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ORIGINAL ARTICLE

Cluster modelling of amorphization pathways in nanostructured arsenic monosulphide

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Abstract

Competitive amorphization scenarios in arsenic monosulphide AsS under nanostructurization from directly-synthesized β-As_4S_4 polymorph are identified employing ab-initio quantum-chemical modelling route with cluster-simulation code CINCA. Geometrically-optimized configurations of As_4S_4 cage-like molecule and its network-forming derivatives responsible for amorphization are simulated and parameterized. Most plausible are found to be single-broken As_4S_4 clusters keeping one hexagon and two adjacent pentagons in atomic arrangement, which are responsible for uncontrolled amorphization in directly-synthesized β-As_4S_4 polymorph. Completely-polymerized triple- and quadruple-broken As_4S_4 clusters in chain configurations without any small-ring entities are character for milling-driven amorphization in monoparticulate β-As_4S_4- and biparticulate β-As_4S_4-Fe_3O_4 composites. In contrast, in triparticulate 1·β-As_4S_4-4·ZnS-1·Fe_3O_4 solution, the amorphizing network is built of double-broken As_4S_4 molecules keeping pentagon-type rings. Combined configuration-enthalpic model showing amorphization diversity in mechanoactivated arsenic monosulphide is developed.

Keywords Nanocluster · Amorphization · Nanostructure · Nanonization · Arsenic monosulphide · Mechanical milling

Background

In many practically important materials composed of coexisting crystalline phases, transition to nanosized state (viz. nanonization, nanostructurization) is related to complicated inter-nanophase transformations supplemented by structural disordering through solid-state *amorphization* (see, e.g. Zhao et al. 1999; Piot et al. 2013; Qiao et al. 2017). The high-temperature modification of tetra-arsenic tetra-sulphide β-As_4S_4 can be mentioned as typical example. Indeed, being directly synthesized from elemental ingredients, this arsenic monosulphide polymorph always contain unidentified amorphous phase (Hruby 1978). Under mechanoactivation due to high-energy nanomilling, this compound demonstrates strong propensity to be stabilized in a variety of metastable disordered phases following diversity in the respective amorphization scenarios (see Baláž et al. 2017; Shpotyuk et al. 2018, 2019a, b). The objective of current research is to compare energetically these amorphization pathways in arsenic monosulphide employing ab-initio quantum-chemical modelling route with cluster-simulation code CINCA (Shpotyuk et al. 2013, 2015; Shpotyuk and Hyla 2017).

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Method

Ab-initio quantum-chemical modelling of molecular-network forming tendencies in arsenic monosulphide with atomic cluster-simulation code CINCA

The geometrically-optimized configurations of cage-like As_4S_4 molecule and its different network-forming derivatives responsible for amorphization in arsenic monosulphide AsS (equivalently, the β-As_4S_4) were simulated with ab-initio

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quantum-chemical modelling developed within cation-interlinking network cluster approach, CINCA (Shpotyuk et al. 2013, 2015; Shpotyuk and Hyla 2017).

The network-forming clusters were reconstructed by breaking As_4S_4 molecule possessing D_{2d} symmetry on distinct fragments linked with atomic surrounding by sulphur bridges $S_{1/2}…S_{1/2}$. The HyperChem Release 7.5 program based on restricted Hartree–Fock self-consistent field method with split-valence double-zeta basis set and single polarization function 6-311G* (Hehre et al. 1969; McLean and Chandler 1980) was used for cluster energy calculation. Final geometrical optimization and single-point energy calculations for selected As_4S_4 clusters were performed with Fletcher-Reeves conjugate gradient method until the root-mean-square gradient of 0.1 kcal/(Å mol) was reached. The calculated cluster-forming energies E_f were corrected on the energy of terminated H atoms transforming "open" network-forming configurations in "closed" (self-consisternt) molecular ones according to procedure developed elsewhere (see, e.g., Jackson 2000; Holomb et al. 2009; Shpotyuk et al. 2013) and finally defined in respect to the energy of single $AsS_{3/2}$ pyramid approaching − 79.404 kcal/mol (Shpotyuk and Hyla 2017).

