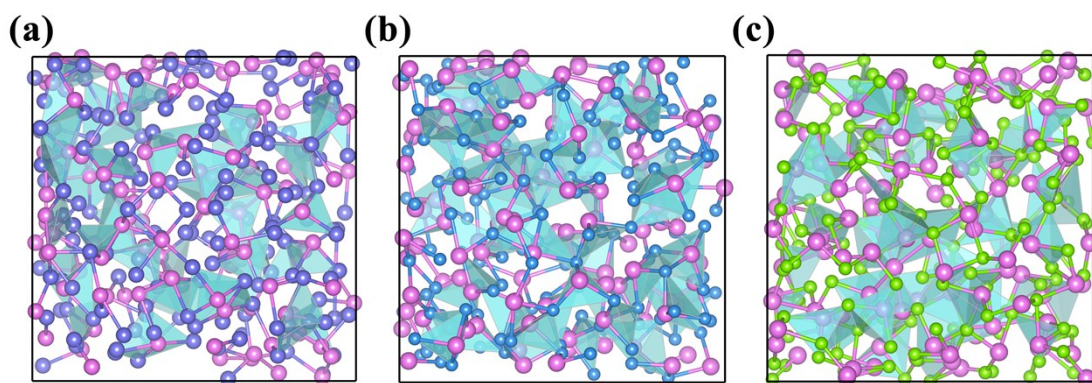

Figure S3. Amorphous models of Sb_2Te_3, Sb_2Se_3 and Sb_2S_3, and the Sb-center polyhedron is shown. All of them mainly form defective octahedral motifs, as most Sb atoms are 3-coordinated and form ~90° bonding angle.
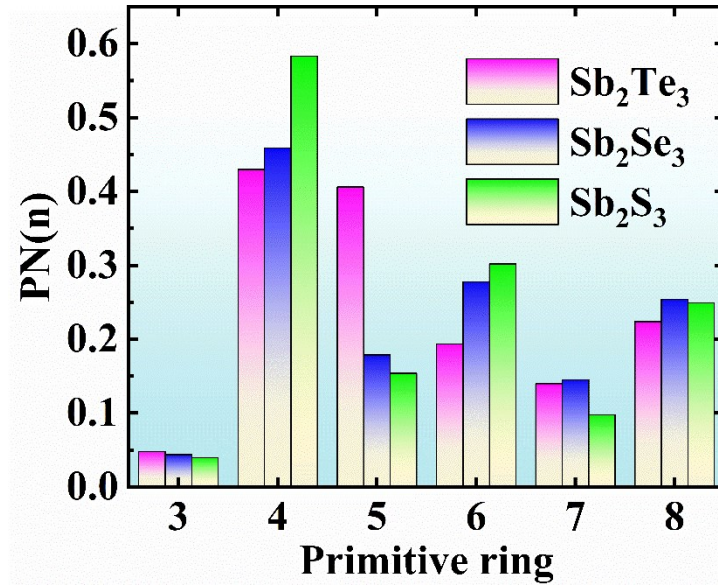
Figure S4. Primitive ring distribution is calculated through the RINGS-code. Here PN(n) shows the connectivity of various rings, i.e., shared atoms between rings. Sb_2S_3 and Sb_2Se_3 have more 4-fold rings than Sb_2Te_3 (Figure 2a), meanwhile their 4-fold rings have more shared atoms.

