Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for "Temperature, strain and charge mediated multiple and dynamical phase changes of selenium and tellurium."

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In this Supporting Information we present, (i) “Calculated Phonon Dispersion Curves (Bands), "Calculated Electronic Energy Bands” of neutral t-Se and t-Te Structures covering various directions of the Brillouin zone ; (ii) "Energy Bands of new sc-, bct-, bco-structures" of Se and Te together with the bands of their free standing, quasi 1D and 2D substructures; (iii) "Band Gap Closing under Electrostatic Charging of t-Se and t-Te"; (v) "Ab-initio MD calculations of New Phases charged by an excess charge q_o corresponding their minimum energy” to provide additional details related with the paper “***Temperature, strain and charge mediated multiple and dynamical phase changes of Selenium and Tellurium”.***

Phonon and Energy Bands of t-Se and t-Te Structures

As detailed in the main text, the dispersion curves of phonon modes (or phonon bands) of neutral t-Se and t-Te are calculated with plane basis set using the VASP code along the symmetry directions of the Brillouin zone. $\omega > 0$ at every k-point assures the dynamical stability at $T = 0$ K. Phonons of new phases occurring under excess charge attained imaginary frequencies when $q = 0$.

The electronic energy band structure of t-Se and t-Te are calculated using plane-wave basis set within the generalized gradient approximation (GGA) with Perdew, Burke, and Ernzerhof (PBE) functional[1] including spin-orbit coupling, (SOC). These band energies are corrected by using hybrid functionals (HSE)[2] as explained in the section of Methods of Calculation. Our results are presented in Fig. S2 for various symmetry directions of the Brillouin zone, which were not included in the text in Fig. 1c and d. Both crystals, t-Se and t-Te, are semiconductor with HSE fundamental band gap of 1.35 eV and 0.28 eV, respectively. The difference of energy between the direct and indirect band gap is minute.[3] In particular, t-Te displays large spin-orbit splitting, unusual band dispersions and small band gap, which are crucial for topologically non-trivial behavior. The band structure of an isolated (free-standing) chain is also presented in the same panel for the sake of comparison. Upon the transition from trigonal structure to isolated chains, while the bands (identified as S_2) become more dispersive, specific bands (identified as S_1) originating from non-bonding orbitals in the absence of interchain interaction are flattened along the chain axis in Fig. 1c and d. Apparently, electronic structure of free chains are different from bulk bands of t-phases.

Charge distribution of S_1 and S_2 states depicted in Fig. S2e confirms this interpretation. Additionally, the significant dispersions of the bands along the $\Gamma - \mathrm{K}$ direction support the isotropy in electrical conductivity.

