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# Deciphering Fast Ion Transport in Glasses: a Case Study of Sodium and Silver Vitreous Sulfides

Mohammad Kassem,<sup>1</sup> Tinehinane Bounazef,<sup>1</sup> Anton Sokolov,<sup>1</sup> Maria Bokova,<sup>1</sup> Daniele Fontanari,<sup>1</sup> Alex C. Hannon,<sup>2</sup> Igor Alekseev,<sup>1</sup> and Eugene Bychkov<sup>1\*</sup>

<sup>1</sup> Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte d'Opale, 59140 Dunkerque, France

<sup>2</sup> ISIS Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX, U.K.

## ABSTRACT

High-capacity solid-state batteries are promising future products for large-scale energy storage and conversion. Sodium fast ion conductors including glasses and glass ceramics are unparalleled materials for these applications. Rational design and tuning of advanced sodium sulfide electrolytes needs a deep insight into the atomic structure and dynamics in relation with ion transport properties. Using pulsed neutron diffraction and Raman spectroscopy supported by first principles simulations, we show that preferential diffusion pathways in vitreous sodium and silver sulfides are related to isolated sulfur  $S_{\text{iso}}$ , that is, the sulfur species surrounded exclusively by mobile cations with a typical stoichiometry of  $M/S_{\text{iso}} \approx 2$ . The  $S_{\text{iso}}/S_{\text{tot}}$  fraction appears to be a reliable descriptor of fast ion transport in glassy sulfide systems over a wide range of ionic conductivities and cation diffusivities. The  $S_{\text{iso}}$  fraction increases with mobile cation content  $x$ , tetrahedral coordination of the network former and, in case of thiogermanate systems, with germanium disulfide metastability and partial disproportionation,  $\text{GeS}_2 \rightarrow \text{GeS} + \text{S}$ , leading to formation of additional sulfur, transforming into  $S_{\text{iso}}$ . A research strategy enabling to achieve extended and interconnected pathways based on isolated sulfur would lead to glassy electrolytes with superior ionic diffusion.

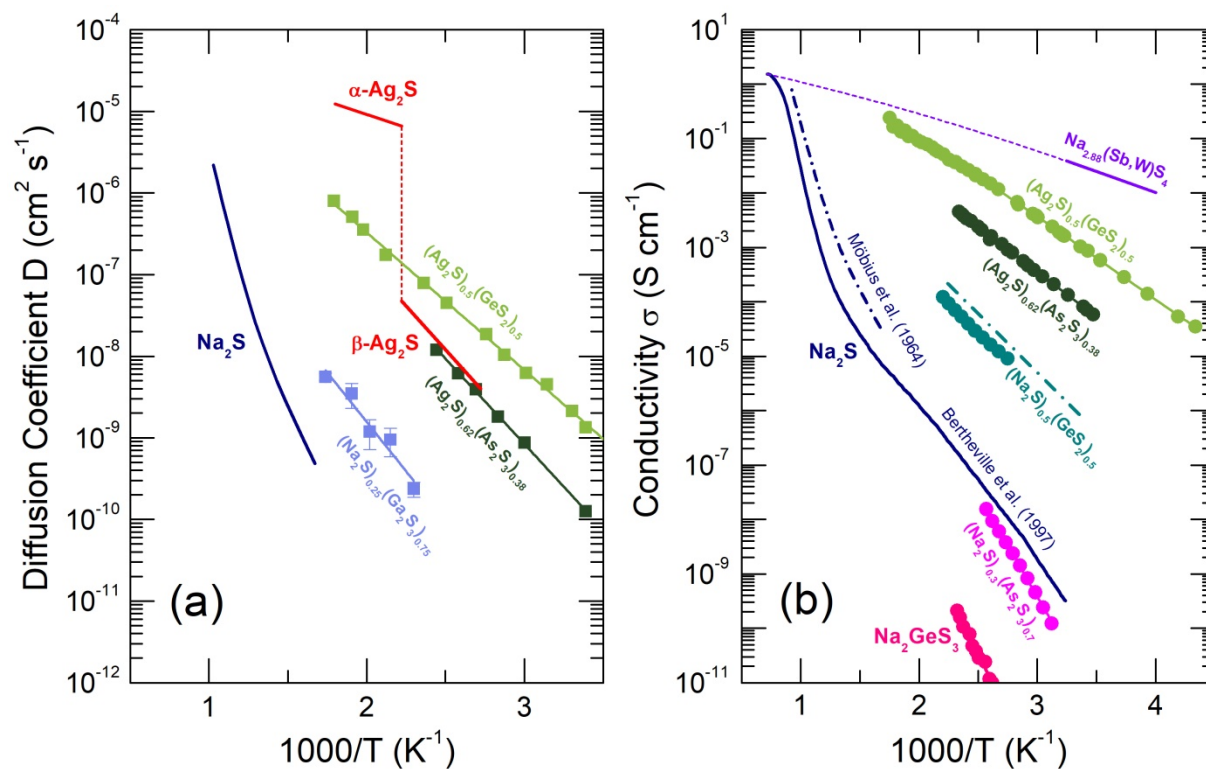
## 1. INTRODUCTION

Carbon-neutral alternative energy production and consumption implies a wide range of large-scale energy storage and conversion including low-cost stationary and mobile sodium devices and installations. Amorphous and crystalline sodium ternary or complex sulfides belong to promising advanced materials for solid-state batteries.<sup>1-3</sup> Rational design of these compounds requires a deep insight into the atomic structure and relationships between the origin of fast ion transport and chemical or structural features. A seminal discovery of cubic Na<sub>3</sub>PS<sub>4</sub> with room-temperature ionic conductivity  $\sigma_i = 0.2 \text{ mS}\cdot\text{cm}^{-1}$ , obtained by crystallization from the glassy state,<sup>4</sup> has triggered an avalanche of research work in this direction, and numerous sodium sulfides and selenides (Na<sub>3</sub>PSe<sub>4</sub>, Na<sub>10</sub>SnP<sub>2</sub>S<sub>12</sub>, Na<sub>3</sub>SbS<sub>4</sub>, Na<sub>11</sub>Sn<sub>2</sub>PnS<sub>12</sub>, where Pn = Sb, P; etc.) were reported,<sup>5-11</sup> reaching  $\sigma_i = 32 \text{ mS}\cdot\text{cm}^{-1}$  at 298 K.<sup>10</sup> A large majority of superionic sodium chalcogenides consist of isolated PnX<sub>4</sub> and/or TX<sub>4</sub> tetrahedra, where X = S, Se; and T = Si, Ge, Sn, connected by sodium.

Fast Li<sup>+</sup> and Na<sup>+</sup> ion transport in superionic solid conductors as Li<sub>10</sub>GeP<sub>2</sub>S<sub>12</sub> or Na<sub>3</sub>SbS<sub>4</sub> is often associated with 3D diffusion pathways representing either a combination of one-dimensional channels crossing diffusion planes<sup>12</sup> or orthogonal channels, parallel to crystallographic axes.<sup>13</sup> Nevertheless, superior ionic mobility requires both disorder, as tetragonal remnants in a cubic lattice,<sup>14</sup> and defects (vacancies, interstitials) in the cationic sublattice.<sup>8-11</sup> Aliovalent substitution, when Ge replaces phosphorus in Li-bearing argyrodites, Li<sub>6+x</sub>P<sub>1-x</sub>Ge<sub>x</sub>S<sub>5</sub>I, causes both anionic (S/I) and cationic site disorder,<sup>15</sup> leading to a significant increase in ionic conductivity up to 4 orders of magnitude. A paddle-wheel mechanism,<sup>16</sup> representing a coupling of tetrahedral rotation and cation translation, is also considered as a favorable factor and a research strategy,<sup>17</sup> enabling to achieve even higher ionic conductivity, especially in glassy electrolytes with lower atomic number density.<sup>18</sup> Another approach consists in using systems composed of super-tetrahedral clusters, that is, B<sub>10</sub>S<sub>20</sub>, revealing a large void space and accommodating highly disordered alkali and sulfide ions, or alkali-halide pairs forming a 'liquid-like' disordered sublattice with enhanced cation mobility.<sup>19</sup>

We should however note that the best Na<sup>+</sup> superionic solids exhibit room-temperature ionic conductivity comparable or lower than the extrapolated conductivity of *hypothetical* high-temperature Na<sub>2</sub>S after experiencing a diffuse second-order phase transition from a regular low-conducting fcc structure to a highly disordered isostructural antifluorite polymorph,<sup>20,21</sup> see also Figure 1 and related references. Similar trend is observed for vitreous silver sulfides suggesting the chemical and topological origin of preferential diffusion pathways is reminiscent of superionic  $\alpha$ -Ag<sub>2</sub>S, Figure 1. The only difference between the two families resides in a high-temperature character of the type-II superionic transition at  $T_c$  in Na<sub>2</sub>S ( $T_c/T_m \approx 0.7$  and  $T_m = 1442 \text{ K}$ ) and Ag<sub>2</sub>S (a type-I transition,  $T_c/T_m \approx 0.4$  and  $T_m = 1115 \text{ K}$ ).<sup>21</sup> Lithium counterparts reveal an intermediate case; fcc Li<sub>2</sub>S has high- $T$  melting,  $T_m = 1465 \text{ K}$ , but  $T_c/T_m \approx 0.5$ .<sup>20</sup> Basically, similar origin of high ionic conductivity was intensively discussed in the past for silver sulfide and silver iodide glasses based essentially on a double extrapolation: (i) from high to ambient temperatures for  $\alpha$ -Ag<sub>2</sub>S or  $\alpha$ -AgI, and (ii) a compositional extrapolation of ambient  $\sigma_i(x)$  to  $x = 1$  for glasses. Nevertheless, no direct structural evidence was found except for crystallization of  $\alpha$ -AgI on splat or roller quenching in glassy (AgI) <sub>$x$</sub> (Ag<sub>3</sub>BO<sub>3</sub>)<sub>1- $x$</sub> , where  $0.78 \leq x \leq 0.90$ .<sup>31,32</sup>

High-resolution diffraction studies using spallation neutron sources and/or 3G synchrotron facilities supported by first-principles simulations enable a better understanding of disordered systems. The structural motifs in crystalline references can be compared in details with their glassy counterparts and reveal previously unnoticed structural features. In particular, it was found that the equilibrium phase diagrams only partially reflect short and intermediate range order in the glass systems in addition to expected structural disorder. Primarily, a topological disorder should be mentioned when unexpected structural motifs were discovered in glasses.



**Figure 1.** (a) <sup>22</sup>Na and <sup>110m</sup>Ag tracer diffusion, and (b) ionic conductivity for benchmark sodium (Na<sub>2</sub>S,<sup>22,23</sup> Na<sub>2.88</sub>Sb<sub>0.88</sub>W<sub>0.12</sub>S<sub>4</sub><sup>10</sup>) and silver (Ag<sub>2</sub>S<sup>24</sup>) fast ion conductors and respective sodium and silver thioarsenate, thiogallate and thiogermanate glasses,<sup>25-30</sup> as well as monoclinic Na<sub>2</sub>GeS<sub>3</sub>.<sup>28</sup>

Sodium and silver, (M<sub>2</sub>S)<sub>x</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>1-x</sub> (M = Na, Ag) and (Ag<sub>2</sub>S)<sub>x</sub>(GeS<sub>2</sub>)<sub>1-x</sub>, vitreous sulfides, where 0.3 ≤  $x$  ≤ 0.6, exhibit isolated sulfur species S<sub>iso</sub>, that is, sulfur without direct contacts to arsenic or germanium and only surrounded by silver or sodium with a typical stoichiometry M/S<sub>iso</sub> ≈ 2.<sup>29,30</sup> Isolated sulfur is not a unique phenomenon for glassy alloys. In crystalline thioarsenates and thiogermanates, S<sub>iso</sub> appears above well-defined stoichiometry limits, M<sub>2</sub>S/As<sub>2</sub>S<sub>3</sub> > 3 ( $x > 3/4$ ) and M<sub>2</sub>S/GeS<sub>2</sub> > 2 ( $x > 2/3$ ), when As or Ge concentration is insufficient to ensure connections to all available sulfur. Superionic silver argyrodite Ag<sub>8</sub>GeS<sub>6</sub> contains 1/3 of S<sub>iso</sub> and 2/3 of terminal sulfur S(*t*) species.<sup>33</sup> However, sodium and silver vitreous sulfides violate the stoichiometry rules and equilibrium phase diagrams; the isolated sulfur species appear well below the crystalline limits.

The ionic conductivity and cation diffusion increases as a function of S<sub>iso</sub>/S<sub>tot</sub> fraction. Glassy (Ag<sub>2</sub>S)<sub>0.5</sub>(GeS<sub>2</sub>)<sub>0.5</sub> and (Ag<sub>2</sub>S)<sub>0.625</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>0.375</sub> have identical silver content, 33.3 at.% Ag, but their <sup>110m</sup>Ag tracer diffusion coefficients appear to be different by a factor of 11±2 at room temperature, Figure 1a, coherent with S<sub>iso</sub>/S<sub>tot</sub> = 17.6±1.4% (As-glass) and 20.6±1.9% (Ge-glass).<sup>29</sup> Vitreous (Na<sub>2</sub>S)<sub>0.3</sub>(As<sub>2</sub>S<sub>3</sub>)<sub>0.7</sub> with a modest S<sub>iso</sub> fraction, 6.2%,<sup>30</sup> exhibits a much lower

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3 room-temperature ionic conductivity  $\sigma_i$  compared to more concentrated  $g\text{-(Ag}_2\text{S)}_{0.6}\text{(As}_2\text{S}_3)_{0.4}$   
4 (the difference in  $\sigma_i$  of 11 orders of magnitude) but also considering sodium thiogallate and  
5 thiogermanate glasses with identical Na content (the difference is roughly a factor of  $10^4$ ), Figure  
6 1b and Figure S1 (Supporting Information). For a detailed analysis, advanced studies of vitreous  
7  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  are required, unraveling the structural and chemical roots of fast ion  
8 transport in glasses, in particular, the nature of mobile cations, that of the host glassy matrix, as  
9 well as relations with equilibrium phase diagrams and crystalline references. This system was  
10 already studied,<sup>25,34-37</sup> but a combined approach involving pulsed neutron diffraction, Raman  
11 spectroscopy, DFT modeling of vibrational properties and first-principles studies of atomic  
12 structure and dynamics, related to well-established ion transport properties, is still missing.  
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## 18 2. EXPERIMENTAL AND SIMULATION DETAILS

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21 **2.1. Synthesis.** Glassy sodium thiogermanates,  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  ( $0.0 \leq x \leq 0.6$ ), and crystalline  
22 references:  $\text{Na}_4\text{Ge}_4\text{S}_{10}$ ,  $\text{Na}_2\text{GeS}_3$ , and  $\text{Na}_6\text{Ge}_2\text{S}_7$ , were obtained by direct synthesis of metallic  
23 sodium (Sigma-Aldrich, 99.9%), sulfur pellets (Alfa Aesar, 99.999%), and previously synthesized  
24 glassy  $\text{GeS}_2$  placed in vitreous carbon crucibles in evacuated silica tubes. The tubes were heated  
25 slowly to 1125-1300 K depending on  $x$ , maintained at this temperature for 24-72 h with  
26 periodic stirring of the melt, and finally quenched in icy salt water. In contrast, the crystalline  
27 thiogermanates after high-temperature homogenization were additionally annealed at 950 K for  
28 at least two weeks and cooled down slowly to room-temperature. The preparation procedures  
29 have been carried out in a glovebox with controlled humidity. Other information related to  
30 temperature regimes and synthesis details was reported elsewhere.<sup>30,38</sup> A Bruker D8 Advance  
31 diffractometer was used to verify the crystal structure of the synthesized references, which was  
32 found to be coherent with the reported results.<sup>39-41</sup>  
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37 **2.2. Raman Spectroscopy Measurements.** The vibrational properties of sodium  
38 thiogermanate glasses and crystals were studied using a LabRAM HR Evolution micro-Raman  
39 spectrometer (Horiba Scientific) in the  $70\text{-}850\text{ cm}^{-1}$  spectral range with a 785 nm solid state  
40 laser as an excitation source. The samples were held in evacuated silica tubes to avoid  
41 interactions and hydrolysis with ambient air humidity. Several spectra at different locations  
42 were taken for each sample to ensure homogeneity and reproducibility of the Raman results.  
43 The spectral background subtraction and data analysis were described in details previously.<sup>42,43</sup>  
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47 **2.3. Neutron Diffraction Measurements.** Pulsed neutron diffraction experiments have been  
48 carried out at the ISIS spallation neutron source (Rutherford Appleton Laboratory, UK). The  
49 GEM diffractometer<sup>44</sup> was used for these measurements at room temperature in vacuum-tight  
50 vanadium containers to avoid hydrogen contamination from atmospheric moisture. No impurity  
51 hydrogen signal was detected. The neutron diffraction data were corrected<sup>45</sup> for background  
52 and container scattering, multiple scattering, self-attenuation, and inelasticity (Placzek) effects  
53 using the GUDRUN program.<sup>46</sup> A vanadium–niobium rod was also measured and used for data  
54 normalization.  
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57 **2.4. Sodium Tracer Diffusion Measurements.** The  $^{22}\text{Na}$  tracer (the life-time  $t_{1/2} = 2.6027$   
58 years, iThemba LABS, Faure, South Africa, radionuclide purity 99.9%) was used for tracer  
59 diffusion experiments in a thin-layer geometry. A drop of radioactive  $^{22}\text{NaCl/HCl}$  solution (pH 2)  
60