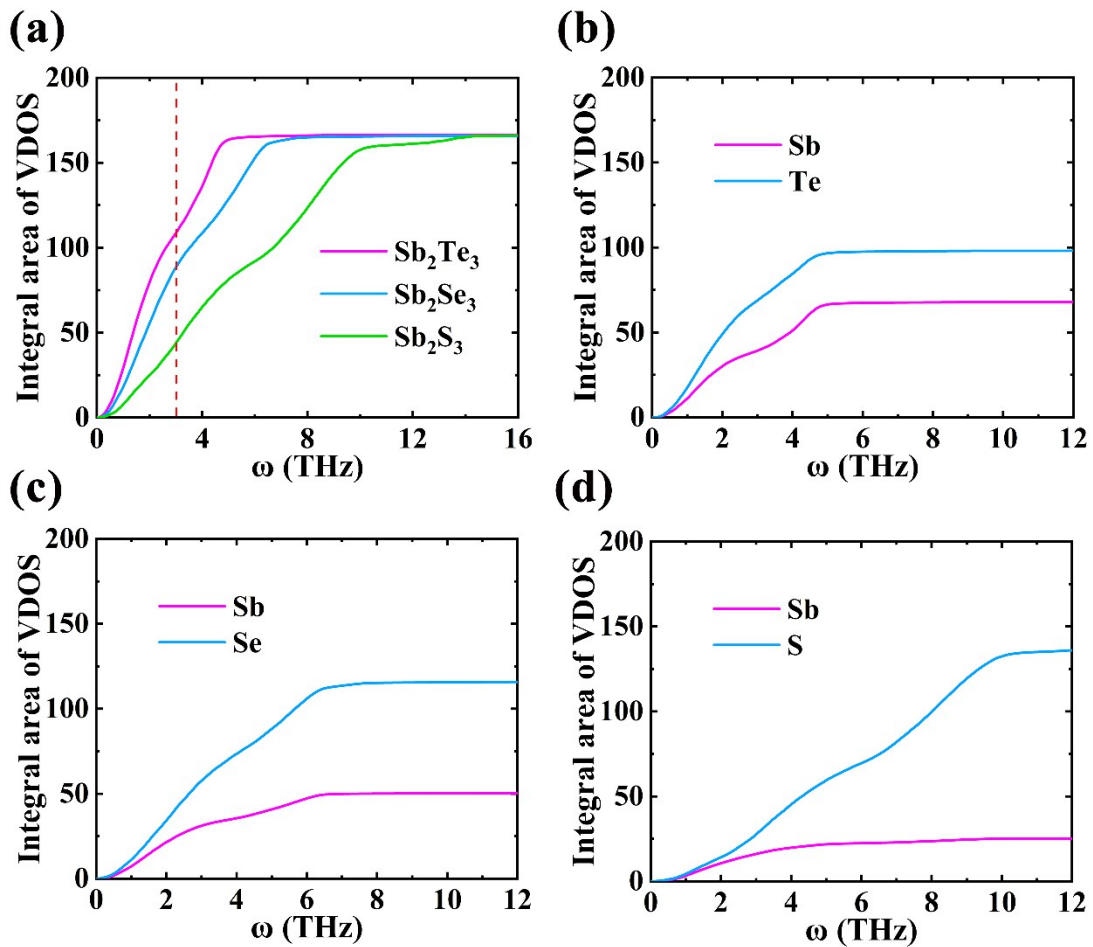Figure S5 a) All of Sb_2Te_3 and Sb_2Se_3 and Sb_2S_3 have the same integral areas of VDOS

(~166) at high enough frequency (~14THz), it confirms their total vibrational mode numbers keep the same. It also shows more low-frequency (below 3THz) modes and less high-frequency of Sb_2Te_3. b-d) Total integral areas are divided into two parts by elements. Their areas under the curves are ~67.9 of Sb and ~98.1 of Te, ~50.2 of Sb and ~115.8 of Se, ~25.3 of Sb and ~140.7 of S. Obviously the sums of two curves remain the same, equal to the total VDOS. Se and S have much more contribution to vibrational modes than Sb, meanwhile they have less low-frequency modes than Te, thus leads to less low-frequency modes of total VDOS.
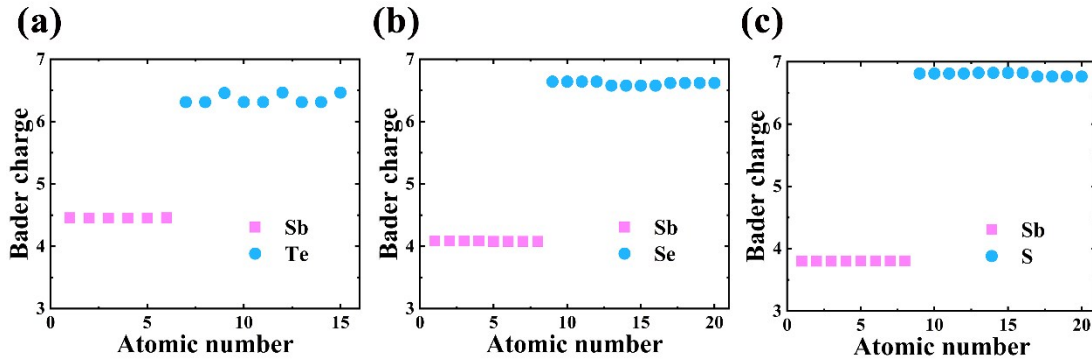