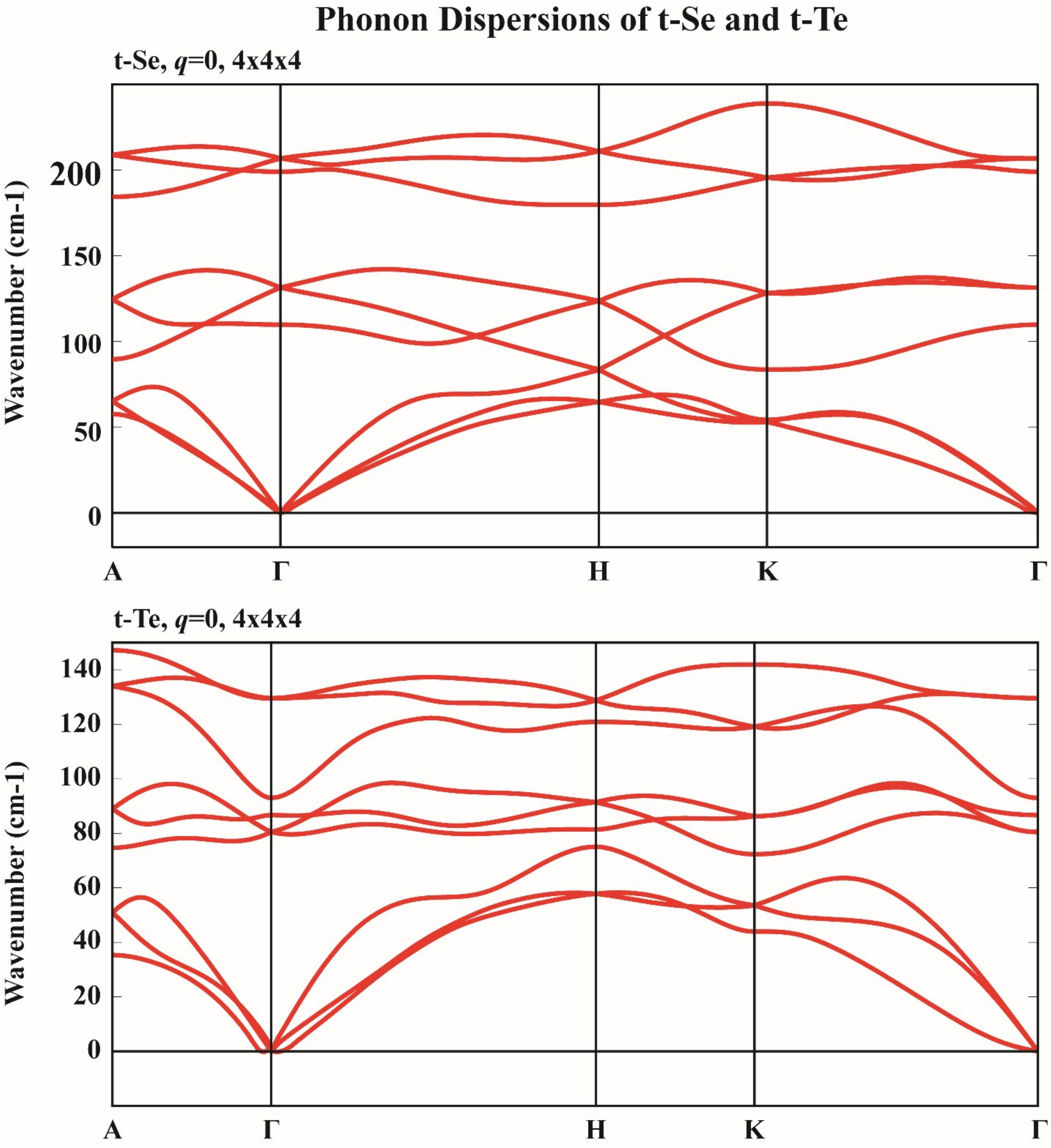

Fig. S1. Phonon bands of t-Se and T-Te along the symmetry directions of BZ.