Amorphization scenarios realized as destruction of As_4S_4 molecule were examined in multiparticulate As_4S_4-based grinding media activated by high-energy mechanical milling in a dry mode under protective Ar atmosphere. Commercial arsenic sulphide β-As_4S_4 of 95% purity purchased in Sigma-Aldrich (USA) and natural mineral magnetite Fe_3O_4 were used as starting materials in grinding media preparation (for monoparticulate and biparticulate β-As_4S_4-Fe_3O_4 grinding solutions), while zinc acetate and sodium sulphide were used as precursors for ZnS preparation through chemical reactions (for triparticulate 1·β-As_4S_4-4·ZnS-1·Fe_3O_4 solution). The milling was performed during 20 min in ball mill Pulverisette 6 (Fritsch, Germany), in 250 mL WC milling chamber with 50 balls (10 mm in diameter) under rotational speed $n = 200–600\ min^{-1}$ (for more details on milling route, see Baláž et al. 2017; Shpotyuk et al. 2018, 2019a, b).

Results and discussion

It was shown that As_4S_4 cage-like molecule character for mineral realgar α-As_4S_4 (see Ito et al. 1952; Mullen and Nowacki 1972) composes principal source of solid-state amorphization in directly-synthesized β-As_4S_4 subjected to nanostructurization through high-energy mechanical milling (see Shpotyuk et al. 2018). Employing ab initio quantum-chemical modelling with cluster-simulation code CINCA, the geometrically-optimized configurations and stabilization energies E_f for these network-forming nanoclusters built by respective breaking of bonds at S atoms linking them with surrounding can be reconstructed and parameterized. The geometrically optimized parameters of these nanoclusters depicted on Fig. 1 are analyzed in our preliminary research (see Shpotyuk et al. 2019a, b), while their cluster-forming energies E_f (in respect to the energy of $AsS_{3/2}$ pyramid) and some topological characteristics such as number of small-ring entities (pentagons and/or hexagons), and number of averaged mechanical constraints per atom n_c calculated in respect to Phillips-Thorpe constraint-counting algorithm for stretching and bending forces ascribed to covalent bonds (see Phillips, 1979; Thorpe 1983, 1995) being given in Table 1. Energetic specificity of molecular-network forming tendencies in arsenic monosulphide AsS is reflected in the developed combined configuration-enthalpy model shown in Fig. 2, evolving configuration-coordinate presentation of calculated cluster-forming energies E_f superimposed with thermodynamic enthalpy diagram of structural relaxation in the respective nanostructured system (Shpotyuk et al. 2019a, b).

Parent realgar-type As_4S_4 cage-like molecule of D_{2d} symmetry evolving eight small-ring entities (four outer pentagons and four inner hexagons) built of eight heteronuclear As-S and two homonuclear As-As covalent bonds is depicted in Fig. 1a, its cluster-forming energy approaching $E_f = -$ 0.58 kcal/mol being most dominated over all other arsenic monosulphide clusters (see Table 1). If a whole matrix of such solid is assumed to be formed only from such As_4S_4 cages, the averaged constraints per atom n_c reaches 2.875, that is smaller than dimensionality of space (3.00), thus corresponding to under-constrained floppy network. Two crystalline structures formed from these As_4S_4 molecules differ in space packing, these being low-temperature α-As_4S_4 character for mineral realgar and high-temperature β-As_4S_4 proper to arsenic monosulphide directly synthesized from elemental ingredients (Bonazzi and Bindi 2008). Within developed configuration-enthalpic model (see Fig. 2), this specificity is reflected in doublet presentation of crystalline state, where the highest well corresponds to As_4S_4 molecules in β-As_4S_4 polymorph (equilibrated with initial 0 kcal/mol level in potential energy barrier), and the lower one is attributed to these molecules in α-As_4S_4. No downhill β-to-α ordering transition can be expected for these As_4S_4 molecules (due to cross-shaded section of inter-well barrier in Fig. 2), despite uphill α-to-β disordering transition is observed under high-energy mechanical milling of mineral realgar α-As_4S_4 (see, e.g., Baláž et al. 2007).

Among different network-forming derivatives of As_4S_4 cage-like molecule, the smallest cluster-forming energy $E_f = -$ 1.29 kcal/mol is character for single x1-broken $As_4S_5H_2$ clusters keeping one hexagon and two pentagons in atomic arrangement (see Fig. 1b). This cluster is optimally constrained in view of $n_c = 3.0$ corresponding to space dimensionality. Due to very low barrier with