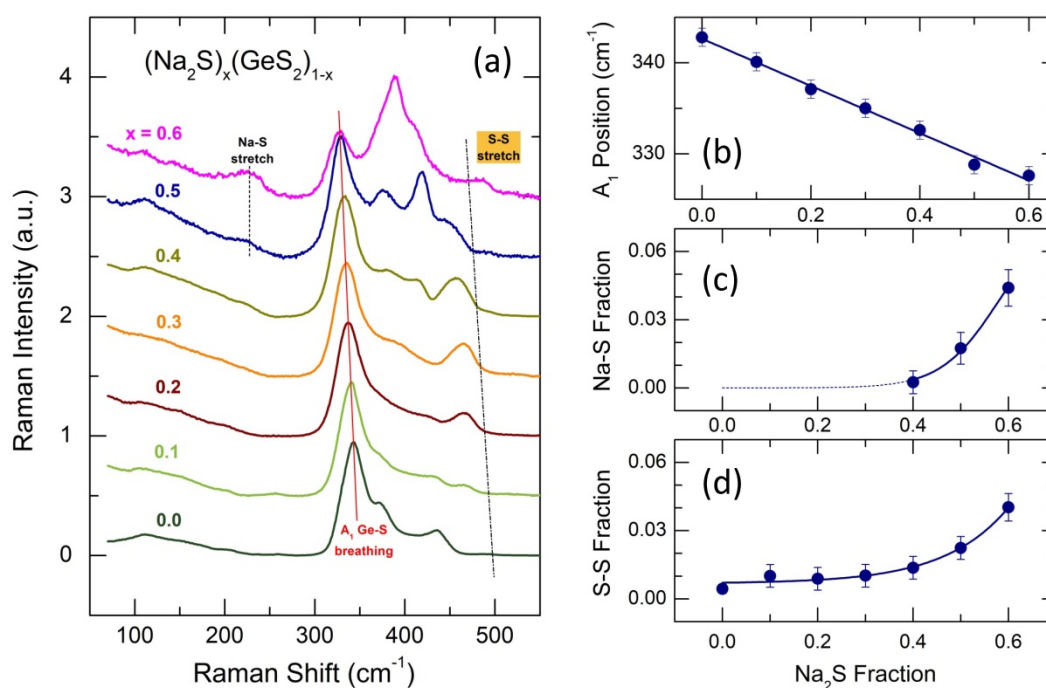
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3 was deposited onto one face of the plane-parallel sample, kept there for 25-30 minutes (a typical  
4 time for isotopic sodium exchange and sorption), wiped with a filter paper, washed twice with a  
5 distilled water and then ethyl alcohol, and dried. The sample was wrapped in aluminum foil,  
6 evacuated and sealed in a Pyrex tube at  $\approx 1$  Pa. The diffusion anneals in a furnace at  $448 \pm 2$  K  
7 were from 20 to 55 days and terminated by quenching the samples in air. The sides of the  
8 sample parallel to the diffusion direction were ground to eliminate surface diffusion effects. The  
9 sample was then sectioned on a parallel grinder. The thickness of each section was determined  
10 either from the density, cross-sectional area, and weight change of the sample or by direct  
11 thickness measurements. Further details on tracer diffusion are given in Supporting  
12 information, including Figures S2 and S3, and were published elsewhere.<sup>47,48</sup>

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16 **2.5. DFT Modeling of Raman Spectra.** The DFT simulations of Raman spectra were carried out  
17 using Gaussian 16 software.<sup>49</sup> The structural optimization and harmonic vibrational frequency  
18 calculations were realized for size-limited Ge-S, Na-S and Na-Ge-S clusters:  $\text{Ge}_4\text{S}_4$ ,  $\text{S}_2\text{Na}_2$ ,  $\text{S}_2\text{Na}_3$ ,  
19  $\text{GeS}_4\text{Na}_4$ ,  $\text{Ge}_2\text{S}_6\text{Na}_2\text{H}_3$ ,  $\text{Ge}_2\text{S}_6\text{Na}_4$ ,  $\text{Ge}_2\text{S}_7\text{Na}_6$ ,  $\text{Ge}_3\text{S}_9\text{Na}_6$ ,  $\text{Ge}_3\text{S}_{10}\text{Na}_6\text{H}_2$ , and  $\text{Ge}_4\text{S}_{10}\text{Na}_4$ . The Becke  
20 three-parameter hybrid exchange functional<sup>50</sup> and the Lee–Yang–Parr correlation functional  
21 (B3LYP)<sup>51</sup> were used for DFT simulations. The small-core relativistic pseudopotential basis set  
22 (cc-pVTZ-PP)<sup>52</sup> and the effective core potentials<sup>53</sup> were applied for cluster geometry  
23 optimization and calculations of harmonic vibrations. Most of the structures were optimized  
24 using the tight convergence option, ensuring adequate convergence and reliability of computed  
25 wavenumbers. An extra quadratically convergent self-consistent field procedure<sup>54</sup> was used for  
26 difficult convergence cases. Further details of the DFT simulations are published elsewhere.<sup>55,56</sup>

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30 **2.6. First-Principles Molecular Dynamics (FPMD) Simulations.** The Born–Oppenheimer  
31 molecular dynamics implemented within the CP2K package<sup>57</sup> was used for structural modeling  
32 of glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ . The generalized gradient approximation (GGA) and the PBE0 hybrid  
33 exchange–correlation functional<sup>58,59</sup> combining the exact Hartree–Fock and DFT approaches  
34 were used. The van der Waals dispersion corrections D3BJ<sup>60</sup> were also applied, reported to have  
35 a positive effect for sodium-containing materials and chalcogenide systems.<sup>61,62</sup> Basically, the  
36 FPMD technique was similar to that reported previously.<sup>63,64</sup> The initial atomic configurations  
37 were created and optimized using the RMC\_POT++ code<sup>65</sup> in comparison with the experimental  
38 neutron structure factor  $S_N(Q)$  to reach a good agreement. The size of the cubic simulation box,  
39 containing 450 atoms (150 Na, 75 Ge and 225 S), was chosen to match the experimental number  
40 density. Further optimization was carried out using DFT, applying the molecularly optimized  
41 correlation consistent polarized triple-zeta valence basis set TZVP along with the norm-  
42 conserving relativistic Goedecker–Teter–Hutter-type pseudopotentials.<sup>66</sup> FPMD simulations  
43 were performed using a canonical *NVT* ensemble with a Nosé–Hoover chain of length 3 as a  
44 thermostat. The simulation boxes were heated from 300 K to 600 K (a supercooled liquid state)  
45 using 100 K steps for 8-10 ps each. At 600 K, the systems were equilibrated for 13 ps and cooled  
46 down to 300 K using the same temperature steps but with a longer simulation time (15-20 ps).  
47 Final equilibration and data collection at 300 K were performed for 20 ps. The connectivity and  
48 ring statistics were analyzed using the R. I. N. G. S. package<sup>67</sup> and a modified connectivity  
49 program.<sup>68</sup> The pyMolDyn code<sup>69</sup> applying the Dirichlet–Voronoi tessellation was used for the  
50 calculation of microscopic voids and cavities.

### 3. RESULTS AND DISCUSSION

**3.1. Raman Spectroscopy.** Typical Raman spectra of the  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses,  $0 \leq x \leq 0.6$ , are shown in Figure 2. Their comparison with the spectra of crystalline sodium thiogermanates of similar or identical chemical composition is given in Figure 3, together with characteristic crystalline motifs in the  $\text{Na}_2\text{S-GeS}_2$  system.<sup>39-41,70,71</sup> Increasing the sodium sulfide content  $x$ , one observes characteristic changes in vibrational properties of both glasses and crystals. The  $A_1$  symmetric in-phase Ge-S breathing in corner-sharing  $\text{CS-GeS}_4$  tetrahedra<sup>55,72-74</sup> remains the most intense vibrational component over the composition range  $x \leq 0.5$  but monotonically shifts to lower frequencies from  $343 \text{ cm}^{-1}$  ( $x = 0$ ) to  $328 \text{ cm}^{-1}$  ( $x = 0.6$ ), Figure 2b, suggesting an increase in Ge-S interatomic distances. In contrast, the  $A_1^c$  companion in-phase Ge-S breathing mode in edge-sharing  $\text{ES-GeS}_4$  tetrahedra at  $373 \text{ cm}^{-1}$  disappears progressively with increasing  $x$ , indicating a significant reduction in population of the ES-units, consistent with exclusively corner-sharing connectivity in crystalline sodium thiogermanates, Figure 3b.

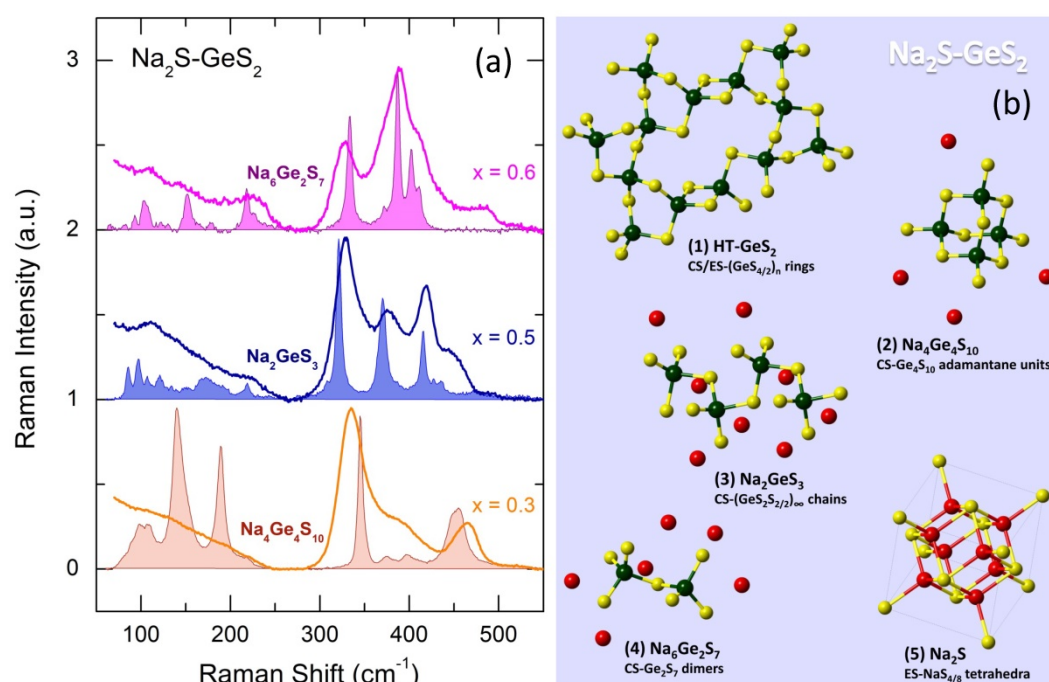


**Figure 2.** (a) Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses; the  $A_1$  symmetric in-phase Ge-S breathing mode is emphasized by the red solid line, the emerging Na-S stretching at  $\approx 220 \text{ cm}^{-1}$  is indicated by the black dashed line, multiple S-S stretching vibrations are located above  $460-490 \text{ cm}^{-1}$  (the dashed-dotted line); composition dependences of (b) the  $A_1$  symmetric Ge-S breathing frequency, and fractional areas of (c) the Na-S and (d) the S-S stretching modes. See text for further details.

Figure 3a reveals the main spectroscopic features are similar in the glasses and crystals, consistent with previous reports,<sup>25</sup> although remarkable differences still exist. Sodium-poor glasses,  $x \leq 0.3$ , seem to contain adamantane units,  $\text{Ge}_4\text{S}(b)_6\text{S}(t)_4$ , where  $\text{S}(t)$  and  $\text{S}(b)$  are terminal and bridging sulfur, respectively, reflected by emerging and growing high-frequency unresolved symmetric and asymmetric Ge-S( $t$ ) stretching modes centered at  $\approx 465 \text{ cm}^{-1}$ , also confirmed by DFT modeling, Figure 4e and Table S1 (Supporting information). The adamantane cages, that is, super-tetrahedra consisting of four  $\text{CS-GeS}_4$  entities and held together by sodium cations, Figure 3b, represent an essential motif in orthorhombic  $\text{Na}_4\text{Ge}_4\text{S}_{10}$ .<sup>39</sup> The shorter Ge-S( $t$ ) distances,  $2.139 \pm 0.004 \text{ \AA}$  vs.  $2.225 \pm 0.021 \text{ \AA}$  for Ge-S( $b$ ), explain a high-frequency shift of the Ge-



$S(t)$  modes. The most intense  $A_1$  in-phase Ge-S breathing of adamantane cages cannot be distinguished from the  $A_1$  counterpart of glassy  $\text{GeS}_2$ , as well as the respective Ge-S breathing vibrations of higher sodium thiogermanates,  $\text{Na}_2\text{GeS}_3$  and  $\text{Na}_6\text{Ge}_2\text{S}_7$ .<sup>40,41</sup>



**Figure 3.** (a) Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses and crystals with similar or identical chemical composition:  $x = 0.3$  and  $\text{Na}_4\text{Ge}_4\text{S}_{10}$  ( $x = 1/3$ ),  $x = 0.5$  and  $\text{Na}_2\text{GeS}_3$  ( $x = 1/2$ ),  $x = 0.6$  and  $\text{Na}_6\text{Ge}_2\text{S}_7$  ( $x = 3/5$ ); (b) crystalline motifs in the  $\text{Na}_2\text{S}-\text{GeS}_2$  system: (1) high-temperature monoclinic HT- $\text{GeS}_2$  polymorph consisting of edge- and corner-sharing ES-/CS- $\text{GeS}_{4/2}$  tetrahedra,<sup>70</sup> (2) orthorhombic tetrasodium closodecathiotetragermanate  $\text{Na}_4\text{Ge}_4\text{S}_{10}$ , formed by adamantane  $\text{Ge}_4\text{S}_{10}$  units connected by sodium,<sup>39</sup> (3) sodium catena-trithiogermanate  $\text{Na}_2\text{GeS}_3$ , consisting of infinite CS- $(\text{GeS}_2\text{S}_{2/2})_\infty$  chains, where sodium resides in the interchain spaces,<sup>40</sup> (4) sodium heptathiodigermanate  $\text{Na}_6\text{Ge}_2\text{S}_7$ , formed by CS- $\text{Ge}_2\text{S}_7$  dimers and connected by Na species,<sup>41</sup> and finally (5) face centered cubic fcc- $\text{Na}_2\text{S}$ , built-up by ES- $\text{Na}_{4/8}$  tetrahedra.<sup>71</sup>

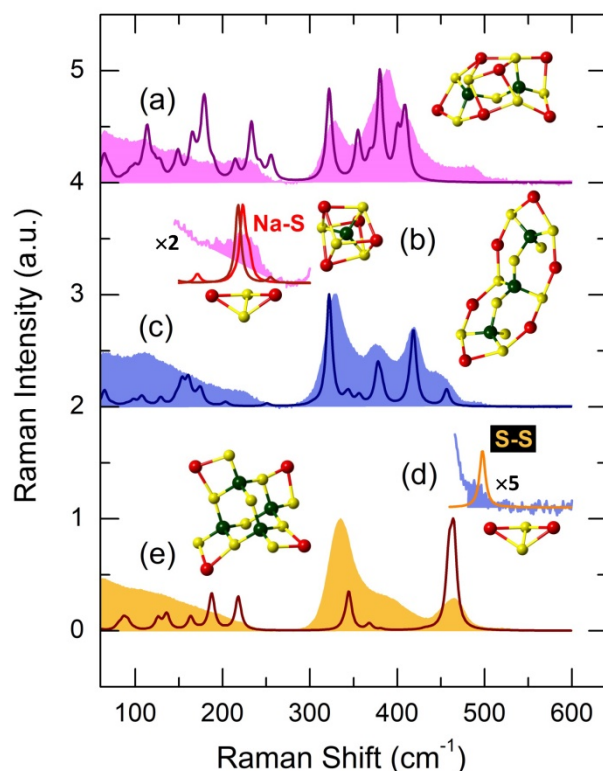
As expected, the dominant separated adamantane units are gradually replaced by CS- $[\text{GeS}(t)_2\text{S}(b)_{2/2}]_\infty$  chains at  $0.3 \leq x \leq 0.5$ , evidenced by two arising mid-frequency vibration features at  $\approx 378$  and  $\approx 416$   $\text{cm}^{-1}$ , corresponding to poorly resolved symmetric and asymmetric Ge-S stretching involving bridging and terminal sulfur, respectively. The DFT Raman spectrum of the optimized CS- $\text{Ge}_3\text{S}_{10}\text{Na}_6\text{H}_2$  cluster reproduces well the main experimental features of the equimolar  $x = 0.5$  glass, Figure 4c. The high-frequency Ge-S( $t$ ) stretching exhibits a step-like red shift above  $x = 0.3$  from 465 to 438  $\text{cm}^{-1}$ , Figure S4 (Supporting information), presumably related to increasing Ge-S( $t$ ) interatomic distances, as in orthorhombic  $\text{Na}_4\text{Ge}_4\text{S}_{10}$ , 2.139 Å, monoclinic  $\text{Na}_2\text{GeS}_3$ ,  $2.16 \pm 0.02$  Å,<sup>40</sup> and monoclinic  $\text{Na}_6\text{Ge}_2\text{S}_7$ ,  $2.192 \pm 0.010$  Å.<sup>41</sup> Finally, vitreous  $(\text{Na}_2\text{S})_{0.6}(\text{GeS}_2)_{0.4}$  at the limit of the glass-forming range reveals the most intense poorly resolved Ge-S stretching modes at  $\approx 389$   $\text{cm}^{-1}$ , similar to pyrothiogermanate  $\text{Na}_6\text{Ge}_2\text{S}_7$ ,<sup>41</sup> consisting of CS- $\text{Ge}_2\text{S}(b)\text{S}(t)_6$  dimers, Figure 3b. Our DFT modeling using CS- $\text{Ge}_2\text{S}_7\text{Na}_6$  clusters shows several symmetric and asymmetric stretching features within this frequency range, involving terminal sulfur species  $S(t)$ , Figure 4a, Tables S1 and S2.