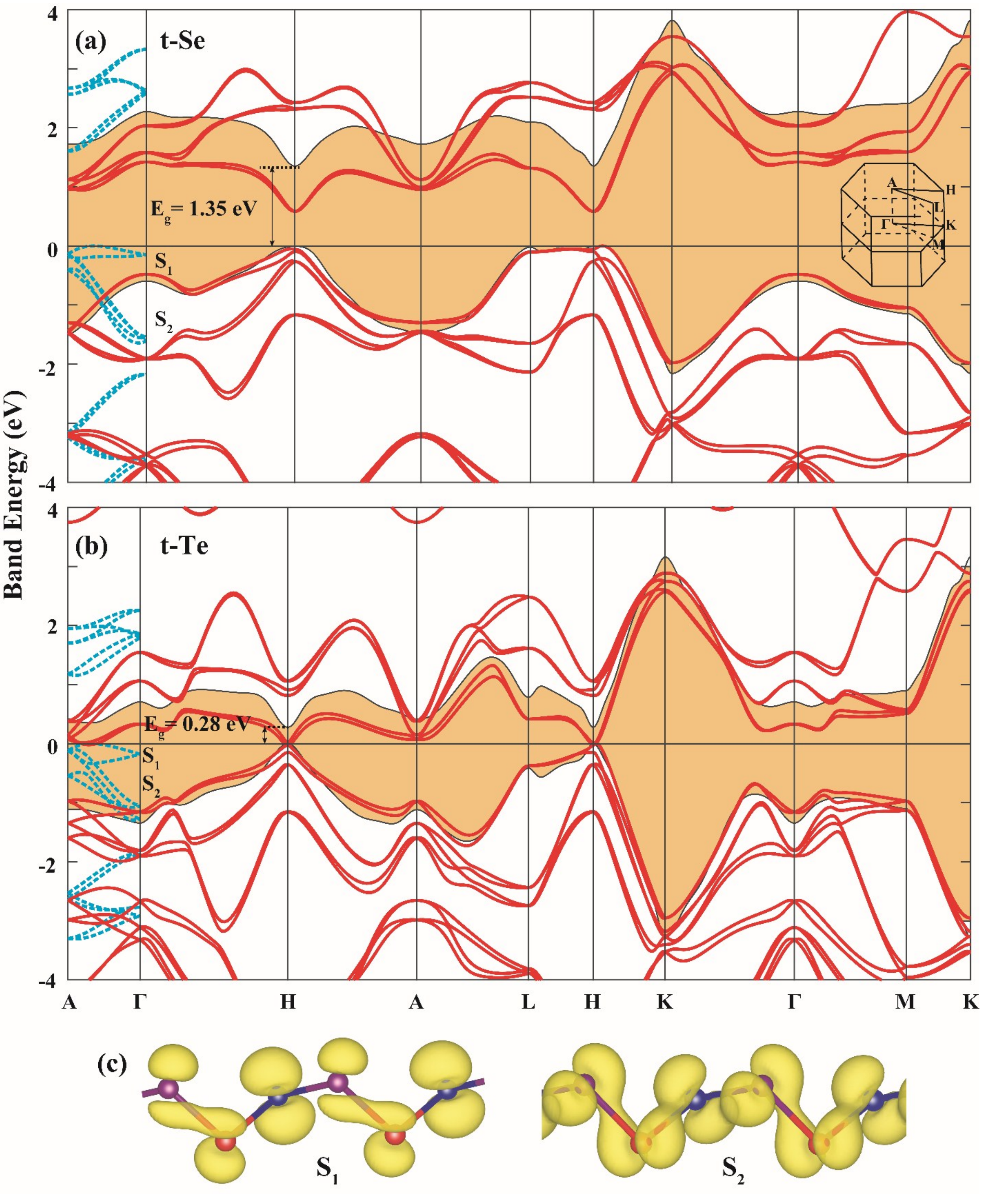

Fig. S2. Electronic energy band structure of t-Se (a), and t-Te (b), calculated by PBE+SOC along various symmetry directions. The fundamental band gaps, which are opened after HSE+SOC calculations are shaded. The bands of isolated helical chains with flat S_1, and dispersive S_2 bands are also shown by dashed lines along chain axis, $\Gamma - A$ direction. (c) The charge density isosurfaces of S_1 and S_2. Zero of energy is set at the top of the valence band.

Energy Bands of New sc-, bct-, bco-Structures

The full electronic energy band structures of sc-, bct- and bco-phases of Se and Te, which are calculated for excess charge q values corresponding to their minimum energies, are presented in Fig. S3 a and b, respectively, to complement the bands in Fig. 3a given only along $\mathrm{X}-\Gamma$ direction. All of these three structures of both Se and Te are metallic due to the bands, which strongly overlap. As discussed above, the overall configurations and the interatomic distances in various directions of these 3D phases let us deduce also specific quasi 2D, quasi 1D substructures. The question of whether the lower dimensionality reflects to the electronic structure is examined by comparing the bands of free 2D square structure related with bct-phase, and also the bands of free 2D rectangular structure, as well as those of 1D monatomic chain related with bco-phase with the bands of parent 3D structures. In Fig. S3 a and b the bands of free 2D and 1D structures are superimposed along the related symmetry directions of the Brillouin zone of parent 3D bct- and bco-structures. The bands of free monolayer of 2D square lattice trace the bands of parent bct-Se and bct-Te, except that the degenerate bands are split in 3D parent bulk due to interlayer interaction as shown in Fig. S3 a and b second row panels. Similar situation arises for the bands of free monolayer of 2D rectangular lattice extracted from bco-Se and bco-Te as depicted in Fig. S3 a and b in the third row panels. Also, the bands of free monatomic chain extracted from bco-phases of Se and Te trace the bands of 3D parent bco-Se and bco-Te along $\Gamma-\mathrm{X}$ direction. These observations justify the assertion that quasi 2D or 1D substructures are inherent in these new 3D crystals of Se and Te stabilized under excess electrostatic charge. These predicted lower dimensionalities are expected to appear in physical properties, in particular in electrical conductivity.