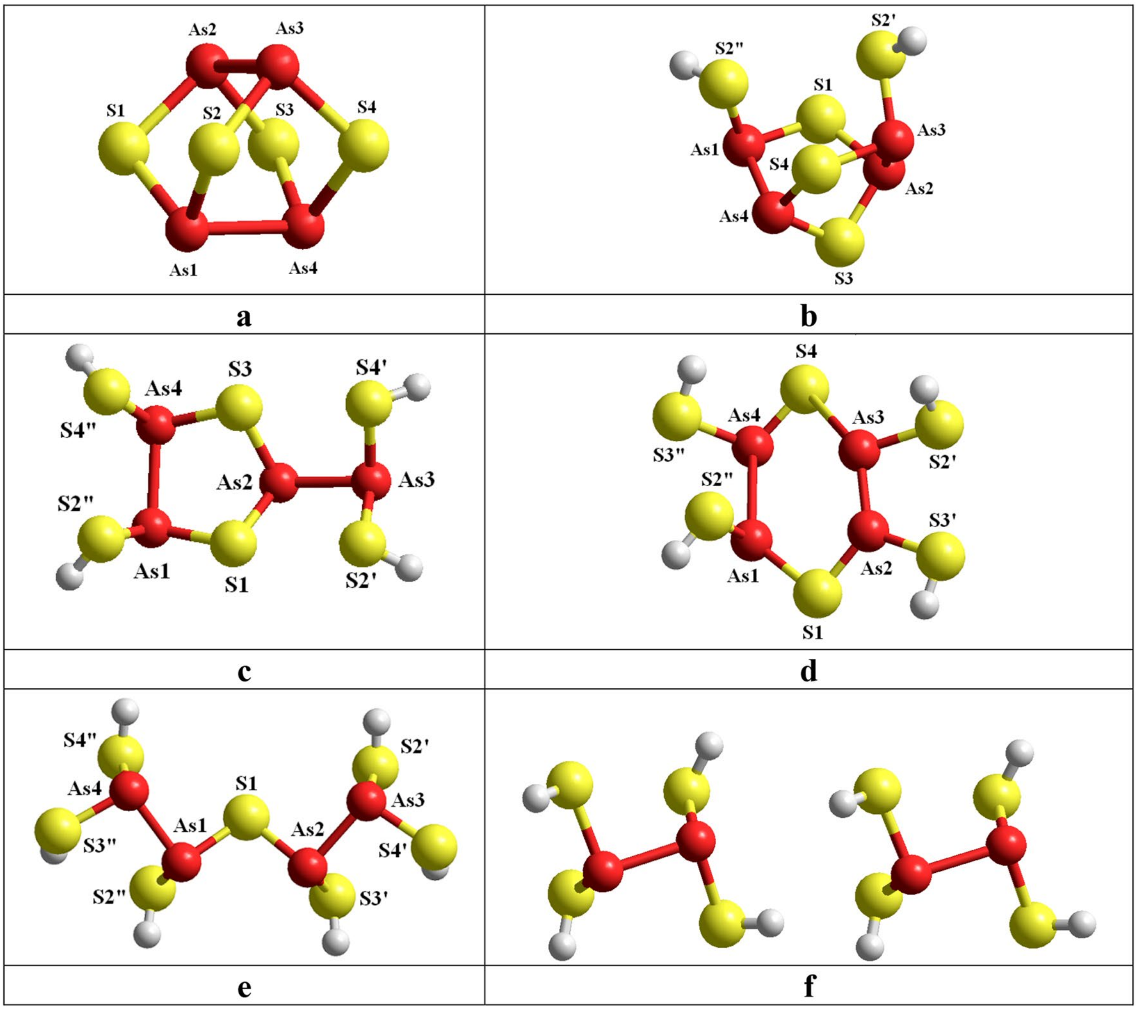

Fig. 1 Geometrically-optimized configurations reconstructed from atomic cluster-simulation code CINCA of realgar-type As_4S_4 cage-like molecule (**a**) and network-forming derivatives formed by single *x*1-break in S1 position (**b**), double *x*2-break in adjusted S1-S3 positions (**c**), double *x*2-break in opposite S1-S4 positions (**d**), triple *x*3-break in S1-S2-S3 positions (**e**), and quadruple *x*4-break in S1-S2-S3-S4 positions (**f**). Terminated H atoms are grey coloured, S and As atoms are depicted by yellow and red balls, respectively, and bonds between atoms are stick-denoted

Table 1 Cluster-forming energies E_f determined in respect to the energy of single $AsS_{3/2}$ pyramid for simulated network-forming derivatives from realgar-type As_4S_4 molecule