The crystalline structural motifs alone cannot explain the Raman spectra of glasses entirely. In particular, we note multiple S-S stretching above 460-490  $\text{cm}^{-1}$ , whose integrated fractional area  $f_{\text{SS}}(\omega)$  increases systematically at  $x \geq 0.3$ , Figure 2c,

$$f_{\text{SS}}(\omega) = \frac{\int_{\omega_{\text{SS}}}^{\omega_{\text{max}}} I_x(\omega) d\omega}{\int_{\omega_{\text{min}}}^{\omega_{\text{max}}} I_x(\omega) d\omega}, \quad (1)$$

where  $I_x(\omega)$  represents the normalized Raman spectrum of a  $\text{Na}_2\text{S-GeS}_2$  glass,  $460 \text{ cm}^{-1} \leq \omega_{\text{SS}} \leq 490 \text{ cm}^{-1}$  depending on  $x$ ,  $\omega_{\text{min}} = 260 \text{ cm}^{-1}$  and  $\omega_{\text{max}} = 600 \text{ cm}^{-1}$ . A typical integration procedure is given in Figure S5 (Supporting information) with additional comments.



**Figure 4.** Experimental Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses and DFT replicas of characteristic vibration features: (a)  $x = 0.6$  (highlighted in magenta) and  $\text{CS-Ge}_2\text{S}_7\text{Na}_6$  (the purple line), (b) Na-S stretching mode in the  $x = 0.6$  glass, and  $\text{S}_2\text{Na}_2$  (the brown line) and  $\text{GeS}_4\text{Na}_4$  (the red line) clusters, (c)  $x = 0.5$  (highlighted in light blue) and  $\text{CS-Ge}_3\text{S}_{10}\text{Na}_6\text{H}_2$  (the dark blue line), (d) S-S stretching mode in the  $x = 0.5$  alloy and  $\text{S}_2\text{Na}_2$  cluster (the orange line), (e)  $x = 0.3$  (yellow) and  $\text{Ge}_4\text{S}_{10}\text{Na}_4$  cluster (the dark brown line). DFT-optimized Na-Ge-S and Na-S clusters are also shown (the insets). The terminal hydrogen species for  $\text{CS-Ge}_3\text{S}_{10}\text{Na}_6\text{H}_2$  are omitted, and the H-related vibrations are removed from the DFT spectrum. See text for further details.

The origins of the S-S stretching are multiple. Stoichiometric glassy matrix  $\text{GeS}_2$  shows a small chemical disorder,  $2\text{Ge-S} \rightarrow \text{Ge-Ge} + \text{S-S}$ . As a result, ethane-like  $\text{ETH-Ge}_2\text{S}_6$  units and S-S dimers appear in the glass network detected by Raman spectroscopy<sup>74-76</sup> and reproduced by first-principles simulations,<sup>55,73-74</sup> see also Figure S6 and corresponding text. On the other hand, Raman studies of fcc  $\text{Na}_2\text{S}$  have shown the presence of two S-S stretching modes at 461 and 479  $\text{cm}^{-1}$  attributed to polysulfide bridges.<sup>77</sup> Basically, the S-S stretching modes in crystalline and glassy sodium polysulfides ( $\text{Na}_2\text{S}_2$ ,  $\text{Na}_2\text{S}_3$ , etc.) are located between 410 and 490  $\text{cm}^{-1}$ ,<sup>78,79</sup> in excellent agreement with our experimental results and DFT simulations. Two types of size-

limited polysulfide clusters were used for DFT modeling:  $S_2Na_2$ , Figure 4d, and  $S_2Na_3$ , Figure S7, representing elements of the structural motifs in  $\alpha$ - and  $\beta$ -polymorphs of  $Na_2S_2$ , Figure S7.<sup>78,79</sup> The S-S stretching frequencies in polysulfide units depend on S-S interatomic distances and vary between  $468\text{ cm}^{-1}$  ( $r_{SS} = 2.16\text{ \AA}$ ) and  $528\text{ cm}^{-1}$  ( $r_{SS} = 2.10\text{ \AA}$ ).

Sodium-rich glasses,  $x > 0.4$ , reveal also a rising spectroscopic feature at  $\approx 220\text{ cm}^{-1}$  (Figure 2a,c), presumably related to Na-S stretching. Face centered cubic  $Na_2S$  shows Raman and IR-active vibrational features between  $190$  and  $220\text{ cm}^{-1}$ ,<sup>77,80</sup> confirmed by inelastic neutron scattering.<sup>81</sup> In addition, our DFT modeling of Na-S and Na-Ge-S clusters is consistent with this assumption, Figures 4b, S7 and S8, Tables S1 and S2.

**3.2. Pulsed Neutron Diffraction.** Two  $Na_2S$ - $GeS_2$  glass compositions have been studied using pulsed neutron diffraction:  $(Na_2S)_{0.3}(GeS_2)_{0.7}$  and  $(Na_2S)_{0.5}(GeS_2)_{0.5}$ . The Faber-Ziman neutron structure factors  $S_N(Q)$  of the studied sodium thiogermanate glasses are shown in Figure 5 together with that for glassy  $GeS_2$

$$S_N(Q) = \sum_{\alpha,\beta} w_{\alpha\beta}^N S_{\alpha\beta}(Q), \quad (2)$$

and the neutron weighting factors are defined as

$$w_{\alpha\beta}^N = (2 - \delta_{\alpha\beta}) \frac{c_\alpha \bar{b}_\alpha c_\beta \bar{b}_\beta}{|\sum_\alpha c_\alpha \bar{b}_\alpha|^2}, \quad (3)$$

where  $c_\alpha$  and  $\bar{b}_\alpha$  are, respectively, the atomic concentration and the average of the neutron-nucleus scattering length of element  $\alpha$ ,  $\delta_{\alpha\beta}$  is the Kronecker delta function. The derived structure factors are similar to previously reported results, obtained for glasses, prepared by mechanical milling.<sup>37</sup>

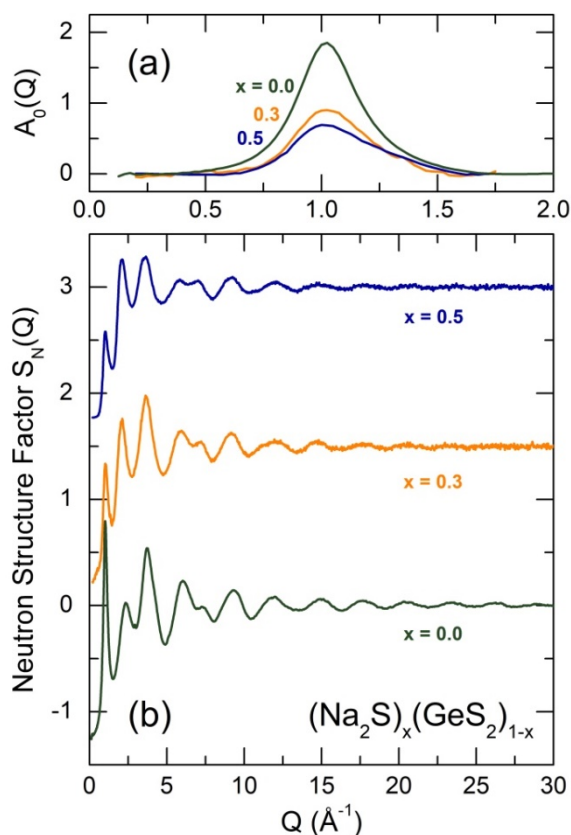
We note a usual decrease of the first sharp diffraction peak (FSDP) at  $Q_0 \approx 1\text{ \AA}^{-1}$  with increasing sodium sulfide content  $x$  and an increase of the principal peak PP at  $Q_1 \approx 2.2\text{ \AA}^{-1}$ . The isolated FSDPs obtained using the subtraction procedure<sup>82,83</sup> are shown in Figure 5a. We note that the FSDP amplitude  $A_0$  has decreased by a factor of  $\approx 2$  between g- $GeS_2$  and  $(Na_2S)_{0.3}(GeS_2)_{0.7}$  glass but further FSDP reduction is less significant. The FSDP position  $Q_0$  remains nearly invariant, however, the FSDP shape becomes increasingly asymmetric.

Similar trend was observed for the PP amplitude and position. The biggest change in the PP amplitude appears to be between  $x = 0$  and  $x = 0.3$ , while the difference between the two sodium thiogermanate glasses is negligible. The PP position  $Q_1$  is shifted from  $2.33$  ( $x = 0$ ) to  $2.09\text{ \AA}^{-1}$  ( $x = 0.3$ ) while the equimolar glass shows  $Q_1 = 2.08\text{ \AA}^{-1}$ .

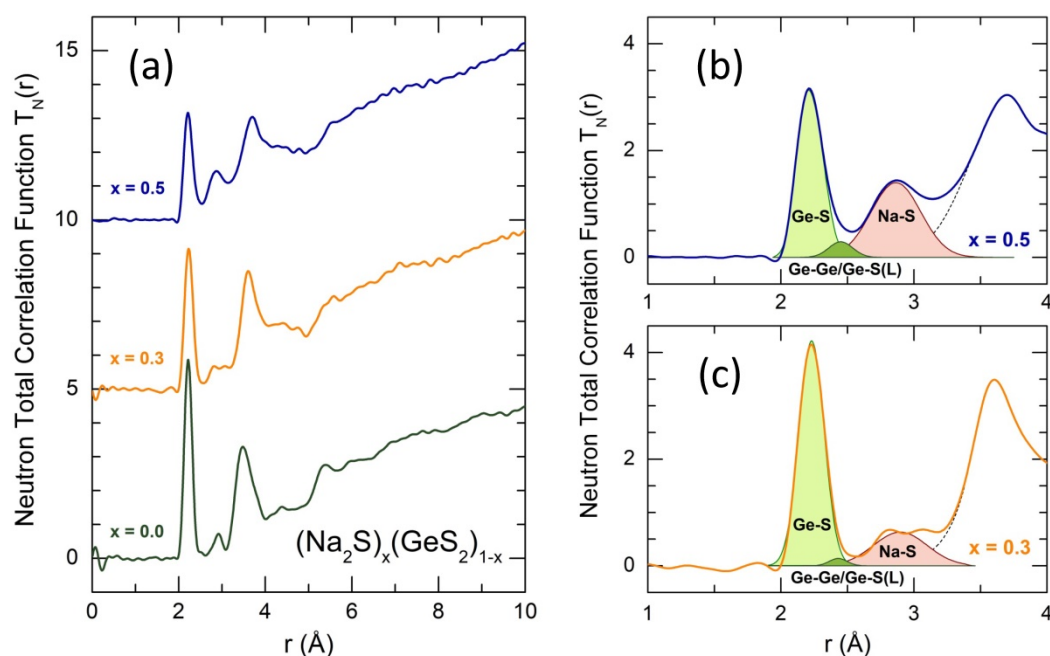
The neutron total correlation functions  $T_N(r)$ , obtained using the Fourier transform with  $Q_{\max} = 30\text{ \AA}^{-1}$ , are shown in Figure 6,

$$T_N(r) = 4\pi\rho_0 r + \frac{2}{\pi} \int_0^{Q_{\max}} Q [S_N(Q) - 1] \sin Qr M(Q) dQ, \quad (4)$$

where  $M(Q)$  is the Lorch modification function and  $\rho_0$  the experimental number density.



**Figure 5.**  $Q$ -space neutron diffraction data for  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses:  $x = 0, 0.3$  and  $0.5$ ; (a) isolated first sharp diffraction peaks  $A_0(Q)$ , (b) neutron structure factors  $S_N(Q)$ . Data for glassy  $\text{GeS}_2$  were taken from our previous work.<sup>82</sup>



**Figure 6.** Real-space neutron diffraction data for  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses:  $x = 0, 0.3$  and  $0.5$ ; (a) neutron total correlation functions  $T_N(r)$ ; fitting results for (b)  $x = 0.5$  and (c)  $x = 0.3$ ; the nearest neighbor correlations are highlighted: Ge-S (light green), Ge-Ge/Ge-S(L) (green) and Na-S (light red). See text for further details.

The first peak at  $\approx 2.2$  Å corresponds to Ge-S nearest neighbors.<sup>37,76,82,84</sup> This peak decreases with  $x$  in accordance with stoichiometric relations in  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses, and its position shifts to larger distances (Table 1) indicating a certain expansion of the  $\text{GeS}_2$  glass matrix with increasing  $x$ . The last trend is also confirmed by a monotonic red shift of the  $A_1$  in-phase Ge-S breathing mode, Figure 2b.

**Table 1.** Interatomic distances  $r_{ij}$  and coordination numbers  $N_{ij}$  in  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses derived from the least-square fitting of the experimental data sets and FPMD modeling ( $x = 0.5$ ).

$x$	S-S		Ge-S		Ge-Ge(1) Ge-S(L)*		Ge-Ge(ES)		Na-S	
	$r_{ij}$ (Å)	$N_{ij}$	$r_{ij}$ (Å)	$N_{ij}$	$r_{ij}$ (Å)	$N_{ij}$	$r_{ij}$ (Å)	$N_{ij}$	$r_{ij}$ (Å)	$N_{ij}$
Neutron diffraction										
0	–	–	2.218(5)	3.93(5)	2.43(2)	0.03(2)	2.90(2)	0.49(5)	–	–
0.3	–	–	2.231(5)	3.65(5)	2.43(2)	0.07(4) 0.09(5)*	–	–	2.90(5)	4.1(3)
0.5	–	–	2.250(5)	3.46(5)	2.45(2)	0.23(8) 0.33(11)*	–	–	2.86(3)	4.4(2)
FPMD modeling										
0.5	2.10	0.27	2.22**	3.58	2.45**	0.09	3.19	0.27	2.79**	4.5(5)

The 2.44(1) Å peak corresponds either to Ge-Ge(1) first nearest neighbors/Ge-Ge homopolar bonds and/or to long Ge-S(L) distances; Ge-Ge(ES) corresponds to short Ge-Ge second neighbors in edge-sharing ES- $\text{GeS}_4$  tetrahedra; \* Ge-S(L) partial coordination number; \*\* strongly asymmetric peaks.

The second peak in g- $\text{GeS}_2$  at 2.9 Å corresponds to short Ge-Ge second neighbor distances related to edge-sharing ES- $\text{GeS}_4$  tetrahedra. The monoclinic lattice of high-temperature HT- $\text{GeS}_2$  polymorph<sup>70</sup> is built-up by corner-sharing CS- $\text{GeS}_4$  and edge-sharing ES- $\text{GeS}_4$  units, Figure 3b. Similar situation exists in glassy  $\text{GeS}_2$ .<sup>76,82,84</sup> In sodium thiogermanate glasses, the presence of short Ge-Ge distances is questionable since an emerging new feature appears at  $\approx 2.9$  Å, related to Na-S nearest neighbors and similar to that in  $\text{Na}_2\text{S-As}_2\text{S}_3$  glasses.<sup>30</sup> Consequently, this peak may have two contributions: short Ge-Ge second neighbors and Na-S nearest contacts. We note however a decrease of the  $A_1^c$  companion mode at 373  $\text{cm}^{-1}$  in Raman spectra of thiogermanate glasses, Figure 2a, suggesting less populated edge-sharing units.

