

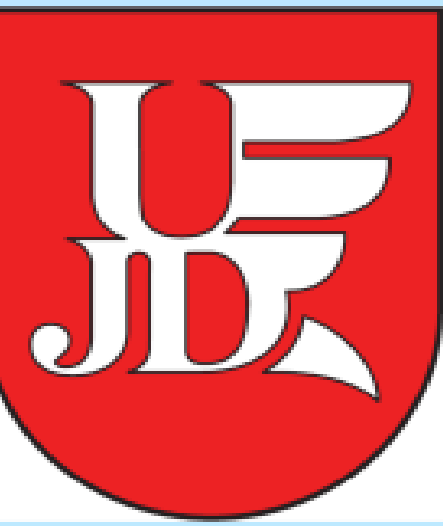
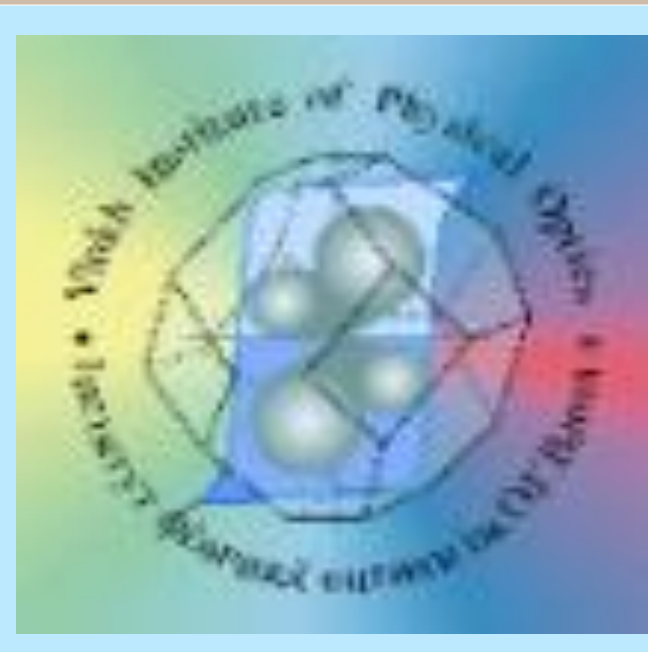
Cluster modeling of nanostructurization-driven reamorphization in glassy arsenoselenides