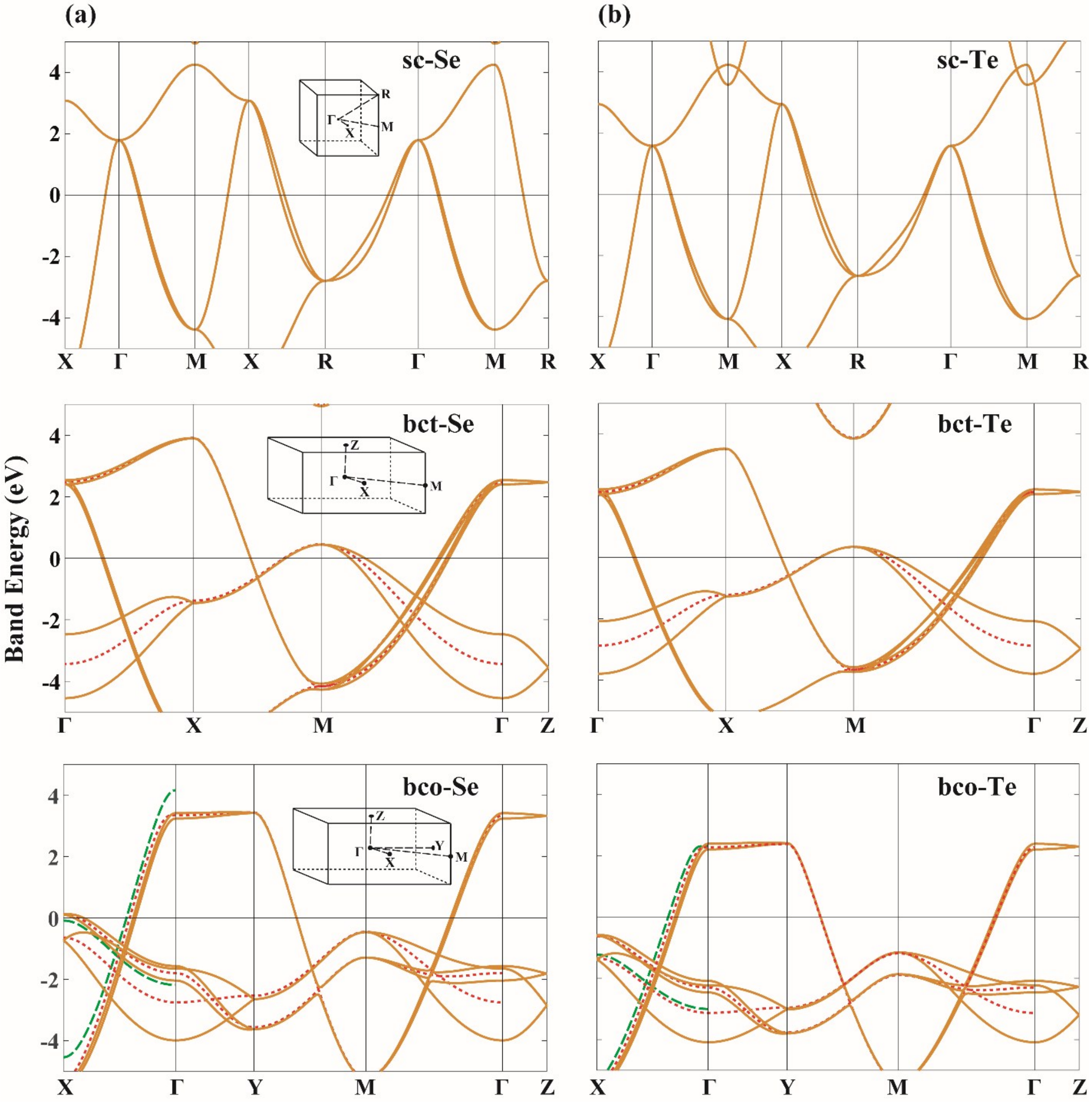

Fig. S3. Full band structures of different metallic phases transformed from semiconducting t-phase. (a) Right panels: Energy band structures of sc-, bct- and bco-Se are calculated for the excess charge q corresponding to the minimum energy for each phase. Zero of energy is set to the Fermi level. (b) Same for Te. The bands associated with the free-standing 2D and 1D substructures are marked on the corresponding directions of the 3D Brillouin zone by dotted and dashed lines, respectively.