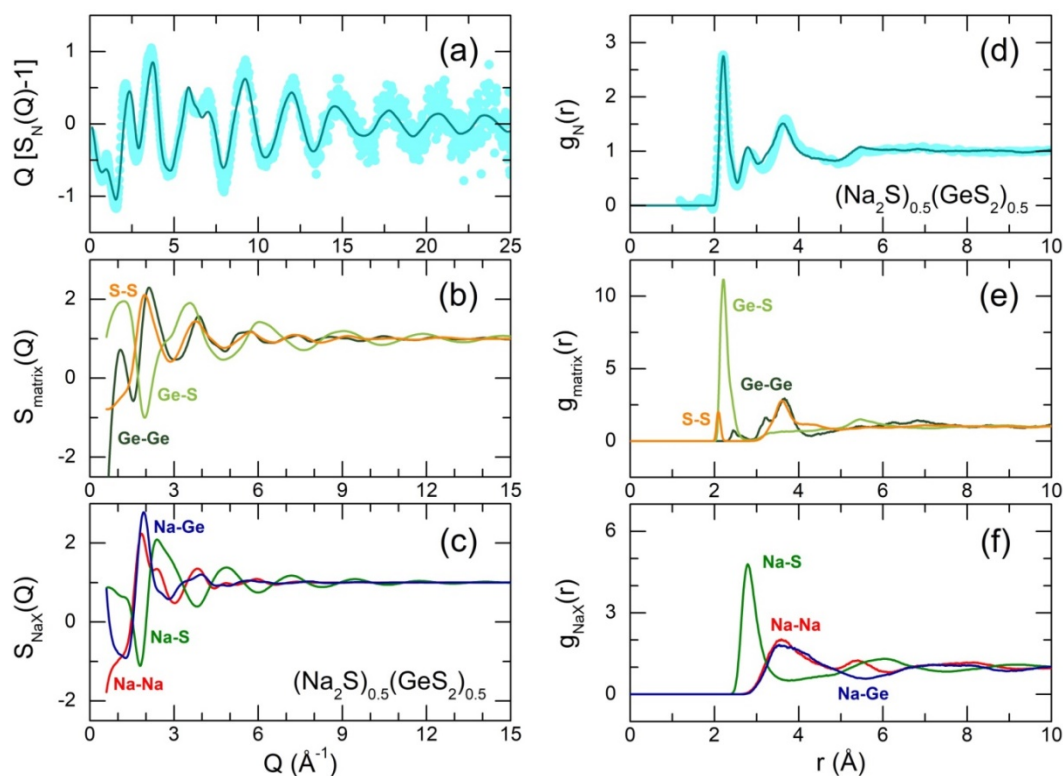
The second neighbor peak at 3.5 Å in g- $\text{GeS}_2$  also shifts to higher  $r$  with increasing  $x$  and appears at 3.7 Å for sodium thiogermanate glasses, confirming the network expansion. More distant features above 5 Å are becoming flat indicating disappearance of the intermediate range order, characteristic of the  $\text{GeS}_2$  glassy host, also confirmed by decreasing FSDP.

A close inspection of the asymmetric first neighbor peak shows the presence of an additional feature at  $\approx 2.44$  Å. This feature in Ge-rich binary sulfide glasses has a dual nature: (a) Ge-Ge first neighbors indicating the presence of a small fraction of homopolar Ge-Ge bonds, or (b) Ge-S(L) long distances with three-fold coordinated sulfur  $\text{S}_{3\text{F}}$  and germanium  $\text{Ge}_{3\text{F}}$ .<sup>82</sup>

Typical fitting procedure of  $T_N(r)$  using Gaussian functions is shown in Figure 6b,c. The fitting results are summarized in Table 1. Two limiting values are given for the 2.44 Å peak,  $N_{\text{Ge-Ge}(1)}$  and  $N_{\text{Ge-S(L)}^*}$ , calculated assuming the absence of long Ge-S(L) or Ge-Ge(1) first neighbors, respectively. The tetrahedral local coordination of germanium,  $\text{Ge}_{4\text{F}}$ , remains mostly intact,  $N_{\text{Ge-X}} \geq 3.7$  or  $\text{Ge}_{4\text{F}}$  fraction  $\geq 70\%$ , where  $N_{\text{Ge-X}} = N_{\text{Ge-S}} + N_{\text{Ge-Ge}}$ . Nevertheless, the exact

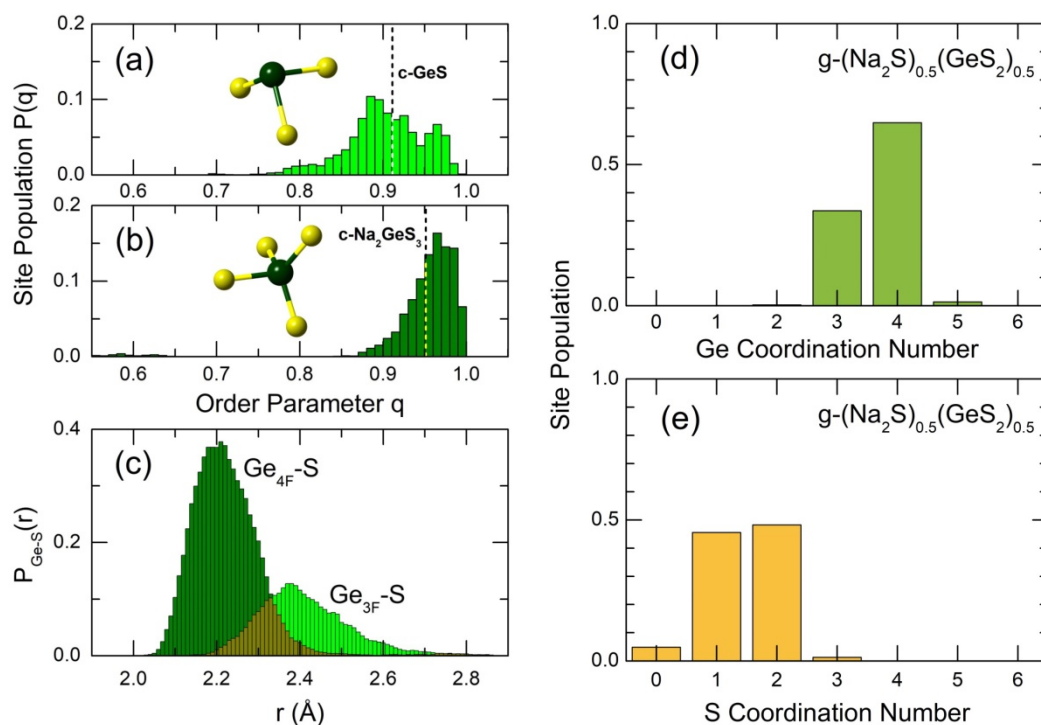
values may change from  $N_{\text{Ge-S}} = 3.8$  ( $x = 0.5$ ,  $N_{\text{Ge-Ge}(1)} = 0$ ) to  $N_{\text{Ge-X}} = 3.7$  ( $x = 0.5$ ,  $N_{\text{Ge-S(L)}} = 0$ ). The sodium local coordination appears to be  $4.1 \leq N_{\text{Na-S}} \leq 4.4$ , assuming the absence of ES-tetrahedra with short Ge-Ge second neighbors. We should however note that this value was obtained by direct fitting with symmetric functions. The sodium local environment in crystalline thiogermanates is characterized by a distribution of Na-S distances, and the above approach could lead to underestimated  $N_{\text{Na-S}}$ . Similar situation was already observed in  $\text{Na}_2\text{S-As}_2\text{S}_3$  glasses, requesting an advanced modeling using the first-principles molecular dynamics.<sup>30</sup>

**3.3. FPMD Modeling of  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ .** The simulated neutron interference function  $Q[S_{\text{N}}(Q) - 1]$  is shown in Figure 7a together with experimental data. The FPMD modeling using hybrid GGA/PBE0 functional describes the obtained neutron diffraction results reasonably well. The oscillation amplitudes and periodicity are in good agreement with the experiment. A typical problem of the small FPMD simulation boxes, related to heavy computational costs, is a lower amplitude of the FSDP and PP at  $1.0$  and  $2.1 \text{ \AA}^{-1}$ , respectively. In case of  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ , we also observed a small shift of the PP to higher  $Q$ . The experimental and simulated neutron pair-distribution functions  $g_{\text{N}}(r)$  are shown in Figure 7d. We also note a good agreement for the nearest neighbors ( $r \lesssim 3 \text{ \AA}$ ) and a slight shift to lower  $r$  for more distant correlations.



**Figure 7.** FPMD of equimolar  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ : (a) neutron interference function  $Q[S_{\text{N}}(Q) - 1]$  (the solid line) plotted together with obtained experimental data (the light cyan circles); partial structure factors  $S_{ij}(Q)$  for (b) Ge-Ge (dark green), Ge-S (light green), S-S (yellow), and (c) Na-S (green), Na-Na (red), and Na-Ge (dark blue) correlations; (d) FPMD (the solid line) and experimental (the light cyan circles) neutron pair-distribution functions  $g_{\text{N}}(r)$ ; partial pair-distribution functions  $g_{ij}(r)$  for (e) Ge-Ge, Ge-S, S-S, and (f) Na-S, Na-Na, and Na-Ge atomic pairs.

The partial structure factors  $S_{ij}(Q)$  are shown in Figure 7b,c. We note that the main contribution to the FSDP comes from Ge-Ge and to some extent from Ge-S correlations while a large negative contribution is related to the Na-Ge partial structure factor. The FPMD partial pair-distribution functions  $g_{ij}(r)$  are summarized in Figure 7e,f. As expected, the main first nearest neighbor peak essentially consists of Ge-S atomic pairs centered at 2.22 Å. The peak is strongly asymmetric consisting of short  $\text{Ge}_{4\text{F}}\text{-S}$  and long  $\text{Ge}_{3\text{F}}\text{-S}$  distances as in crystalline  $\text{GeS}_2$  or sodium thiogermanates,  $2.14 \leq r_{\text{Ge}_{4\text{F}}\text{-S}} \leq 2.26$  Å,<sup>39-41,70</sup> and orthorhombic  $\text{GeS}$ ,  $r_{\text{Ge}_{3\text{F}}\text{-S}} = 2.443$  Å.<sup>85</sup> The statistical analysis of FPMD simulation boxes in thermal equilibrium at 300 K yields  $\text{Ge}_{4\text{F}}\text{-S}$  and  $\text{Ge}_{3\text{F}}\text{-S}$  distance distributions, Figure 8c, centered at 2.22 Å and 2.38 Å, respectively.



**Figure 8.** FPMD structural parameters for Ge-S subnetwork in glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ : (a,b) orientational order parameter  $q$  and (c) Ge-S distance distributions for four-fold  $\text{Ge}_{4\text{F}}$  and three-fold  $\text{Ge}_{3\text{F}}$  germanium species; (d) germanium and (e) sulfur local coordination distributions. The  $q$ -parameters for crystalline  $\text{GeS}$  and  $\text{Na}_2\text{GeS}_3$  are also shown.

We also note a small fraction of homopolar Ge-Ge bonds at 2.45 Å, seen in the diffraction and Raman experiments (Figure S6 and respective comments), and an S-S first neighbor peak at 2.10 Å. A weak amplitude of the S-S homopolar bonds makes impossible to detect them in a neutron scattering experiment, taking into account a small neutron coherent scattering length for sulfur ( $\bar{b} = 2.847$  fm) compared to germanium (8.185 fm) and sodium (3.58 fm). Nevertheless, Raman spectroscopy of equimolar glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  shows the S-S stretching, Figure 4d, supported by DFT modeling with consistent S-S interatomic distances.

The FPMD partial coordination numbers are collected in Table 1, revealing a good agreement with the experimental values. In particular, the total germanium coordination was also found to be below four:  $N_{\text{Ge-X}} = N_{\text{Ge-S}} + N_{\text{Ge-Ge}} = 3.58 + 0.09 = 3.67$ . It means that the Ge-centered polyhedra contain both tetrahedral  $\text{GeX}_4$  and trigonal  $\text{GeX}_3$  entities. The Ge coordination distribution is shown in Figure 8d and reveals  $\frac{2}{3}$  of tetrahedra and  $\frac{1}{3}$  of pyramids with negligible population of under- and over-coordinated Ge-X units.



The tetrahedral shape of  $\text{GeX}_4$  entities clearly shows the orientational order parameter  $q$ ,<sup>86,87</sup> Figure 8a and b, extended beyond the tetrahedral geometry<sup>88-90</sup>

$$q = 1 - \frac{3}{8} \sum_{j=1}^{n-1} \sum_{k=j+1}^n \left( \cos \psi_{jk} + \frac{1}{3} \right)^2, \quad (5)$$

where  $\psi_{jk}$  is the X-Ge-X angle of a given  $\text{GeX}_n$  unit, see also Figure S9 and related more detailed comments. The non-tetrahedral fraction is negligible, 2.6%. Basically, the  $\text{GeX}_4$  tetrahedra are slightly more distorted than those in monoclinic  $\text{Na}_2\text{GeS}_3$ , confirmed also by the S-Ge<sub>4F</sub>-S bond angle distribution  $B_{\text{SGeS}}(\theta)$ , Figure S10b. In contrast to tetrahedral germanium, the  $\text{GeX}_3$  trigonal pyramids are highly distorted in comparison with orthorhombic GeS evidenced by  $P(q)$ , Figures 8a and S9a, and  $B_{\text{SGeS}}(\theta)$ , Figure S10a.

The partial sulfur local coordination,  $N_{\text{S-X}} = N_{\text{S-Ge}} + N_{\text{S-S}} = 1.19 + 0.27 = 1.46$ , is below two. In addition to usual bridging sulfur S(*b*),  $N_{\text{S}(b)\text{-Ge}} = 2$ , glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  contains a comparable fraction of terminal sulfur S(*t*),  $N_{\text{S}(t)\text{-Ge}} = 1$ , Figure 8e. Ideally, these two fractions should be identical for equimolar composition:  $\text{Na}_2\text{S} + \text{GeS}_2 = \text{GeS}(t)_2\text{S}(b)_{2/2} + 2\text{Na}^+$ . The simulated values are very close to these expectations. We should also note a non-negligible fraction of isolated sulfur, which does not have Ge nearest neighbors. We will discuss the role of these sulfur species later.

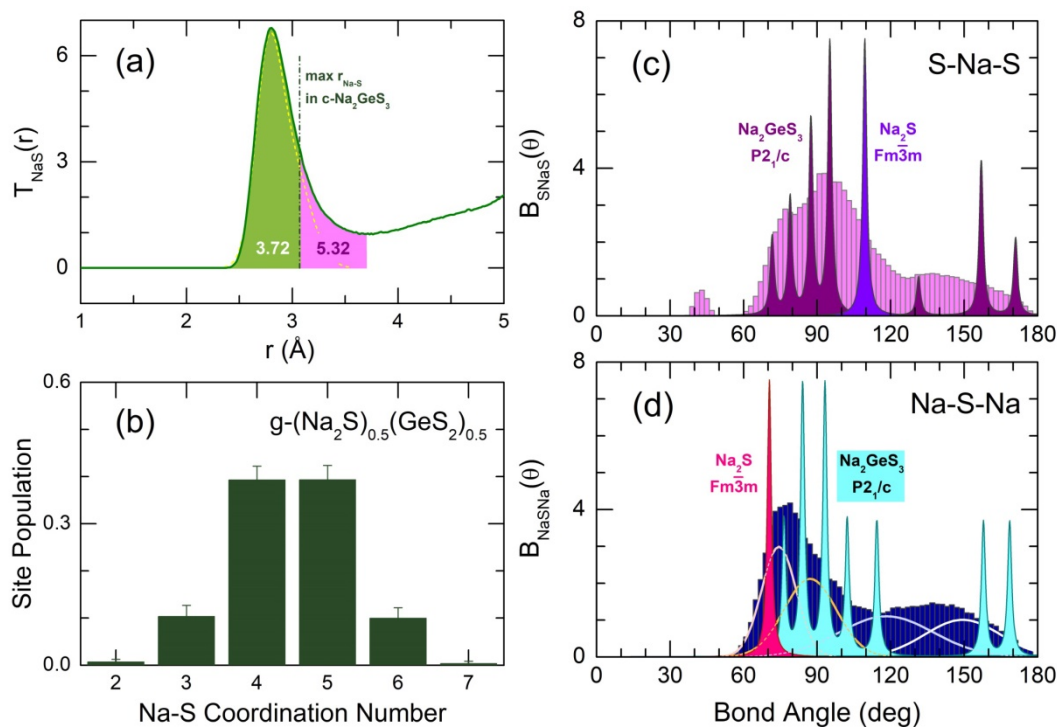
The Ge-Ge second neighbor correlations exhibit a bimodal shape, Figure 7e. The short Ge-Ge second neighbor distances at 3.19 Å are related to edge-sharing units, supported by the low- $\theta$  shoulder for  $B_{\text{SGeS}}(\theta)$  and bimodal distributions of  $B_{\text{GeSGe}}(\theta)$ , Figure S10. The longer Ge-Ge correlations at 3.67 Å correspond to CS-tetrahedra/pyramids. The fraction of the ES-entities is lower in glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ ,  $f_{\text{ES}} = 0.27$ , compared to  $f_{\text{ES}} = 0.49 \pm 0.05$  for g- $\text{GeS}_2$  (Table 1). The tetrahedral connectivity, reflected by Ge<sub>4F</sub>-S-Ge<sub>4F</sub> bond angles, is reminiscent of monoclinic HT- $\text{GeS}_2$ ,<sup>70</sup> Figure S10d, although both trigonal and tetrahedral connectivities are rather different in comparison with crystalline references.