Cluster	Cluster-forming pathway	Short-ring entities: pentagons-hexagons		n_c	E_f (kcal/mol)
As_4S_4	No break (*x*0—break)	4	4	2.875	− 0.58
$As_4S_5H_2$	Single *x*1—break in S1 position	2	1	3.00	− 1.29
$As_4S_6H_4$	Double *x*2—break in S1-S3	1	–	3.125	− 3.47
$As_4S_6H_4$	Double *x*2—break in S1-S4	–	1	3.25	− 12.59
$As_4S_7H_6$	Triple *x*3—break in S1-S2-S3	–	–	3.25	− 1.69
$As_4S_8H_8$	Quadruple *x*4—break in S1-S2-S3-S4	–	–	3.25	− 1.72

ground state of parent As_4S_4 molecule ($\Delta E_f = 0.71$ kcal/mol), transformation from molecular to network arrangement occurs as activated uphill tunnelling even in directly synthesized arsenic monosulphide (see Fig. 2), being a source of uncontrolled amorphization (Baláž et al. 2017; Shpotyuk et al. 2018).

$As_4S_6H_4$ clusters represent double *x*2-broken derivatives from As_4S_4 molecule formed by bond breaking on two S

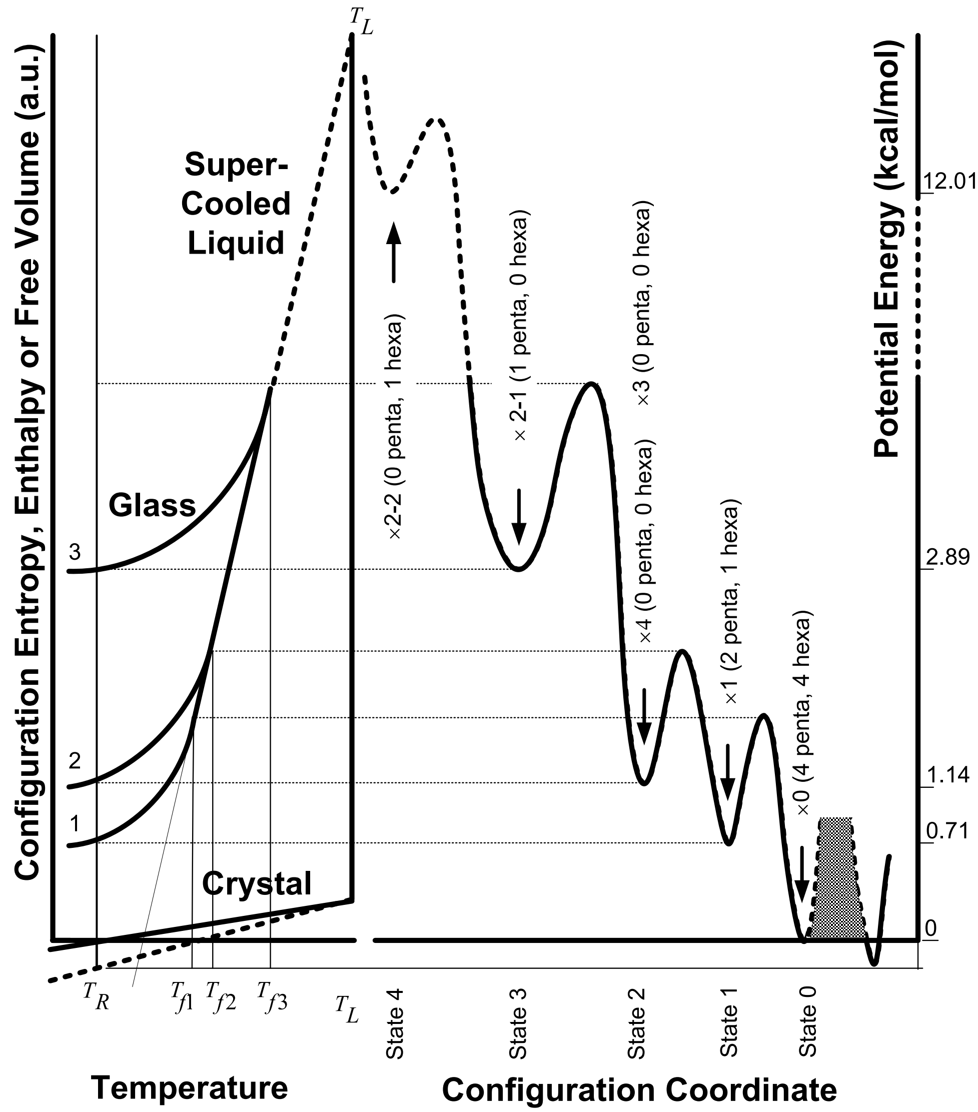

Fig. 2 Combined configuration-enthalpic model of amorphization diversity in nanostructurized arsenic monosulphide AsS

atoms in adjusted and opposite configurations, respectively shown in Fig. 1c, d.