Figure S6. Bader charge distributions of Sb_2Te_3, Sb_2Se_3 and Sb_2S_3 crystal. All of crystalline Te (6.36), Se (6.61) and S (6.80) get more electrons (~0.1) than in amorphous state. It shows an ionicity increase of three materials upon crystallization, which could be also responsible for property difference between amorphous and crystalline states. Meanwhile Sb_2Se_3 and Sb_2S_3 crystals still keep more ionic than Sb_2Te_3.
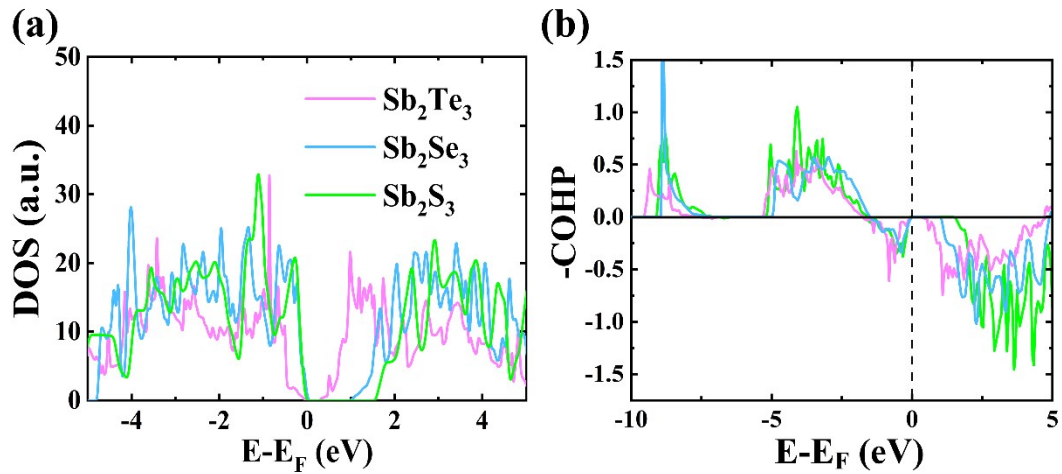
Figure S7. a) Total DOS of Sb_2Te_3, Sb_2Se_3 and Sb_2S_3 crystals. b) Average -COHP of Sb_2Te_3, Sb_2Se_3 and Sb_2S_3 crystals. All of them show antibonding state below fermi energy. Sb_2Te_3 has slightly more antibonding state thus Sb-Te bonding is weaker.

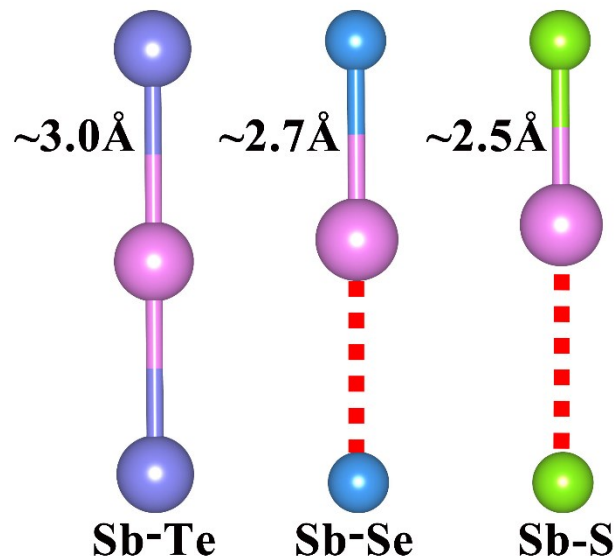Figure S8. All amorphous Sb_2Te_3, Sb_2Se_3 and Sb_2S_3 form a large number of bonding angles close to 180°. Sb would like to form similar bond lengths with two Te atoms. Once Se and S take place of Te, Sb atoms would move towards one side, leading to Peierls-like distortions.
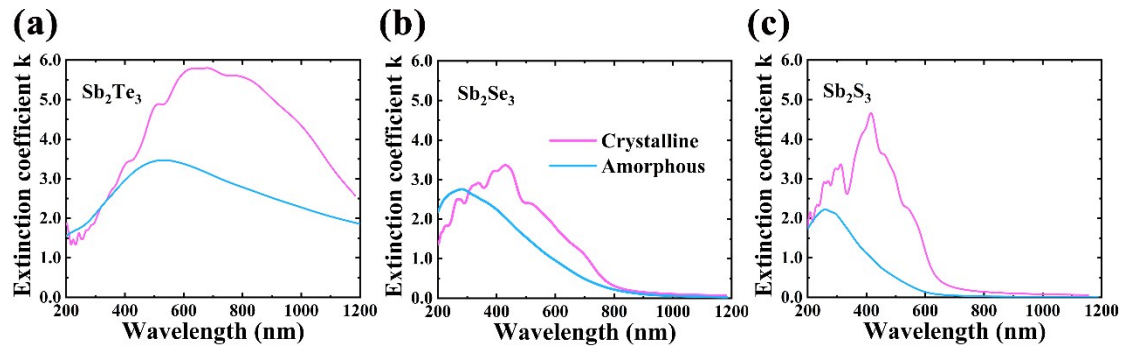
Figure S9. Calculated extinction coefficient k of both crystalline and amorphous states of three Sb-based materials. Sb_2Te_3 has great extinction coefficient i.e. high optical loss of both amorphous and crystalline states until 1200 nm, thus not suitable for visible tuning photonics. Then Sb_2Se_3 and Sb_2S_3 show really low extinction coefficient at 800 nm in both amorphous and crystalline states, thus more popular in visible photonic device.