Similar to  $\text{Na}_2\text{S-As}_2\text{S}_3$  glasses,<sup>30</sup> the local sodium coordination is ill-defined. The  $g_{\text{NaS}}(r)$  partial function, Figure 7f, exhibits a long high- $r$  tail for the Na-S nearest neighbors overlapping with the second coordination sphere. As a result, the correct evaluation of the local sodium environment appears to be difficult. Fitting the  $T_{\text{NaS}}(r)$  partial correlation function with multiple Gaussians, we can reproduce the asymmetric shape of the nearest neighbor peak, Figure 9a. Assuming the first two contributions are related to the Na-S nearest neighbors and more distant contributions correspond to the second coordination sphere, we obtain the Na-S local coordination number  $N_{\text{Na-S}} = 4.12$ . Taking the maximum Na-S distance in crystalline  $\text{Na}_2\text{GeS}_3$  as a cutoff, one obtains  $N_{\text{Na-S}} = 3.72$ . Finally, taking a shallow minimum of  $T_{\text{NaS}}(r)$  at 3.70 Å as a cutoff, the Na-S local coordination number appears to be 5.32. Averaging these values, our estimation of the local sodium coordination number is  $N_{\text{Na-S}} = 4.5 \pm 0.5$ . The sodium coordination distribution corresponding to this average value is shown in Figure 9b. As expected, the populations of 4-fold and 5-fold coordinated sodium sites are nearly identical. The distribution is symmetric with the less populated under- and over-coordinated sodium species.

The sodium environment is strongly distorted as evidenced by the  $B_{\text{SNaS}}(\theta)$  bond angle distribution, Figure 9c. Roughly, the sodium local surroundings appear to be a broadened deformed version of sodium polyhedra in monoclinic  $\text{Na}_2\text{GeS}_3$  and fcc  $\text{Na}_2\text{S}$ . The polyhedral



connectivity reflected by  $B_{\text{NaSNa}}(\theta)$  is also rather similar to that in the above crystalline mixture although the Na-S-Na angles between  $120^\circ \lesssim \theta \lesssim 150^\circ$  are missing in both  $\text{Na}_2\text{GeS}_3$  and  $\text{Na}_2\text{S}$ .



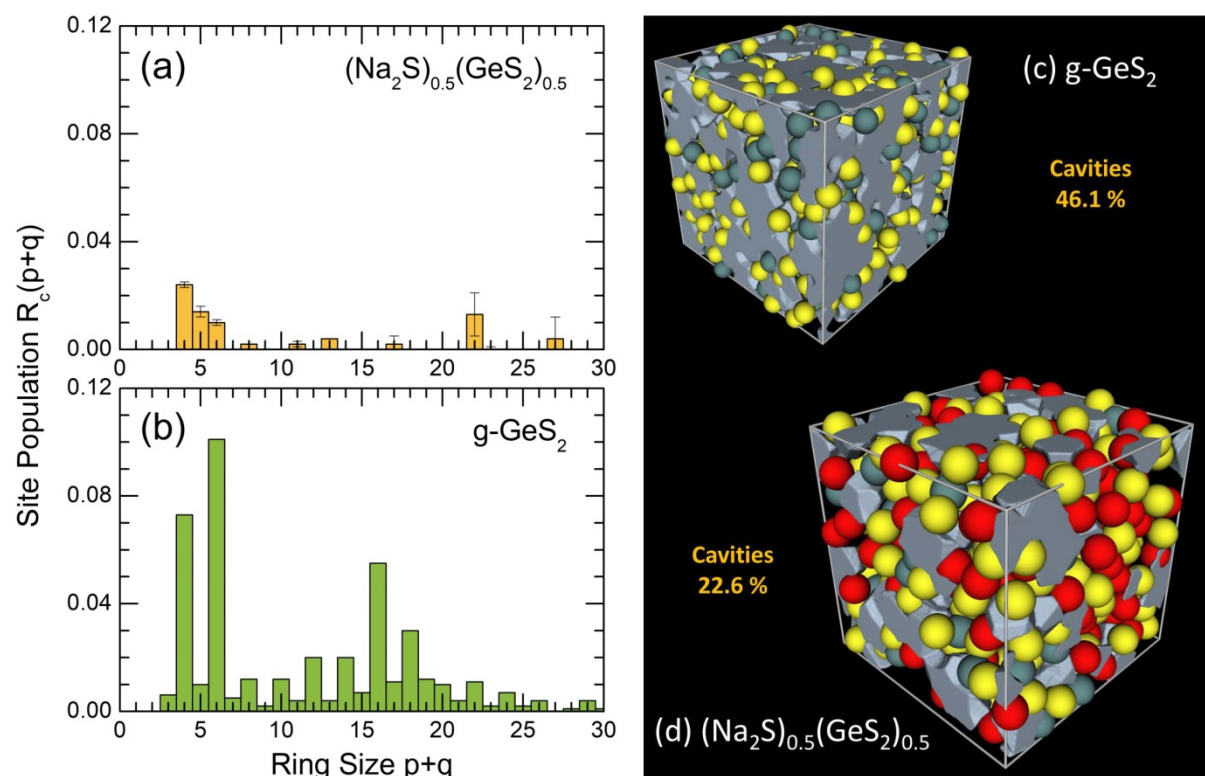
**Figure 9.** FPMD structural parameters for Na-S subnetwork in glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ : (a) various approaches to determine sodium coordination environment; the yellow dashed line represents the sum of two Gaussian functions related to Na-S nearest neighbors, the black dash-dotted line shows the maximum Na-S distance in monoclinic  $\text{Na}_2\text{GeS}_3$ ; (b) Na-S coordination distribution,  $B(\theta)$  angular distributions for (c) S-Na-S and (d) Na-S-Na bond angles. The  $B_{\text{SNaS}}(\theta)/B_{\text{NaSNa}}(\theta)$  functions for crystalline  $\text{Na}_2\text{GeS}_3$  and  $\text{Na}_2\text{S}$  are also shown.

The connectivity analysis shows that 61% of Ge and S atoms are still forming a single connected Ge-S fragment in the simulation box. The remaining 39% represent either isolated S atoms or small oligomeric fragments, Figure S11. The obtained results are very different from crystalline  $\text{Na}_2\text{GeS}_3$ , consisting of infinite corner-sharing chains  $\text{CS}[\text{GeS}(t)_2\text{S}(b)_{2/2}^-]_\infty$  held together by sodium cations.<sup>40</sup> The small oligomeric fragments represent isolated tetrahedra  $\text{ISO-GeS}_4$  or trigonal pyramids  $\text{ISO-GeS}_3$ , corner-  $\text{CS-Ge}_2\text{S}_5$  and edge-sharing  $\text{ES-Ge}_2\text{S}_6$  dimers or mixed oligomeric  $\text{ES/CS}$ -chains, all connected by sodium. The single large connected fragment is roughly a complicated chain consisting of  $\text{CS}$ - and  $\text{ES}$ -segments, including also small rings and homopolar S-S and Ge-Ge dimers. A chain-like character of the connected fragments confirms a clear majority ( $\approx 4/5$ ) of corner-sharing polyhedra,  $\text{CS-GeX}_4$  and  $\text{CS-GeX}_3$ , which are predominantly forming chains,  $N_{\text{Ge-Ge}}^{\text{CS}} = 1.82$ . Figure S12 and related comments reveal that trigonal Ge is distributed rather randomly in the glass network with the average  $\text{Ge}_{3\text{F}}\text{-Ge}_{3\text{F}}$  separation distance of  $5.7 \pm 0.5 \text{ \AA}$ . In contrast, the  $\text{Ge}_{4\text{F}}$ -centered units are forming complex  $n$ -membered chains,  $n \leq 35$ .

The DFT vibrational signatures of typical Na-Ge-S clusters observed in FPMD appear to be consistent with experimental Raman spectra of sodium thiogermanate glasses, Figure S8. In particular, a lower frequency symmetric  $\text{Ge}_{3\text{F}}\text{-S}$  breathing explains the red shift of the broad

unresolved  $A_1$  glassy breathing mode over the spectral range  $343 \leq \omega_{A_1} \leq 328 \text{ cm}^{-1}$  (Figure 2b) with corresponding increase of the average Ge-S interatomic distances (Table 1).

The derived ring statistics in comparison with that in glassy  $\text{GeS}_2$  is shown in Figure 10. We note an enormous difference in size,  $(p+q)$ , and population  $R_c(p+q)^{67}$  of  $\text{Ge}_p\text{S}_q$  rings between the two glasses, revealing a complete disappearance of the intermediate range order typical for g- $\text{GeS}_2$ . One should however mention that this is not a simple network fragmentation, since 61% of Ge and S are still connected but a profound transformation of the original  $\text{GeS}_2$  host with sodium sulfide additions.



**Figure 10.** Rings and voids:  $\text{Ge}_p\text{S}_q$  ring statistics in (a) equimolar  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  and (b) glassy  $\text{GeS}_2$ ; microscopic cavities in (c) vitreous  $\text{GeS}_2$  and (d) glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ .

This transformation can also be seen differently, analyzing the microscopic voids and cavities. Using the pyMolDyn code<sup>69</sup> and the Dirichlet–Voronoi tessellation, we have found a significant decrease of the total volume of cavities  $V_c$ , normalized to the volume of the simulation box,  $0 \leq V_c \leq 1$ , in case of the sodium thiogermanate glass, Figure 10. Glassy  $\text{GeS}_2$  has 46.1% of voids, that is, nearly one half of the glass volume is unoccupied. Alloying with sodium decreases significantly the cavities and voids, and the total volume of voids drops to 22.6%. It could be interpreted as the sodium species are located in previously empty spaces within the glass network. More importantly, a two-fold difference in  $V_c$  indicates a more dense packing of sodium thiogermanate glasses also reflected by the increased amplitude of the principle peak PP in the neutron structure factor for  $\text{Na}_2\text{S-GeS}_2$  glasses, Figure 5.

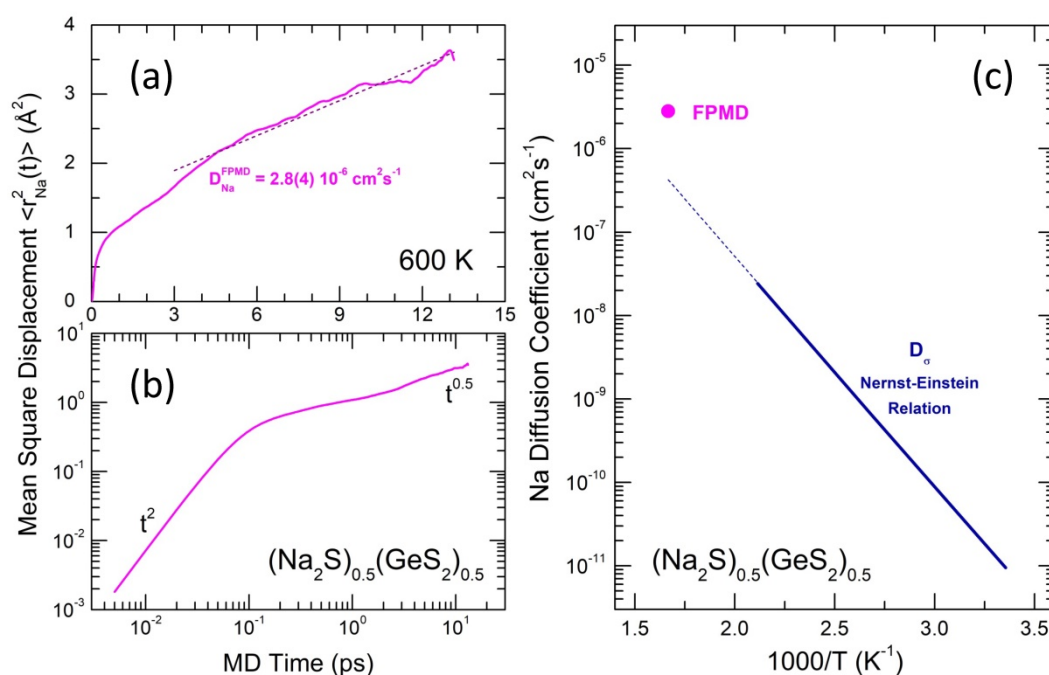
The FPMD sodium local dynamics can be compared with long-range sodium diffusion calculated from the experimental ionic conductivity  $\sigma_i$  using the Nernst-Einstein relation,

$$D_{\sigma} = \frac{k_{\text{B}}T}{c_i(Ze)^2} \sigma_i, \quad (6)$$

where  $D_{\sigma}$  is the diffusion (conductivity) coefficient,  $c_i$  the atomic sodium concentration,  $Ze$  the electric charge of the carrier ion,  $k_{\text{B}}$  and  $T$  have their usual meaning. The sodium mean square displacements  $\langle r_{\text{Na}}^2(t) \rangle$  as a function of time  $t$  are defined as

$$\langle r_{\text{Na}}^2(t) \rangle = \left\langle \frac{1}{N_i} \left\{ \sum_{i=1}^{N_i} [r_i(t) - r_i(0)]^2 \right\} \right\rangle, \quad (7)$$

where  $r_i(0)$  and  $r_i(t)$  are the positions of sodium atom  $i$  for the initial time and time  $t$ , respectively,  $N_i$  the total number of sodium in the simulation box, and the angle brackets represent the average over initial times. The  $\langle r_{\text{Na}}^2(t) \rangle$  values are shown in Figure 11 on linear and log-log scales for the highest FPMD temperature of 600 K, corresponding to supercooled liquid above  $T_{\text{g}} = 498 \pm 2$  K.



**Figure 11.** FPMD atomic dynamics in equimolar  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ ; sodium mean square displacements at 600 K on (a) linear and (b) log-log scales, (c) the derived sodium diffusion coefficients  $D_{\text{Na}}^{\text{FPMD}}(\text{eff})$  and  $D_{\sigma}$ . See text for further details.

As expected, the ballistic regime is observed at low  $t \lesssim 30$  fs, Figure 11b, revealing a slope  $s = 2$  on a log-log scale<sup>91</sup>

$$\langle r_{\text{Na}}^2(t) \rangle \propto \left( \frac{k_{\text{B}}T}{m_{\text{Na}}} \right) t^2, \quad (8)$$

where  $m_{\text{Na}}$  is the sodium atomic mass, followed by transient phenomena and the beginning of diffusive motion for the last 10 ps. Nevertheless, a long-range Brownian diffusion process, characterized by a linear function of time,<sup>92</sup>

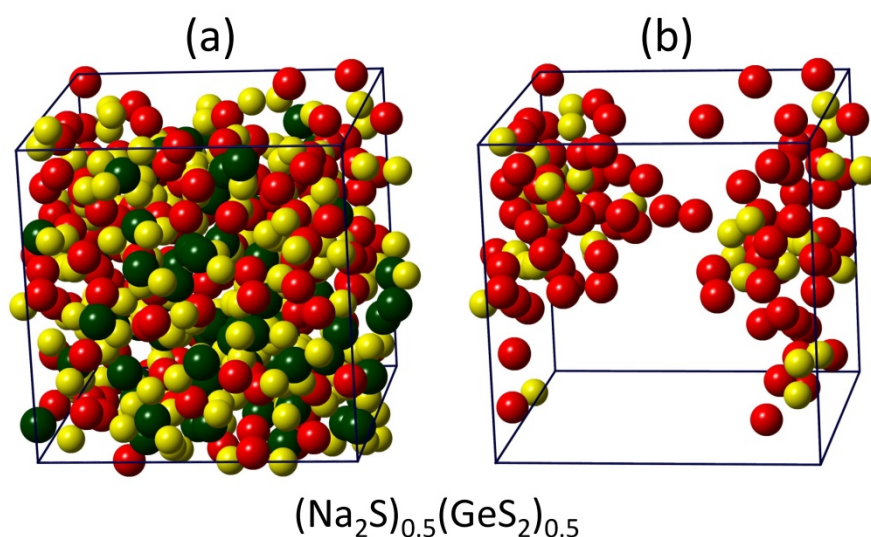
$$\langle r_{\text{Na}}^2(t) \rangle \propto D_{\text{Na}}^{\text{FPMD}} t^1, \quad (9)$$

where  $D_{\text{Na}}^{\text{FPMD}}$  is the average sodium diffusion coefficient, has not been observed over the used temperature – time domain, mostly limiting the sodium mobility to localized displacements. A typical evolution of the atomic dynamics over a wide temperature – time range is given in Figure S13.<sup>93</sup> The derived effective sodium diffusion coefficient  $D_{\text{Na}}^{\text{FPMD}}(\text{eff})$

$$D_{\text{Na}}^{\text{FPMD}}(\text{eff}) = \frac{1}{6} \lim_{t \rightarrow t_{\text{max}}} \frac{\partial \langle r_{\text{Na}}^2(t) \rangle}{\partial t}, \quad (10)$$

where the time domain is restricted by the last 10 ps, appears to be overestimated in comparison with long-range sodium migration, Figure 11c. This is not surprising since cation mobility is faster on a shorter spatial and time scale, see for example,<sup>94</sup> and references therein. It should also be noted that the observed difference,  $D_{\text{Na}}^{\text{FPMD}}(\text{eff})/D_{\sigma} = 7 \pm 2$ , might be lower, while  $D_{\sigma}$  corresponds to a solid glass, and  $D_{\text{Na}}^{\text{FPMD}}(\text{eff})$  to a supercooled liquid. Further discussion on sodium atomic motion will be given below.