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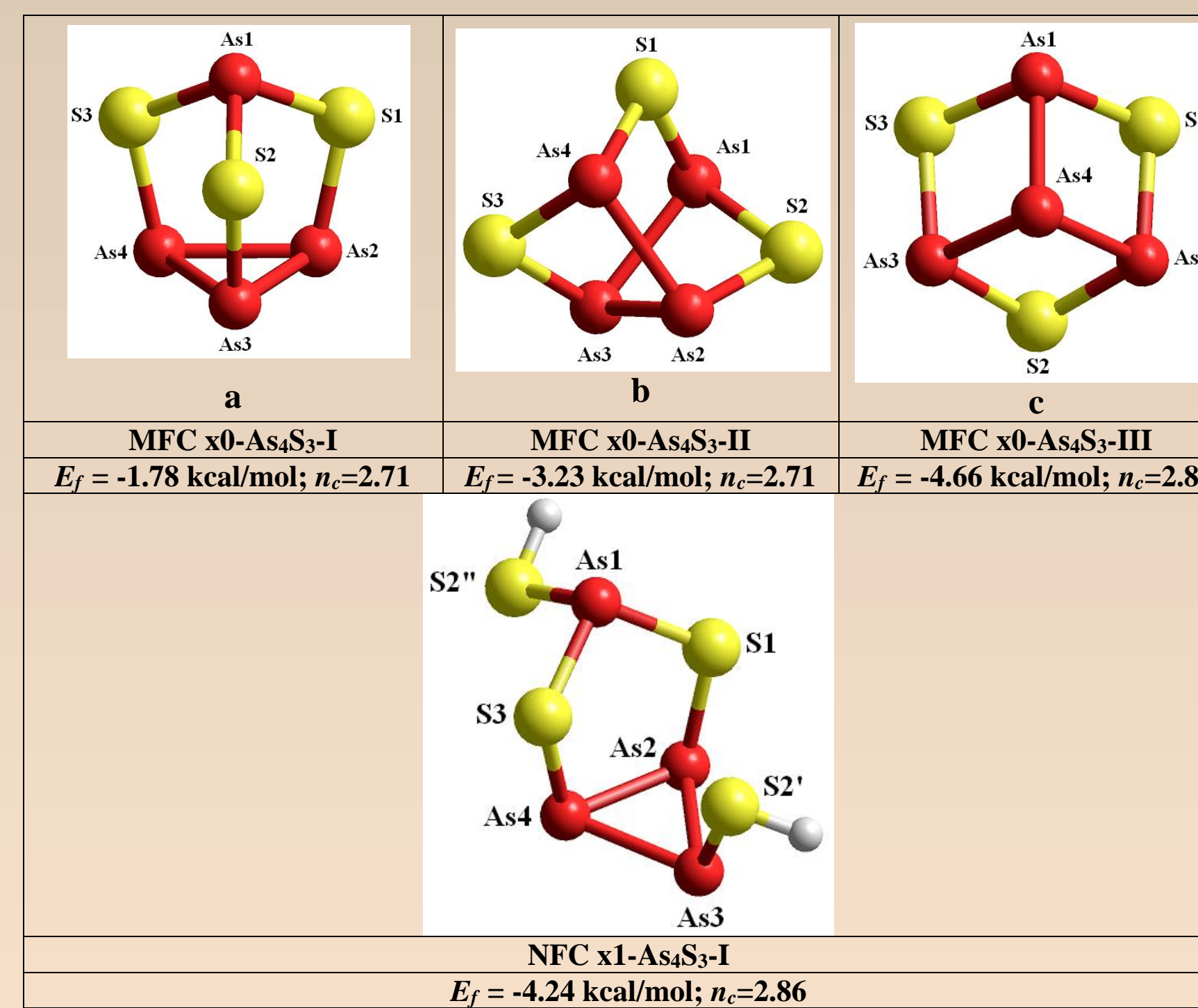
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Abstract:

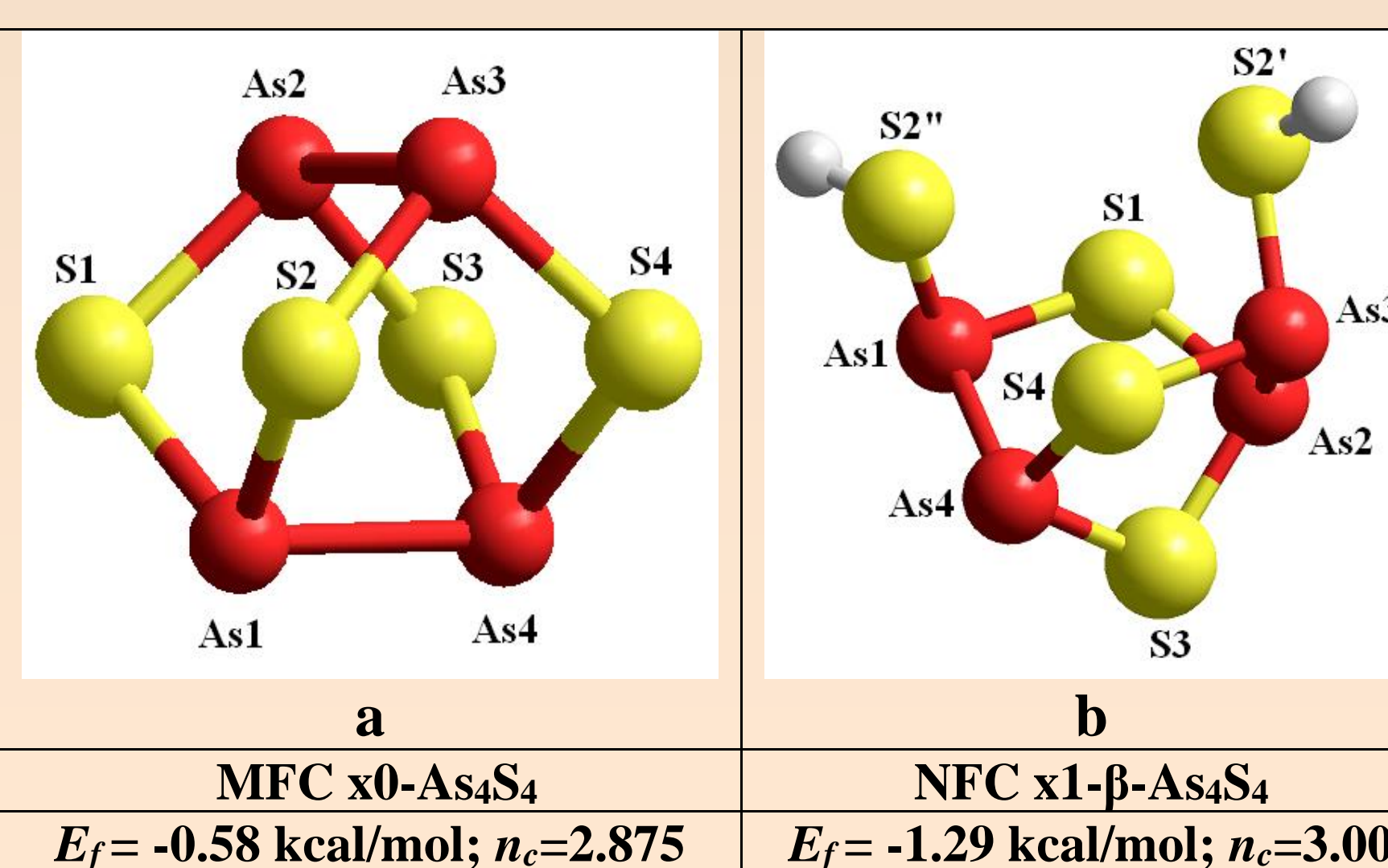
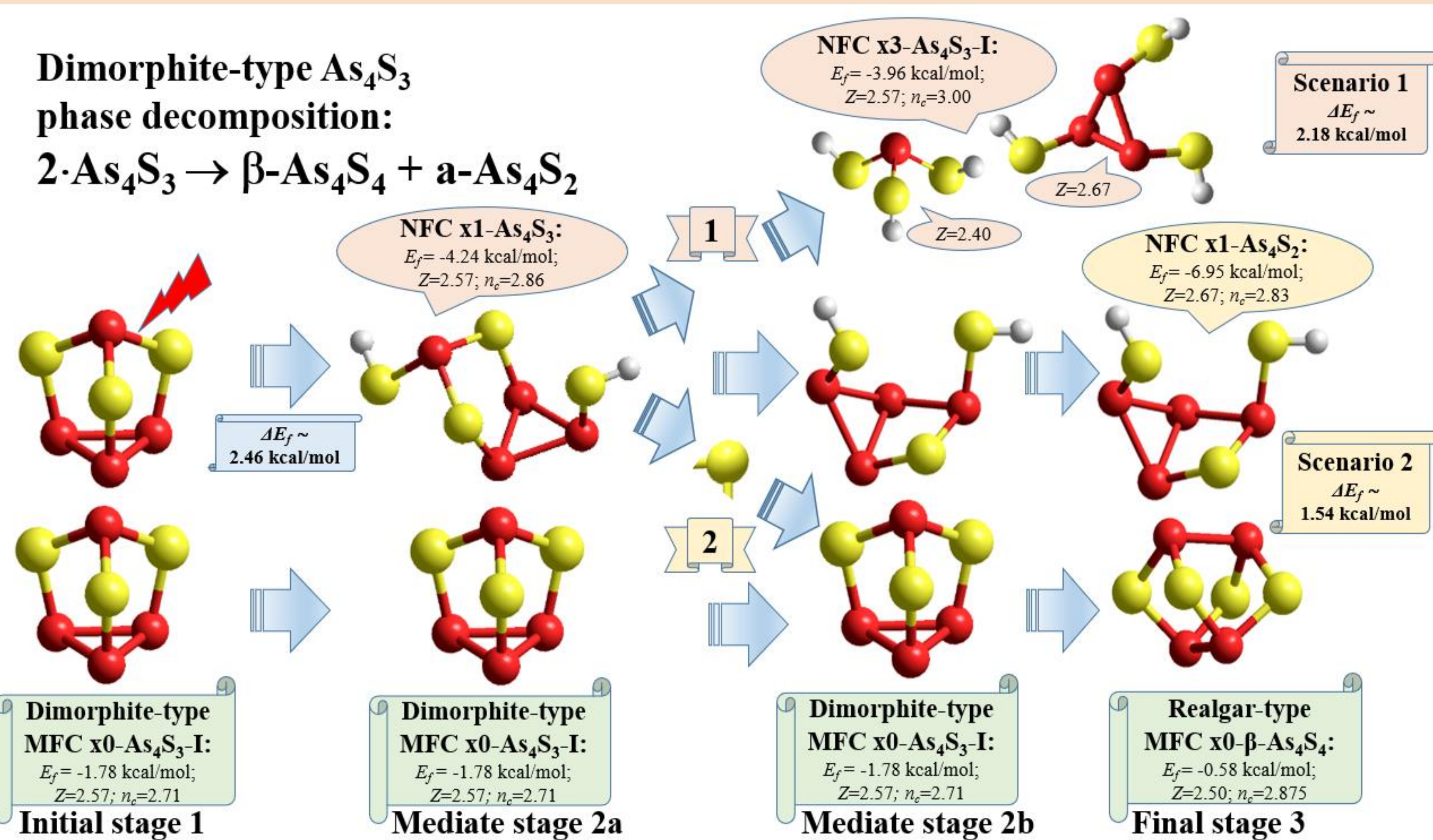
The melt-quenched and nanomilling-derived glassy g-As-Se probes are studied analyzing arrangement of diffuse peak-halos in their XRD patterns ascribed to intermediate- and extended-range ordering, revealed through first and second sharp diffraction peaks (FSDP, SSDP). Straightforward interpretation of the observed changes is developed with modified microcrystalline approach, accepting diffuse halos as originated from superposition of inter-planar- and inter-atomic correlations due to quasi-crystalline remnants, the former contributing through broad reflexes from quasi-crystalline planes (the Bragg-diffraction contribution), and latter contributing through inter-atomic distances belonging to these planes and inter-molecular correlations (the Ehrenfest-diffraction contribution). Balance in molecular-network entities in g-As-Se due to melt-quenching is disturbed at milling, providing evidence on defects with unfavorable energies. Nanomilling destroys cage-like molecules, facilitating transferring towards chain-like network structures. Nanomilling-driven reamorphization results in increase in the FSDP position and width, occurring fragmentation impact on the correlation length of the FSDP-responsible entities. Destruction of intermediate-range ordering under nanomilling is accompanied by changes in extended-range order, revealed in high-angular shift in the SSDP position and broadening in the width. Milling-driven breakdown in intermediate-range ordering in g-As-Se is concomitant with destruction of most distant inter-atomic correlations belonging to remnants of quasi-crystalline planes contributing to FSDP, whereas longer inter-atomic ones become dominant in extended-range order. Complete hierarchy of reamorphization scenarios in g-As-Se connected with cage-like molecules and most energetically favorable network-forming derivatives are examined with ab-initio quantum-chemical modeling CINCA.