Band Gap Closing under Electrostatic Charging

We carried out a series of self-consistent field and structure optimized band calculation of parent t-Se and t-Te for varying values of positive and negative excess charge q as seen below in Fig. S4. Notably, the Fermi level overlaps with the bottom of the conduction band for excess electrons $q < 0$. Subsequently, the band gaps are closed beyond specific values of excess electronic charge, which may impose instability for the parent phases to transform to a new phase. Similarly, for t-Te under excess positive charge (or electron deficiency) the Fermi level first dips in the valence band and then the band gap is closed heralding the transformation to a new phase (simple cubic sc-structure). The band gap of t-Se is reduced for electron deficiency and Fermi level overlaps with the valence band. For $q = 0.33$ e/atom the bad gap is still open, but is expected to be closed for $q = 0.42$ e/atom. The overall changes in bands under excess q are in compliance with the predicted phase changes.

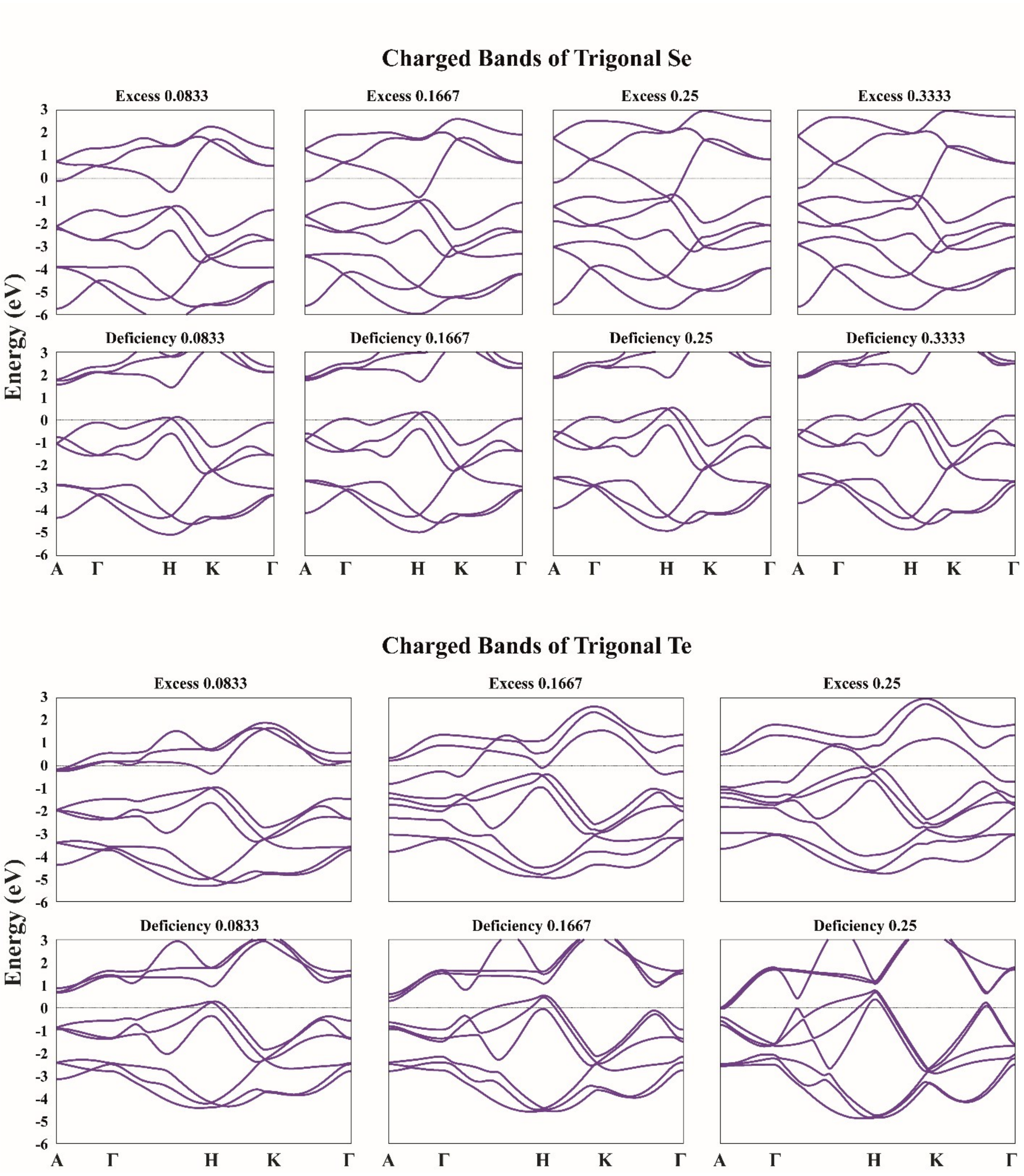

Fig. S4. Energy band structures of t-Se and t-Te calculate for various positive and negative excess charge q.