**3.4. Isolated Sulfur and Preferential Diffusion Pathways.** As emphasized in Introduction, a special attention should be paid to isolated sulfur species  $S_{\text{iso}}$ , that is, the sulfur atoms without direct connections to germanium. The isolated sulfur species are connected only to sodium, and the average Na/ $S_{\text{iso}}$  stoichiometry is approximately  $[\text{Na}]/[S_{\text{iso}}] \approx 2$ . In contrast to the  $(\text{Na}_2\text{S})_{0.3}(\text{As}_2\text{S}_3)_{0.7}$  glass with a modest  $S_{\text{iso}}$  fraction of 6.2%,<sup>30</sup> equimolar  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  exhibits  $S_{\text{iso}}/S_{\text{tot}} = 0.169$ , Figure 12. The derived fraction is still lower than that in superionic  $\text{Ag}_2\text{S}-\text{As}_2\text{S}_3$  or  $\text{Ag}_2\text{S}-\text{GeS}_2$  glasses,  $0.18 \leq S_{\text{iso}}/S_{\text{tot}} \leq 0.21$ ,<sup>29</sup> and even is less significant than the  $S_{\text{iso}}$  fraction in the same glass reported previously, 23.5%.<sup>36</sup> However, the obtained results using identical GGA/PBE0 simulation approach appear to be systematic, and the ratio  $\sigma_{\text{Ag}}/\sigma_{\text{Na}} \approx 1000$  for the silver and sodium equimolar thiogermanate glasses, Figure 1b, is consistent with the difference in  $S_{\text{iso}}/S_{\text{tot}}$ .



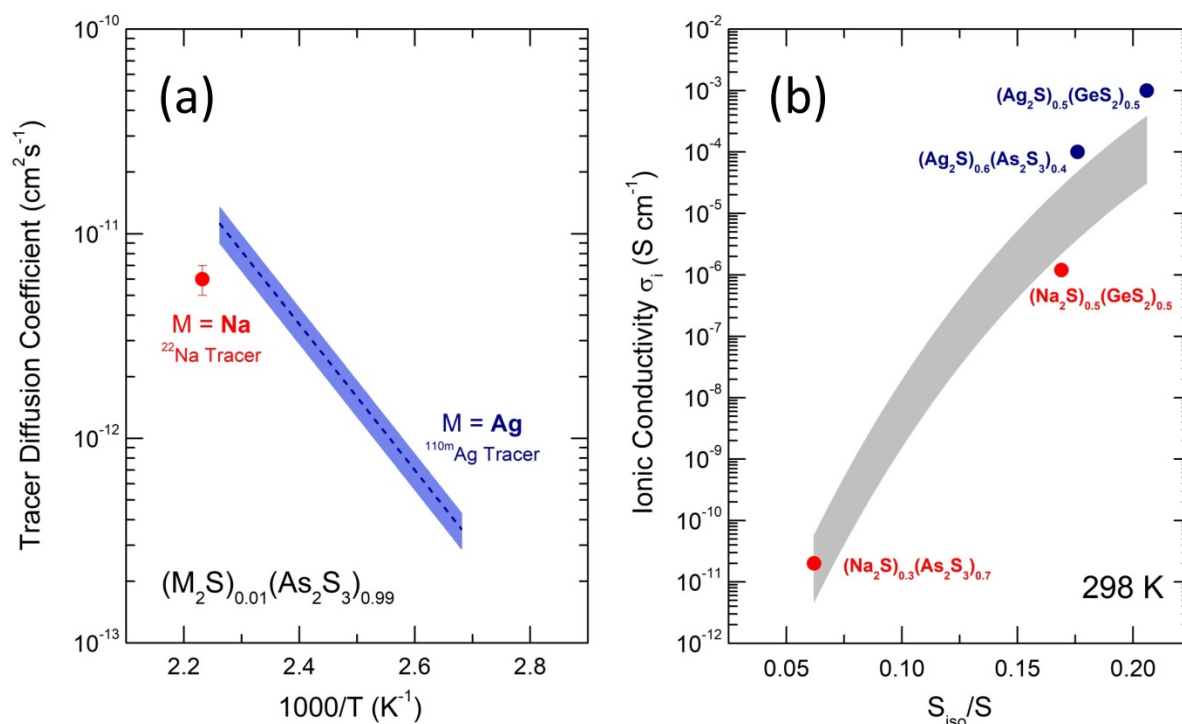
**Figure 12.** Isolated sulfur  $S_{\text{iso}}$  in glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ : (a) the entire FPMD simulation box containing 450 atoms (150 Na, 75 Ge and 225 S), (b) isolated sulfur species with connected sodium atoms.

The isolated sulfur species with connected sodium are located in a close proximity to each other forming preferential conduction pathways. These pathways are still not as efficient as in superionic silver glasses but they are drastically different compared to the  $S_{\text{iso}}$  distribution in



low-conducting  $(\text{Na}_2\text{S})_{0.3}(\text{As}_2\text{S}_3)_{0.7}$ ,<sup>30</sup> where the average distance between  $\text{Na-S}_{\text{iso}}$  units is 6.7 Å for more than 50% of the sodium species involved. Taking into account the  $\text{Na/S}_{\text{iso}}$  stoichiometry, 58% of sodium are connected to  $\text{S}_{\text{iso}}$  species in  $\text{g-}(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ , indicating a predominant role of  $\text{Na}^+$  ion transport via these diffusion channels. In superionic silver ternaries, the fraction of  $\text{Ag-S}_{\text{iso}}$  associates is even higher: 67% for  $(\text{Ag}_2\text{S})_{0.6}(\text{As}_2\text{S}_3)_{0.4}$  and 74% for  $(\text{Ag}_2\text{S})_{0.45}(\text{GeS}_2)_{0.45}$ . We should also note an astonishing contrast in  $\sigma_i$  between glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  and monoclinic  $\text{Na}_2\text{GeS}_3$ , Figure 1b. The crystalline counterpart without isolated sulfur exhibits the room-temperature conductivity by 8 orders of magnitude lower.

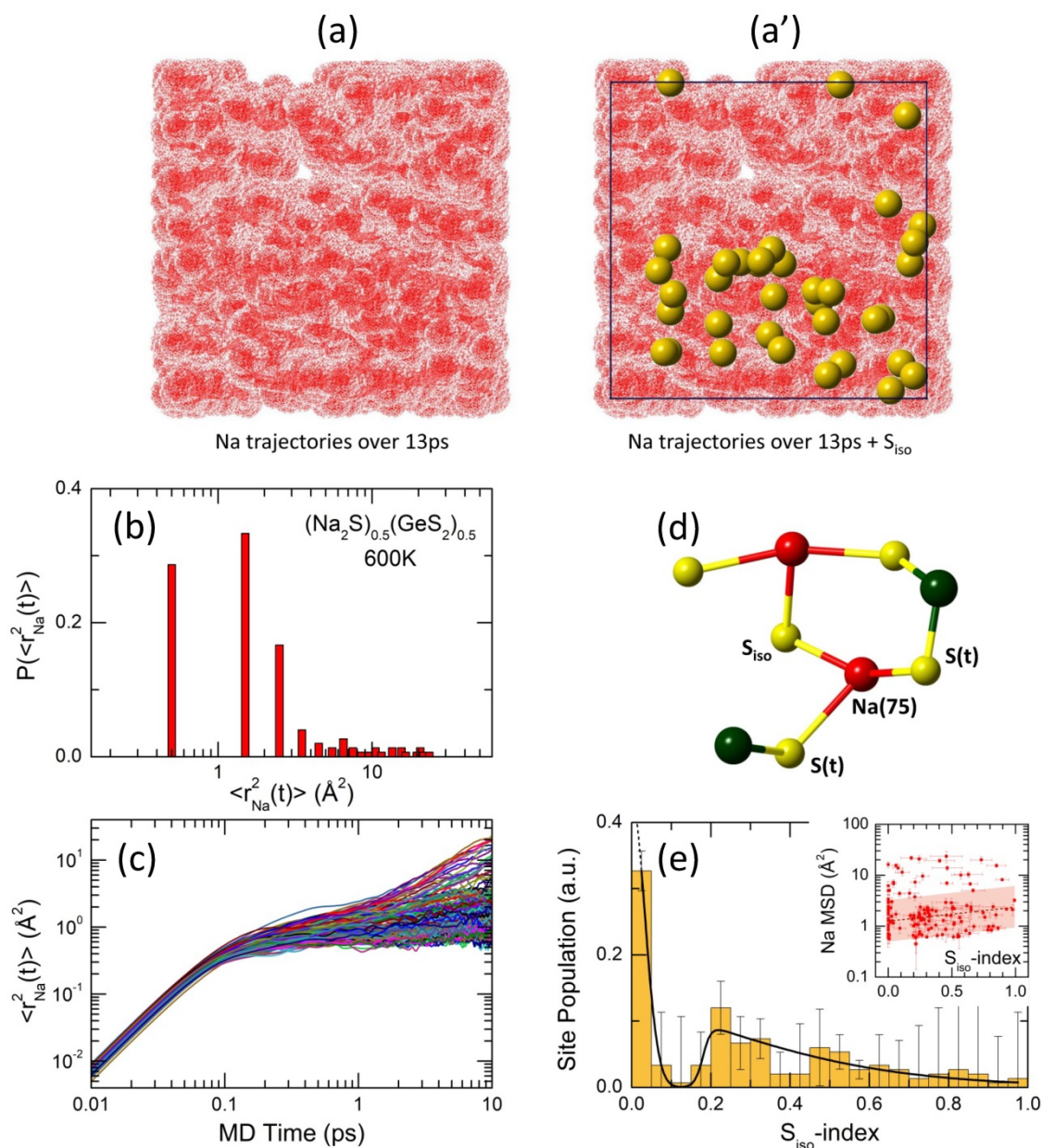
The question arises whether a remarkable  $\sigma_{\text{Ag}}/\sigma_{\text{Na}}$  difference both for  $(\text{M}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  (3 orders of magnitude, Figure 1b) and  $(\text{M}_2\text{S})_{0.3}(\text{As}_2\text{S}_3)_{0.7}$  (4.5 orders of magnitude, Figure S1) glasses may be related to intrinsically low sodium ion mobility in sulfide systems compared to fast  $\text{Ag}^+$  ions. The answer is given in Figure 13a, revealing  $^{22}\text{Na}$  and  $^{110\text{m}}\text{Ag}$  tracer diffusion coefficients in diluted thioarsenate glasses of identical stoichiometry  $(\text{M}_2\text{S})_{0.01}(\text{As}_2\text{S}_3)_{0.99}$ , in which no preferential conduction pathways are yet formed.<sup>27,29</sup> Sodium diffusion was found to be slightly lower,  $D_{\text{Ag}}/D_{\text{Na}} = 2.4 \pm 0.6$  at 448 K, but incomparable with 3 or 4.5 orders of magnitude difference in cation-rich vitreous systems. In other words, the isolated sulfur fraction seems to be an appropriate descriptor of fast ion transport in glasses, at least, for sodium and silver vitreous sulfides, Figure 13b.



**Figure 13.** Ion transport properties in silver and sodium vitreous sulfides: (a)  $^{22}\text{Na}$  (this work) and  $^{110\text{m}}\text{Ag}$  (Ref.<sup>26</sup>) tracer diffusion coefficients in glassy  $(\text{M}_2\text{S})_{0.01}(\text{As}_2\text{S}_3)_{0.99}$ ; (b) room-temperature ionic conductivity  $\sigma_{298}$  for silver and sodium ternary sulfides as a function of isolated sulfur fraction  $S_{\text{iso}}/S_{\text{tot}}$ .

As expected, sodium atomic dynamics is heterogeneous<sup>95</sup> in vitreous  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ , Figure 14b,c. Two-thirds of the sodium mean-square displacements (MSD) at 600 K are below 2 Å<sup>2</sup>, and only 8.7% are characterized by  $\langle r_{\text{Na}}^2(t) \rangle \geq 10$  Å<sup>2</sup>, that is, may be considered as a long-range Brownian motion. The Na trajectories over 13 ps are shown in Figure 14a using the [100] projection of the FPMD simulation box. We note a non-random sodium dynamical distribution,

where dark red domains reflect more dense mobile Na population. A majority of these domains are decorated by isolated sulfur, Figure 14a'.

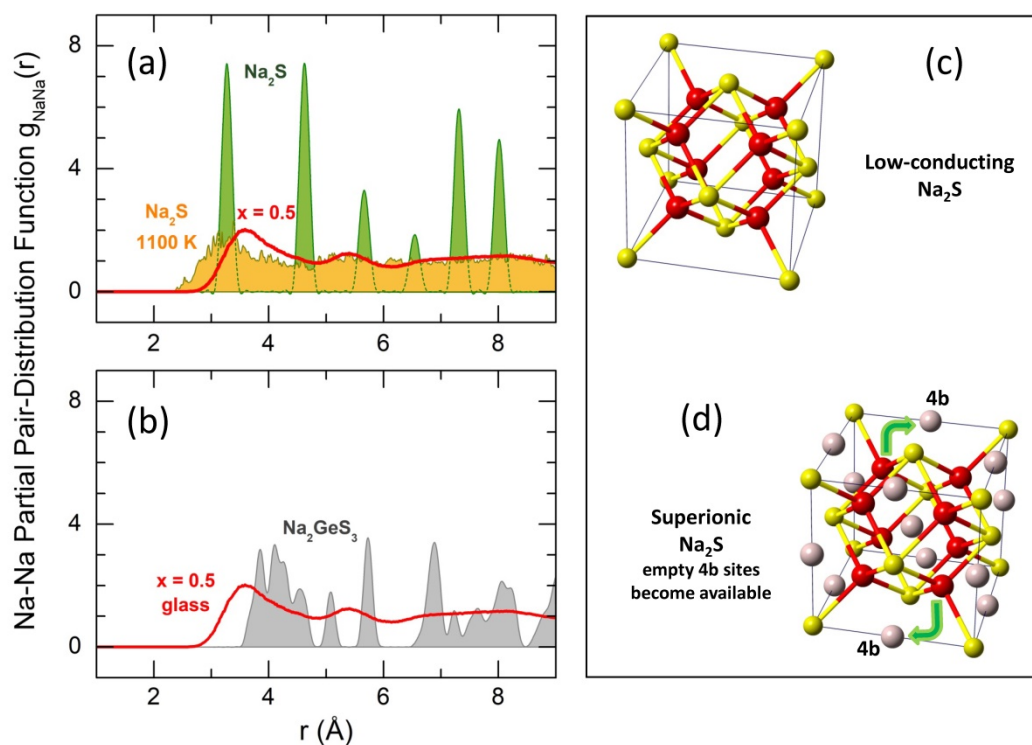


**Figure 14.** Temporal and spatial sodium atomic dynamics in  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  at 600 K. (a,a') Na trajectories over 13 ps using the [100] projection of the FPMD simulation box; heterogeneous sodium dynamics: (b) probability distribution function  $P(\langle r_{\text{Na}}^2(t) \rangle)$  of Na MSD for  $t = 10$  ps, (c) individual Na MSD as a function of time; (d) schematic definition of isolated sulfur index, (e) distribution of time-averaged  $S_{\text{iso}}$ -index for sodium species at 600 K, the inset shows the sodium MSD as a function of  $S_{\text{iso}}$ -index. See text for further details.

A semi-quantitative estimation of a possible correlation between the mobile sodium environment and  $\langle r_{\text{Na}}^2(t) \rangle$  may be given using a time-averaged  $S_{\text{iso}}$ -index, that is, the fraction of  $S_{\text{iso}}$  nearest neighbors in the sodium environment over a particular Na trajectory. Figure 14d shows incomplete, for simplicity, local environment of Na(75), one of the 150 sodium species present in the simulation box for a particular time  $t_i$ . Between three shown sulfur nearest neighbors, two belong to terminal sulfur  $S(t)$  and one is  $S_{\text{iso}}$ . Consequently, the  $S_{\text{iso}}$ -index is

$i_{S_{iso}}(t_i) = 1/3$ . The bimodal distribution of time-averaged  $\langle i_{S_{iso}}(t) \rangle$  for sodium species is given in Figure 14e. About 40% of sodium over the entire trajectories is mostly surrounded by terminal sulfur,  $\langle i_{S_{iso}}(t) \rangle \lesssim 0.1$ . The remaining distribution is asymmetric with a maximum at  $\langle i_{S_{iso}}(t) \rangle \approx 0.25$  and a long tail toward pure  $S_{iso}$  environment,  $\langle i_{S_{iso}}(t) \rangle = 1$ . Nevertheless, the  $S_{iso}$ -rich population,  $\langle i_{S_{iso}}(t) \rangle > 0.5$ , represents only one-quarter. The inset in Figure 14e shows the average sodium MSDs over the last 5 ps as a function of time-averaged  $S_{iso}$ -index. In spite of a strong scatter of the data points and a large temporal variability of  $\langle i_{S_{iso}}(t) \rangle$ , a distinct correlation reveals an increase of the sodium mobility for  $S_{iso}$ -rich environment, roughly by a factor of two.

In this context, additional information yields comparison of Na-Na partial pair-distribution functions  $g_{NaNa}(r)$  for equimolar  $(Na_2S)_{0.5}(GeS_2)_{0.5}$  and crystalline references  $Na_2GeS_3$  and  $Na_2S$ , Figure 15. For sodium sulfide, both room-temperature  $g_{NaNa}(r)$  is given and that at 1100 K. A drastic difference between the Na-Na partials in low-conducting and superionic  $Na_2S$  appears to be consistent with a dramatic change in  $\sigma_i$  and  $D_{Na}$  of 10 orders of magnitude for  $\sigma_i$ , Figure 1.