The first of these network-forming clusters having $E_f = -$ 3.47 kcal/mol keep pentagon-type ring in atomic arrangement (see Fig. 1c), thus being slightly over-constrained (i.e. stress-rigid) in view of $n_c = 3.125$. Such network clusters can be stabilized owing to through-barrier tunneling from ground state of As_4S_4 molecule with $\Delta E_f = 2.89$ kcal/mol barrier (Fig. 2), as it occurs in triparticulate grinding media like 1·β-As_4S_4-4·ZnS-1·Fe_3O_4 with hard magnetite Fe_3O_4 grains (20–25 nm) and large amount of tiny zinc sulphide ZnS particles (2–3 nm) acting as additional milling balls on β-As_4S_4 nanocrystallites (see, e.g. Shpotyuk et al. 2019a, b).

Other network cluster originated from x2-break on two S atoms in opposite positions (Fig. 1d) possesses $E_f = -$ 12.59 kcal/mol suggesting essential changes to accommodate hexagon ring in asymmetric configuration of two neighbouring $S_{1/2}$-As-As-$S_{1/2}$ and = As-S-As = bridges. Such clusters are strongly over-constrained ($n_c = 3.25$), they can be stabilized only after through-barrier tunneling with unrealistic $\Delta E_f = 12.01$ kcal/mol (Fig. 2).

$As_4S_7H_6$ clusters are triple x3-broken derivatives from As_4S_4 molecule producing completely network-forming structure built of S-interlinked $(As_2S_{4/2})_n$ chains without any small-ring structural entities (see Fig. 1e). Despite obviously over-constrained nature ($n_c = 3.25$), such clusters possess respectively low $E_f = -$ 1.69 kcal/mol (Table 1), which seems to be nearly the same as for quadruple x4-broken derivatives from As_4S_4 molecules with $E_f = -$ 1.72 kcal/mol ($As_4S_8H_8$ cluster shown in Fig. 1f). This energetic difference can be accepted as uncertainties in cluster-simulation code CINCA for two $As_2S_{4/2}H_4$ clusters with optimally-constrained ($n_c = 3.00$) bridge = As-S-As = (see Shpotyuk et al. 2013). So to stabilize predominantly chain-like network structure in arsenic monosulphide, the energetic barrier ΔE_f of 1.14 kcal/

mol (close to the barrier for single x1-broken derivatives from As_4S_4 cage-like molecules) should be overcome (see Fig. 2). With respect to previous results of intermediate-range structural studies (Baláž et al. 2017; Shpotyuk et al. 2018), such situation is a character for high-energy milling with increased rotational speed (within 200–600 min^{-1}) in monoparticulate β-As_4S_4 or biparticulate β-As_4S_4-Fe_3O_4 grinding media (Shpotyuk et al. 2019a, b).

Conclusions

Competitive amorphization scenarios in arsenic monosulphide derived under nanostructurization from directly-synthesized tetra-arsenic tetra-sulphide β-As_4S_4 polymorph are identified employing ab-initio quantum-chemical modelling route with cluster-simulation code CINCA (cation-interlinked network cluster approach). Geometrically-optimized configurations of realgar-type As_4S_4 cage-like molecule and its network-forming derivatives responsible for amorphization are parameterized.

Under nanostructurization, most plausible are found to be single-broken As_4S_4 nanoclusters keeping one hexagon and two adjacent pentagons in network-forming arrangement, these clusters being responsible for uncontrolled amorphization in directly-synthesized β-As_4S_4 polymorph. Completely-polymerized triple- and quadruple-broken As_4S_4 clusters in chain configurations without any small-ring entities are character for amorphization in monoparticulate β-As_4S_4- and biparticulate β-As_4S_4-Fe_3O_4 composites under high-energy milling. In triparticulate $1{\cdot}\beta$-As_4S_4-$4{\cdot}ZnS$-$1{\cdot}Fe_3O_4$ grinding solution, the amorphizing network is built of double-broken As_4S_4 molecules keeping pentagon rings.

At the basis of calculated cluster-forming energies, the combined configuration-enthalpic model showing amorphization diversity in mechanoactivated arsenic monosulphide is developed.

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Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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