Ab-Initio Finite Temperature MD Calculations of New Phases

High temperature MD calculations performed at the excess charge corresponding to the minimum energy of each phase further assure the stability under charge. As an example, the snapshots of ab-initio MD calculations performed on sc-Te for $q = 0.25$ e/atom in Fig. S5 shows that this new phase remain stable at $\mathrm{T} = 400$ K. Also, the stability of bct-Te and bco-Te under excess charge of $q = -0.5$ e/atom and $q = -1.4$ e/atom are assured by MD calculations performed at $\mathrm{T} = 400$ K as shown in Fig. S6. We note that the thermal stability assured by high temperature MD calculations indicate that the structure trapped in local minima in the Born-Oppenheimer can remain stable at moderate temperatures. Similar results are obtained for Se.

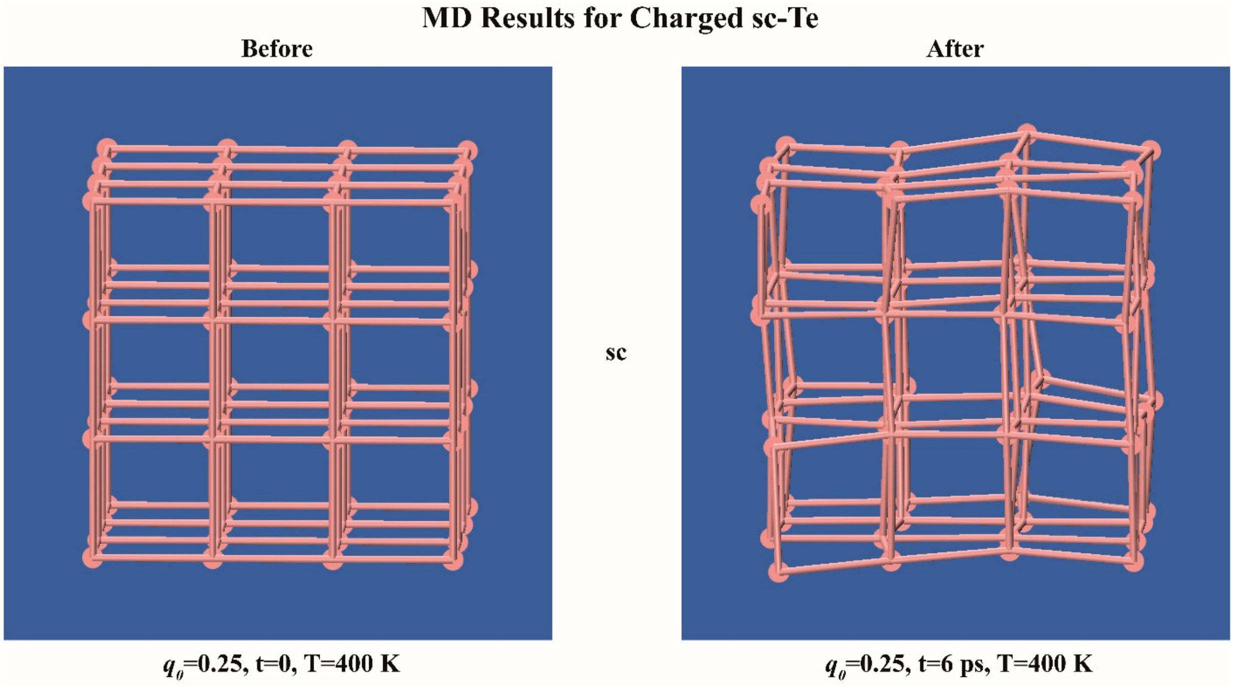

Fig. S5. Snapshots of ab-initio MD calculations show that sc-Te structure remains stable at $\mathrm{T} = 400$ K, when charged by $q_0 = 0.25$ e/atom.