**Figure 15.** Partial Na-Na pair-distribution functions  $g_{NaNa}(r)$  in glassy  $(Na_2S)_{0.5}(GeS_2)_{0.5}$  (the red solid line) and crystalline references: (a)  $Na_2S$  at room-temperature (highlighted in green) and 1100 K (highlighted in yellow), and (b)  $Na_2GeS_3$  (highlighted in light grey). The room temperature crystalline  $g_{NaNa}(r)$  were calculated from the cif files using the XTAL program.<sup>96</sup> Preliminary FPMD results are used for  $Na_2S$  at 1100 K. Face-centered cubic unit cell for (c) low-conducting and (d) superionic  $Na_2S$ . At high temperatures,  $T \gtrsim 1000$  K, empty 4b positions (highlighted in light red) become available for sodium, opening up fast diffusion pathways.

The onset of type-II superionic transition in  $Li_2S$  and  $Na_2S$ , Figure 1, is associated with expected availability of previously empty 4b sites in the fcc lattice for alkalis<sup>20</sup> opening up efficient diffusion pathways for long-range  $Na^+$  migration, Figure 15d. The  $g_{NaNa}(r)$  broadening at 1100 K reflects this trend, especially at low  $r$ , since the partial occupancy of 4b sites reveals Na-Na



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3 correlations centered at  $r = 2.84 \text{ \AA}$ . We note a striking similarity between the Na-Na partials in  
4 equimolar  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$  and superionic  $\text{Na}_2\text{S}$ , Figure 15a, coherent with much higher  $\sigma_i$  and  
5  $D_{\text{Na}}$  for glassy sodium thiogermanates and thiogallates at ambient temperatures in comparison  
6 with low-conducting  $\text{Na}_2\text{S}$  and  $\text{Na}_2\text{GeS}_3$ , Figure 1. This difference is certainly related to the  
7 existence of percolating diffusion pathways based on  $S_{\text{iso}}$  in sodium sulfide glasses.  
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10 The next question is what factors control the  $S_{\text{iso}}/S_{\text{tot}}$  fraction? Basically, the first variable seems  
11 to be the cation content  $x$ . Our FPMD simulations of sodium and silver ternary sulfides show  
12 that 60 to 67% of glassy structural motifs are consistent with equilibrium phase diagrams and  
13 crystalline motifs yet remaining disordered. Although the crystalline stoichiometry limits are  
14 violated in glasses, the basic composition trend persists, and  $S_{\text{iso}}/S_{\text{tot}}$  increases with  $x$ . The  
15 crystalline stoichiometry limits depend on the local coordination of the glass-former, and the  $S_{\text{iso}}$   
16 species appear earlier in systems with four-fold coordinated Ge than in those with trigonal As.  
17 An easy way to form the homopolar bonds can also be beneficial. Taking into account the  
18 energies of homopolar and heteropolar bonds As-As, Ge-Ge, S-S, As-S and Ge-S, the As-As  
19 homopolar bonds should be formed more easily since  $(E_{\text{A-A}} + E_{\text{S-S}})/2E_{\text{A-S}} = 0.94$  for  $A = \text{As}$  and  
20  $0.87$  for  $A = \text{Ge}$ .<sup>97</sup> On the other hand, the chemical disorder in glassy  $\text{GeS}_2$  and  $\text{As}_2\text{S}_3$  is roughly  
21 similar,  $[\text{As-As}]/([\text{As-As}] + [\text{As-S}])$  or  $[\text{Ge-Ge}]/([\text{Ge-Ge}] + [\text{Ge-S}]) = 1-3 \%$ .<sup>82,97</sup> Finally, a structural  
22 instability in glasses can also be noted. In particular, the germanium disulfide glassy systems  
23 exhibit a partial disproportionation:  $\text{GeS}_2 \rightarrow \text{GeS} + \text{S}$ , and trigonal GeS-related structural motifs  
24 appear instead of  $\text{GeS}_4$  tetrahedra, accompanied by additional sulfur, transforming into  $S_{\text{iso}}$ . This  
25 instability was observed in Ge-rich binaries,<sup>82</sup> silver<sup>29</sup> and sodium thiogermanate glasses,  
26 Sections 3.2 and 3.3. An extreme case of tetrahedral metastability shows  $\text{GeTe}_2$  in crystalline<sup>98,99</sup>  
27 and glassy<sup>89</sup> states.  
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33 The equilibrium phase diagrams and glassy  $S_{\text{iso}}/S_{\text{tot}}$  are also correlated differently. The  $\text{Ag}_2\text{S}$ -  
34  $\text{GeS}_2$  ternary system exhibits superionic argyrodite  $\text{Ag}_8\text{GeS}_6$ , which contains  $\frac{1}{3}$  of  $S_{\text{iso}}$ . The silver-  
35 rich thioarsenate counterpart is just  $\text{Ag}_3\text{AsS}_3$ , the composition limit of emerging  $S_{\text{iso}}$ . Broadly  
36 speaking, the isolated sulfur species are more favorable energetically in silver thiogermanates  
37 than in silver thioarsenates. These observations are consistent with glassy  $S_{\text{iso}}/S_{\text{tot}}$  and  
38 composition trends in ionic conductivity and tracer diffusion, Figures 1 and 13.  
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#### 44 4. CONCLUSIONS

45 Pulsed neutron diffraction and Raman spectroscopy supported by first-principles simulations  
46 were used in decoding structural and chemical roots of fast ion transport in vitreous  $\text{Na}_2\text{S}$ - $\text{GeS}_2$   
47 and comparing with its silver counterparts, as well as sodium and silver thioarsenates. It was  
48 found that 60 to 67% of glassy structural motifs follow the equilibrium phase diagrams and  
49 crystalline motifs, remaining strongly disordered; however, the stoichiometry limits are violated  
50 leading additionally to a topological disorder and unexpected chemical and structural features.  
51 In particular, the preferential diffusion pathways in these systems are related to isolated sulfur  
52  $S_{\text{iso}}$ , that is, the sulfur species surrounded exclusively by mobile cations with a typical  
53 stoichiometry  $M/S_{\text{iso}} \approx 2$ . The  $S_{\text{iso}}/S_{\text{tot}}$  fraction appears to be a reliable descriptor of fast ion  
54 transport in glassy systems over a wide range of ionic conductivities and cation diffusivities.  
55 The  $S_{\text{iso}}$  fraction increases with mobile cation content  $x$ , tetrahedral coordination of the network  
56 former and, in case of thiogermanate systems, with germanium disulfide metastability and  
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3 partial disproportionation,  $\text{GeS}_2 \rightarrow \text{GeS} + \text{S}$ , leading to formation of additional sulfur,  
4 transforming into  $\text{S}_{\text{iso}}$ . A research strategy enabling to achieve extended and interconnected  
5 pathways based on isolated sulfur would lead to sodium glassy electrolytes with superior  
6 transport properties.  
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## 10 ASSOCIATED CONTENT

### 11 Supporting Information

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13 The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/>  
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17 Ionic conductivity of vitreous sodium and silver thioarsenates, sodium thiogermanate  
18 and thiogallate; typical gamma-spectrum of  $^{22}\text{Na}$  tracer; typical  $^{22}\text{Na}$  tracer diffusion  
19 profile; Ge-S(t) stretching as a function of  $x$  in the  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses; integration  
20 procedure for Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses; Ge-Ge and S-S stretching in  
21 Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses; experimental and DFT Raman spectra of  
22 Na-S and S-S stretching in glasses; DFT Raman spectra of size-limited Ge-S and Na-Ge-S  
23 clusters; orientational order parameter  $q$ ; bond angle distributions for trigonal and  
24 tetrahedral Ge species; small fragments forming a disconnected Ge-S subnetwork;  
25 connectivity of  $\text{Ge}_{3\text{F-S}}$  and  $\text{Ge}_{4\text{F-S}}$  subsets; gallium mean-square displacements in GaS at  
26 1000 K; optimized geometry of DFT clusters (PDF)  
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## 33 AUTHOR INFORMATION

### 34 Corresponding Author

35  
36  
37 **Eugene Bychkov** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte*  
38 *d'Opale, 59140 Dunkerque, France; orcid.org/0000-0002-3292-1205; Phone: +33 328*  
39 *658250; Email: Eugene.Bychkov@univ-littoral.fr; Fax: +33 328 658244*  
40  
41

### 42 Authors

43  
44 **Mohammad Kassem** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral*  
45 *Côte d'Opale, 59140 Dunkerque, France; orcid.org/0000-0003-0512-0004*  
46

47 **Tinehinane Bounazef** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral*  
48 *Côte d'Opale, 59140 Dunkerque, France*  
49

50  
51 **Anton Sokolov** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte*  
52 *d'Opale, 59140 Dunkerque, France*  
53

54 **Maria Bokova** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte*  
55 *d'Opale, 59140 Dunkerque, France*  
56

57 **Daniele Fontanari** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte*  
58 *d'Opale, 59140 Dunkerque, France*  
59  
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3 **Alex C. Hannon** – *ISIS Facility, Rutherford Appleton Laboratory, Didcot OX11 0QX, U.K.;*  
4 *orcid.org/0000-0001-5914-1295*  
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6 **Igor Alekseev** – *Laboratoire de Physico-Chimie de l'Atmosphère, Université du Littoral Côte*  
7 *d'Opale, 59140 Dunkerque, France; on leave from V. G. Khlopin Radium Institute, 194021 St.*  
8 *Petersburg, Russia*  
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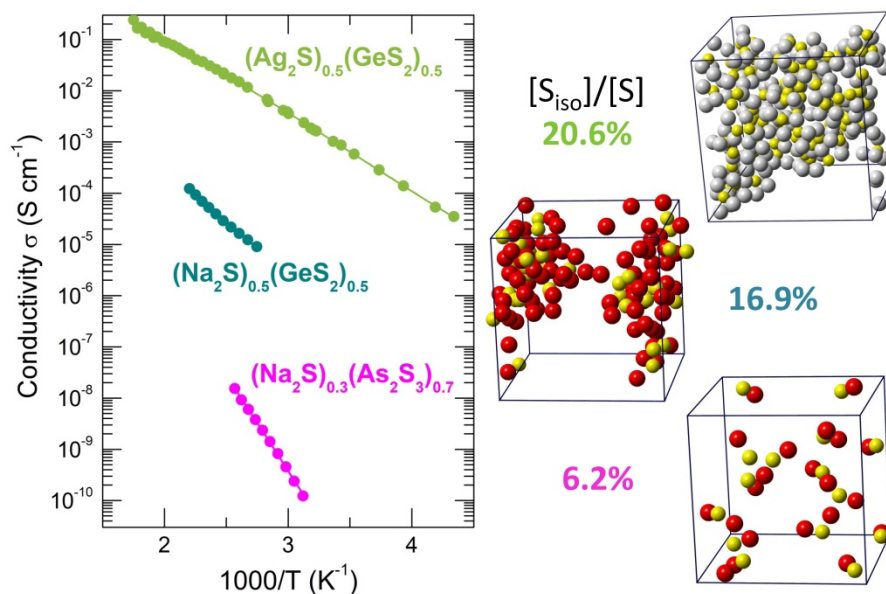
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## TOC Figure and synopsis



Stoichiometry limits of crystalline systems are violated in vitreous sodium and silver sulfides leading to emerging isolated sulfur S<sub>iso</sub>, that is, the sulfur species surrounded exclusively by mobile cations with a typical stoichiometry M/S<sub>iso</sub> ≈ 2. The S<sub>iso</sub>/S<sub>tot</sub> fraction appears to be a reliable descriptor of fast ion transport in glassy systems over a wide range of ionic conductivities and cation diffusivities.

# Supporting Information

## Deciphering Fast Ion Transport in Glasses: a Case Study of Sodium and Silver Vitreous Sulfides

Mohammad Kassem,<sup>1</sup> Tinehinane Bounazef,<sup>1</sup> Anton Sokolov,<sup>1</sup> Maria Bokova,<sup>1</sup> Daniele Fontanari,<sup>1</sup> Alex C. Hannon,<sup>2</sup> Igor Alekseev,<sup>1</sup> and Eugene Bychkov\*,<sup>1</sup>

<sup>1</sup> *Université du Littoral Côte d'Opale, 59140 Dunkerque, France*

<sup>2</sup> *ISIS Facility, Rutherford Appleton Laboratory, Chilton, Didcot, OX11 0QX, U.K.*

**Figure S1.** Ionic conductivity of vitreous sodium and silver thioarsenates, sodium thiogermanate and thiogallate.

**Figure S2.** Typical gamma-spectrum of <sup>22</sup>Na tracer.

**Figure S3.** Typical <sup>22</sup>Na tracer diffusion profile.

**Figure S4.** Ge-S(t) stretching as a function of  $x$  in the  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses.

**Figure S5.** Integration procedure for Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses.

**Figure S6.** Ge-Ge and S-S stretching in Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses.

**Figure S7.** Experimental and DFT Raman spectra of Na-S and S-S stretching in glasses.

**Figure S8.** DFT Raman spectra of size-limited Ge-S and Na-Ge-S clusters.

**Figure S9.** Orientational order parameter  $q$  for trigonal and tetrahedral Ge species.

**Figure S10.** Bond angle distributions for trigonal and tetrahedral Ge species.

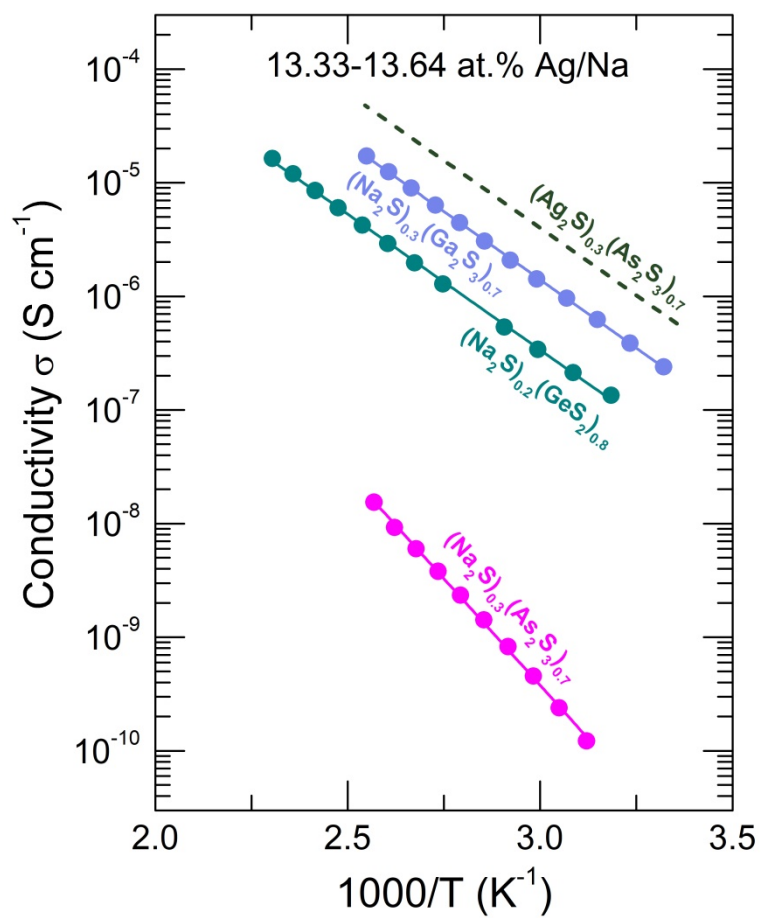
**Figure S11.** Small Ge-S fragments forming a disconnected Ge-S subnetwork in glassy  $(\text{Na}_2\text{S})_{0.5}(\text{GeS}_2)_{0.5}$ .

**Figure S12.** Connectivity of  $\text{Ge}_{3\text{F-S}}$  and  $\text{Ge}_{4\text{F-S}}$  subsets.

**Figure S13.** Gallium mean-square displacements in GaS at 1000 K.

**Tables S1 and S2.** Optimized geometry of DFT clusters

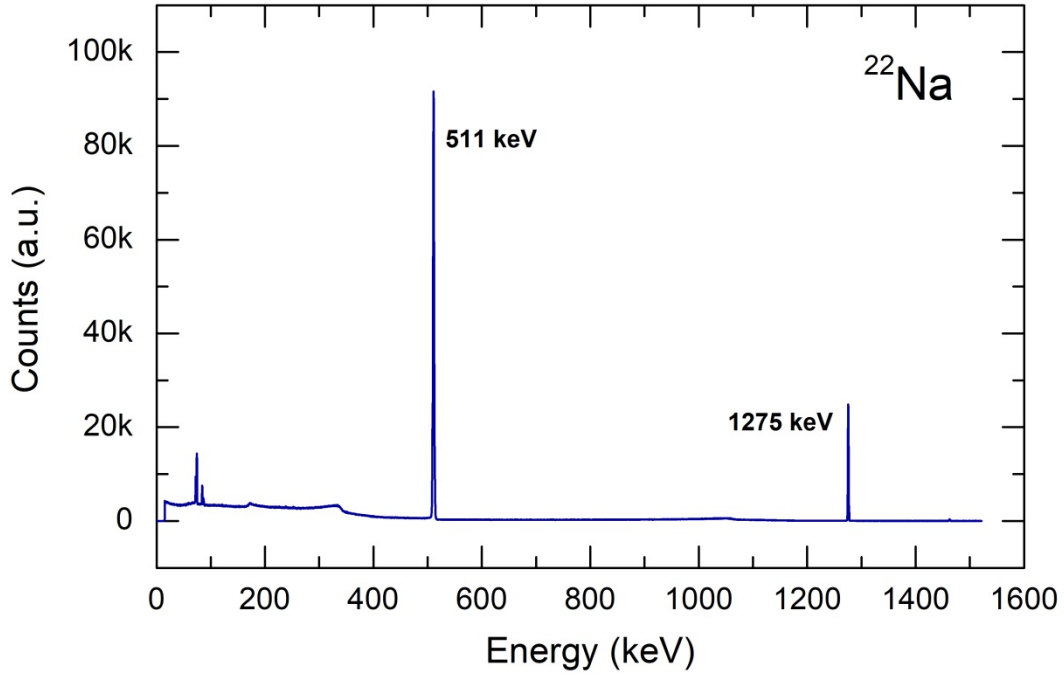
\* Email: Eugene.Bychkov@univ-littoral.fr



**Figure S1.** Ionic conductivity of vitreous  $(\text{Na}_2\text{S})_{0.3}(\text{As}_2\text{S}_3)_{0.7}$  (13.64 at.% Na),<sup>S1</sup>  $(\text{Na}_2\text{S})_{0.2}(\text{GeS}_2)_{0.8}$  (13.33 at.% Na),<sup>S1</sup>  $(\text{Na}_2\text{S})_{0.3}(\text{Ga}_2\text{S}_3)_{0.7}$  (13.64 at.% Na),<sup>S1</sup> and  $(\text{Ag}_2\text{S})_{0.3}(\text{As}_2\text{S}_3)_{0.7}$  (13.64 at.% Ag).<sup>S2</sup>

## <sup>22</sup>Na Tracer Diffusion Experimental Details

A high-purity Ge detector GX1018 and LYNX gamma-spectrometer (Canberra Ind., USA) were used to measure the initial and residual gamma activity of the sample before and after sectioning. Spectrometer calibration in the energy range from 20 keV to 1600 keV was carried out using <sup>109</sup>Cd, <sup>152</sup>Eu, and <sup>241</sup>Am sources. The gamma activity of the samples was determined using two characteristic photopeaks at 511 and 1275 keV, Figure S2.