Geometrically-optimized configurations of dimorphite-type As₄S₃ MFC in *triangle-* (a), *zig-zag chain-* (b) and *star-like* (c) conformations, and molecular precursor (As₄S₄H₂) of x1-As₄S₃-I NFC derived from x0-As₄S₃-I molecule by single x1-breaking in S2 position (d).

The S and As atoms are shown by yellow and red balls, and terminated H atoms are grey-colored. The averaged cluster-forming energies E_f and numbers of topological constraints n_c are given for each cluster.

Dimorphite-type As₄S₃ phase decomposition:



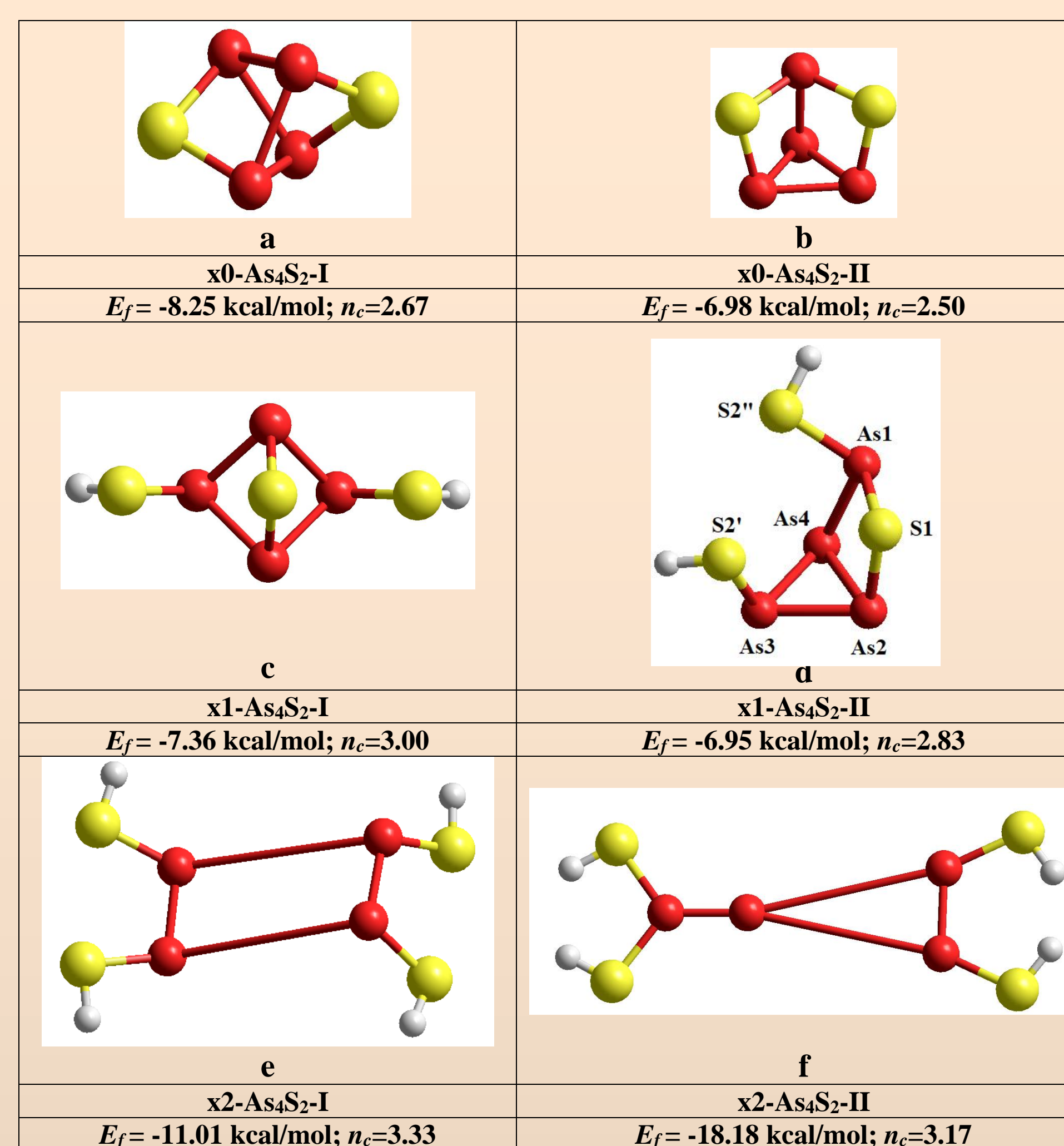
Geometrically-optimized configurations of realgar-type x0-As₄S₄ MFC (a) and molecular precursor (As₄S₅H₂) of x1-β-As₄S₄ NFC derived from x0-As₄S₄ molecule by single x1-breaking in S2 position (b). The S and As atoms are shown by yellow and red balls, respectively, and terminated H atoms are grey-colored. The averaged cluster-forming energies E_f and numbers of constraints n_c are given for each cluster.