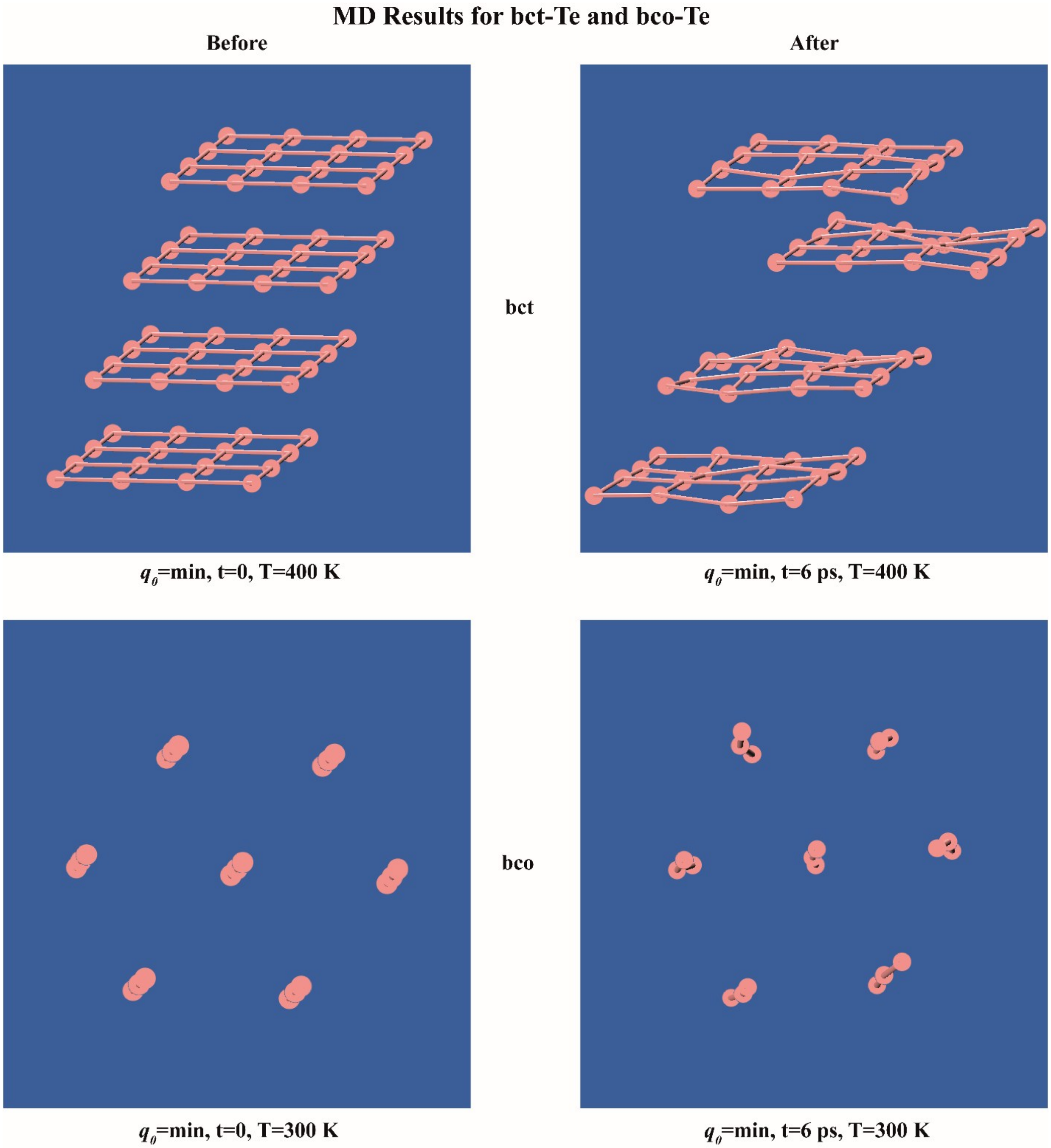

Fig. S6. Snapshots of ab-initio MD calculations show that new phases, bct-Te and bco-Te remain stable at $\mathrm{T} = 400$ K, when charged $q_0 =- 0.5$ e/atom and $q_0 =- 1.4$ e/atom, respectively.

References

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3. X.-X. Xue, Y.-X. Feng, L. Liao, Q.-J. Chen, D. Wang, L.-M. Tang and K. Chen, *J. Phys.: Condens. Matter, 2018,* ***30****, 125001*