Disproportionality pathways in As_xS_{100-x} arsenicals related to *direct* decomposition of *triangle-like* dimorphite-type As₄S₃ MFC in two optimally-constrained NFC with $Z=2.40$ and $Z=2.67$ (scenario 1) and *indirect* decomposition in realgar-type β-As₄S₄ phase supplemented by network-forming amorphous α-As₄S₂ substance (scenario 2).

The optimized configurations of MFC and NFC are reproduced with S and As atoms labeled by yellow and red balls; terminated H atoms are grey-colored. Energetic barriers ΔE_f to be overcome for these disproportionality scenarios, average values of coordination numbers Z , cluster-forming energies E_f and numbers of constraints n_c are given.

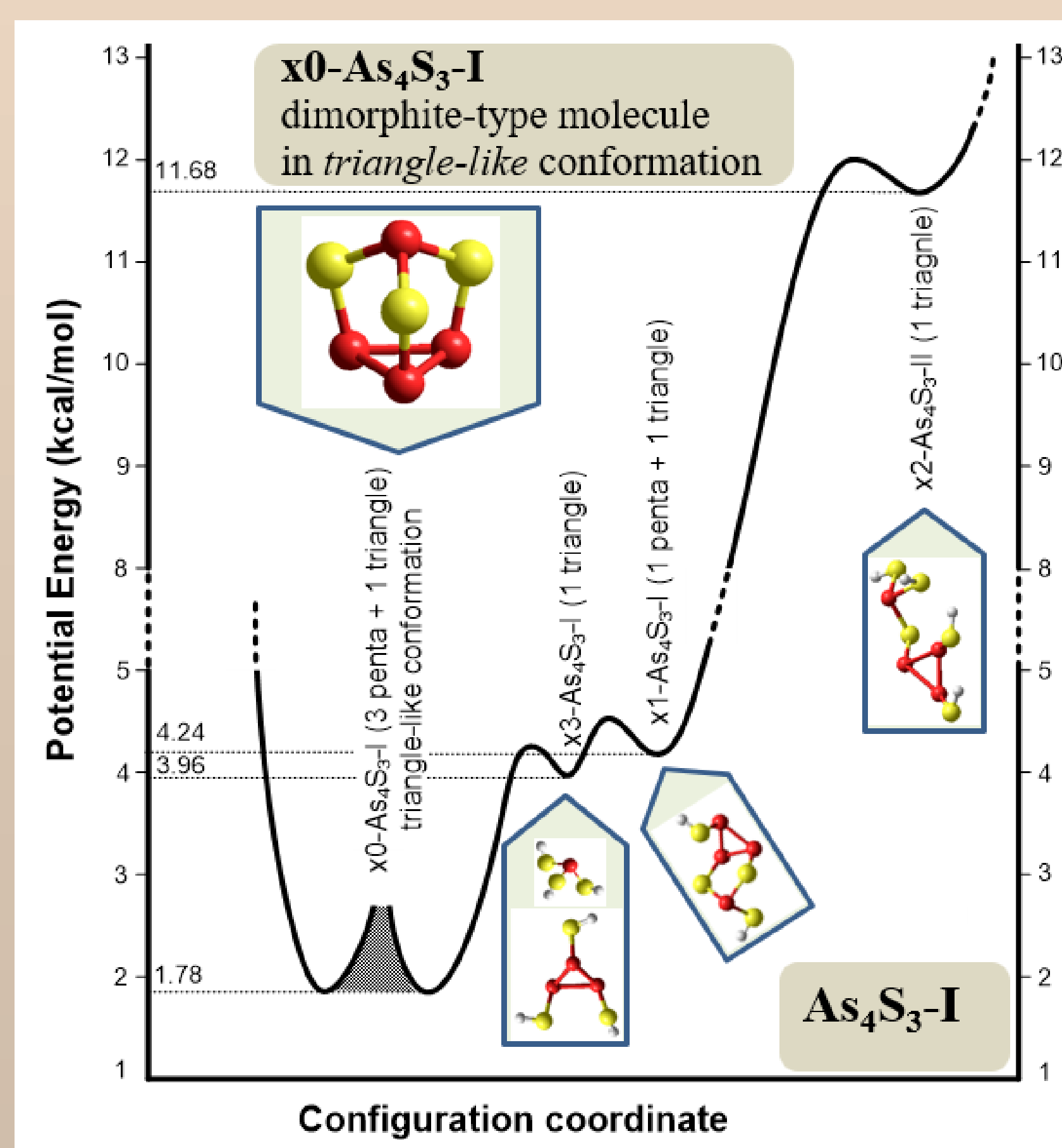
Conclusions:

Competitive pathways of nanostructurization-driven molecular-network disproportionality due to decomposition of dimorphite-type As₄S₃ phase were identified in over-stoichiometric As_xS_{100-x} arsenicals ($57 < x < 67$) employing computational *ab-initio* quantum-chemical modeling code (CINCA). At the ground of calculated cluster-forming energies, it was proved that amorphization related to direct transformation of dimorphite-type As₄S₃ molecules having *triangle-like* conformation in their network-forming derivatives was dominated in nanoarsenicals within As₄S₄-As₄S₃ cut-section ($50 < x < 57$), while it was unfavorable in more As-rich alloys taken from As₄S₃-As₄S₂ cut-section ($57 < x < 67$). In the latter case, nanostructurization-driven disproportionality attained purely *molecular* character, being governed by indirect decomposition of dimorphite-type As₄S₃ molecules in realgar-type β-As₄S₄ phase supplemented by amorphous α-As₄S₂ substance. Complete hierarchy of molecular-network transformations contributing to this decomposition was reconstructed, the most favorable conformations of participating molecular entities and their network-forming derivatives being parameterized in terms of respective cluster-forming energies.



Geometrically-optimized configurations of cage-like As₄S₂ MFC in *chain-like* (a) and *star-triangle-like* (b) geometries, and H-terminated molecular precursors of NFC derived from these molecules by single-breaking (x1-As₄S₂-I - c; x1-As₄S₂-II - d) and double-breaking (x2-As₄S₂-I - e; x2-As₄S₂-II - f) in S atom positions.

The S and As atoms are shown by yellow and red balls, and terminated H atoms are grey-colored. The averaged cluster-forming energies E_f and numbers of topological constraints n_c are given for each cluster.



Potential energy landscapes showing diversity of amorphizing NFC-related states originated from dimorphite-type x0-As₄S₃-I molecule possessing *triangle-like* conformation. The double-well presentation of ground state for x0-As₄S₃-I molecule corresponds to low- and high-temperature modifications of tetra-arsenic trisulphide after Whitfield. The geometrically-optimized configurations of H-terminated molecular precursors derived from this x0-As₄S₃-I molecule by multi-breaking in respective S atom positions are depicted. The settle-points ascribed to the NFC (keeping small rings, such as triangles and pentagons, in parenthesis) are pointed out with cluster-forming energies E_f given on potential energy axis.