**Figure S2.** Typical gamma-spectrum of <sup>22</sup>Na tracer with two characteristic photopeaks at 511 and 1275 keV used for data collection and analysis.

The samples were placed in a polyethylene cell (the radioactive face in the bottom) in a well-defined fixed geometry. The measurements of the initial  $A_0$  and residual  $A(t)$  gamma activity were carried out for 1000 s. A Genie 2000 program (Canberra Ind., USA) was used for data analysis.

Penetration profiles for <sup>22</sup>Na tracer diffusion in a  $(\text{Na}_2\text{S})_{0.01}(\text{As}_2\text{S}_3)_{0.99}$  glass obey the usual solution of Fick's law for an infinitesimally thin deposit of radioactive isotope on a semi-infinite specimen<sup>S3</sup>

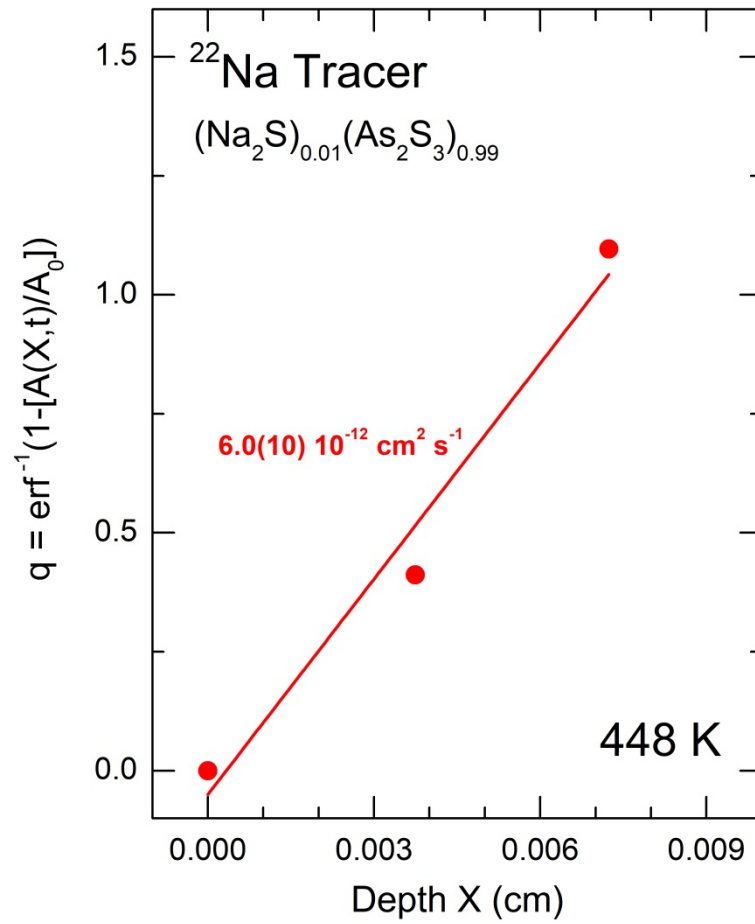
$$1 - \frac{A(X,t)}{A_0} = \text{erf}(q), \quad (\text{S1})$$

and

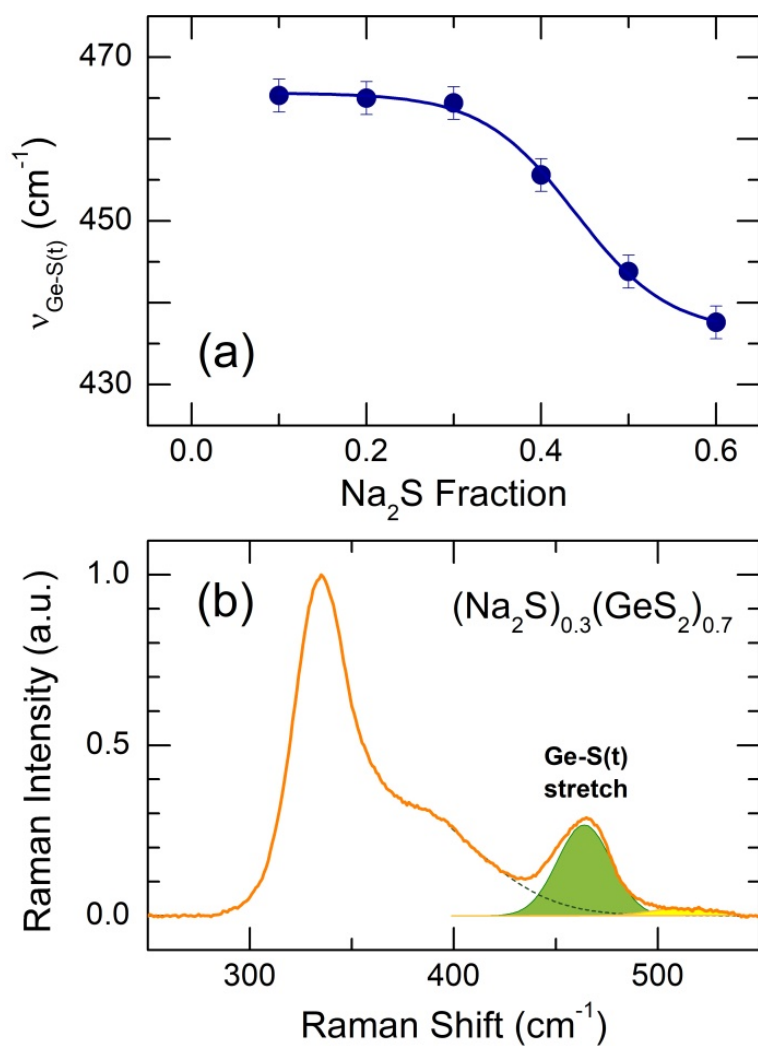
$$q = \frac{X}{2\sqrt{D_{\text{Na}}t}}, \quad (\text{S2})$$

where  $A(X, t)$  is the residual activity of the sample after a thickness  $X$  was removed,  $t$  is the diffusion anneal time,  $D_{\text{Na}}$  the tracer diffusion coefficient, and  $\text{erf}(q)$  is the Gauss error function.

Experimentally determined values of  $A_0$  and  $A(X, t)$  yield  $q$ -values which, when plotted vs.  $X$ , produce a straight line passing through origin, Figure S3.

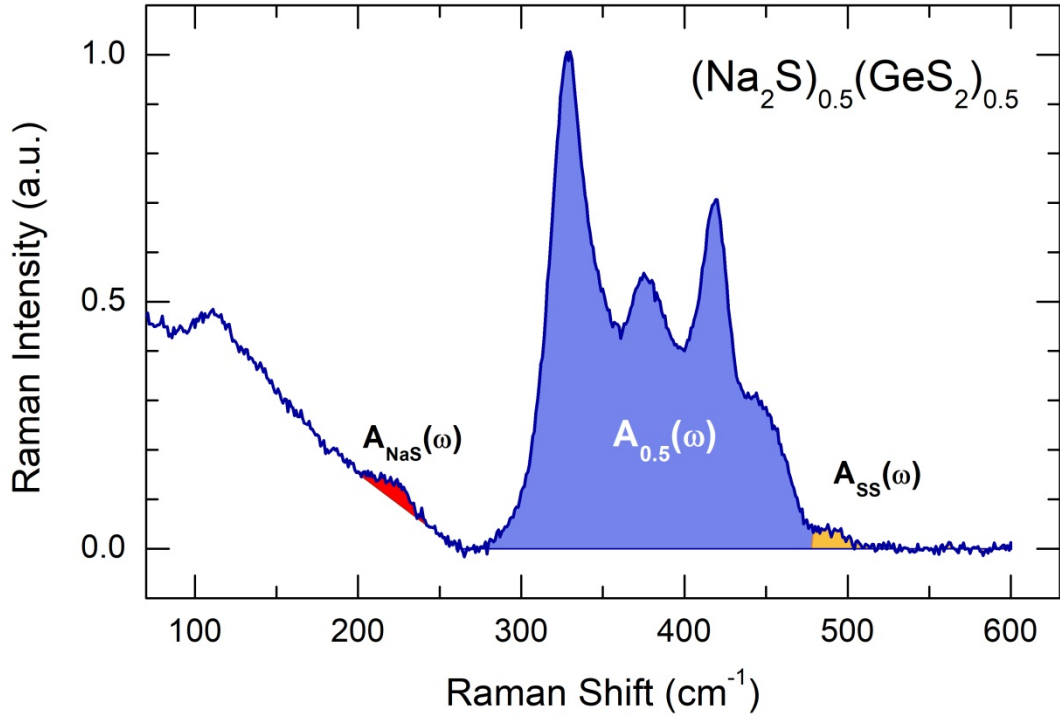


**Figure S3.** Typical  $^{22}\text{Na}$  tracer diffusion profile for a  $(\text{Na}_2\text{S})_{0.01}(\text{As}_2\text{S}_3)_{0.99}$  glass annealed at 448 K for 20 days. The solid line shows a least-square fit of the experimental data points to Eq. (S2), where  $q = \text{erf}^{-1}(1 - \frac{A(X,t)}{A_0})$ .



**Figure S4.** Ge-S(t) stretching as a function of  $x$  in the  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses: (a) composition dependence of the Ge-S(t) stretching frequency, (b) typical fitting procedure to extract the Ge-S(t) stretching position.





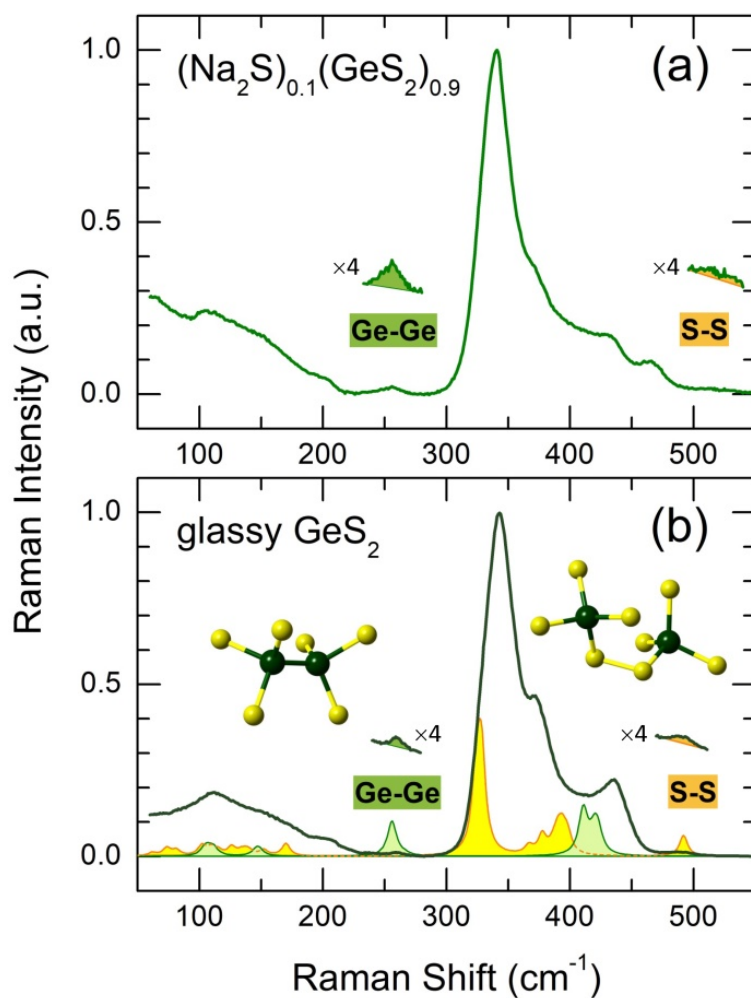
**Figure S5.** Integration procedure for Raman spectra of  $(\text{Na}_2\text{S})_x(\text{GeS}_2)_{1-x}$  glasses, taking the equimolar glass,  $x = 0.5$ , as an example.

The fractional area of the S-S stretching was determined using integration

$$f_{\text{SS}}(\omega) = \frac{\int_{\omega_{\text{SS}}}^{\omega_{\text{max}}} I_x(\omega) d\omega}{\int_{\omega_{\text{min}}}^{\omega_{\text{max}}} I_x(\omega) d\omega} = \frac{A_{\text{SS}}(\omega)}{A_x(\omega)}, \quad (\text{S3})$$

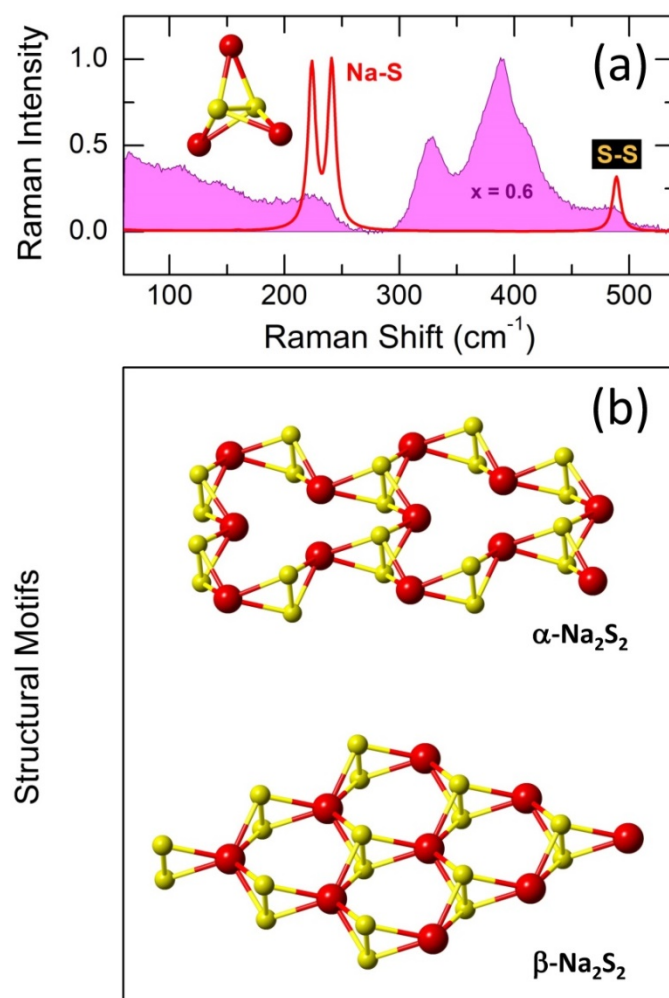
where  $I_x(\omega)$  represents the normalized Raman spectrum of a  $\text{Na}_2\text{S}$ - $\text{GeS}_2$  glass,  $460 \text{ cm}^{-1} \leq \omega_{\text{SS}} \leq 490 \text{ cm}^{-1}$  depending on  $x$ ,  $\omega_{\text{min}} = 260 \text{ cm}^{-1}$  and  $\omega_{\text{max}} = 600 \text{ cm}^{-1}$ . The integrated area of the S-S stretching modes,  $A_{\text{SS}}(\omega)$ , is highlighted in yellow in Figure S5; the summarized integrated area of the Ge-S and S-S stretching features,  $A_x(\omega)$ , is depicted in blue.

The fractional area of the Na-S stretching was also determined by integration, as it is shown in Figure S5. In this case, we did not use a Gaussian least-square fitting similar to that in Figure S4 for Ge-S( $t$ ) stretching. Consequently,  $f_{\text{NaS}}(\omega)$  seems to be underestimated but can be used qualitatively.

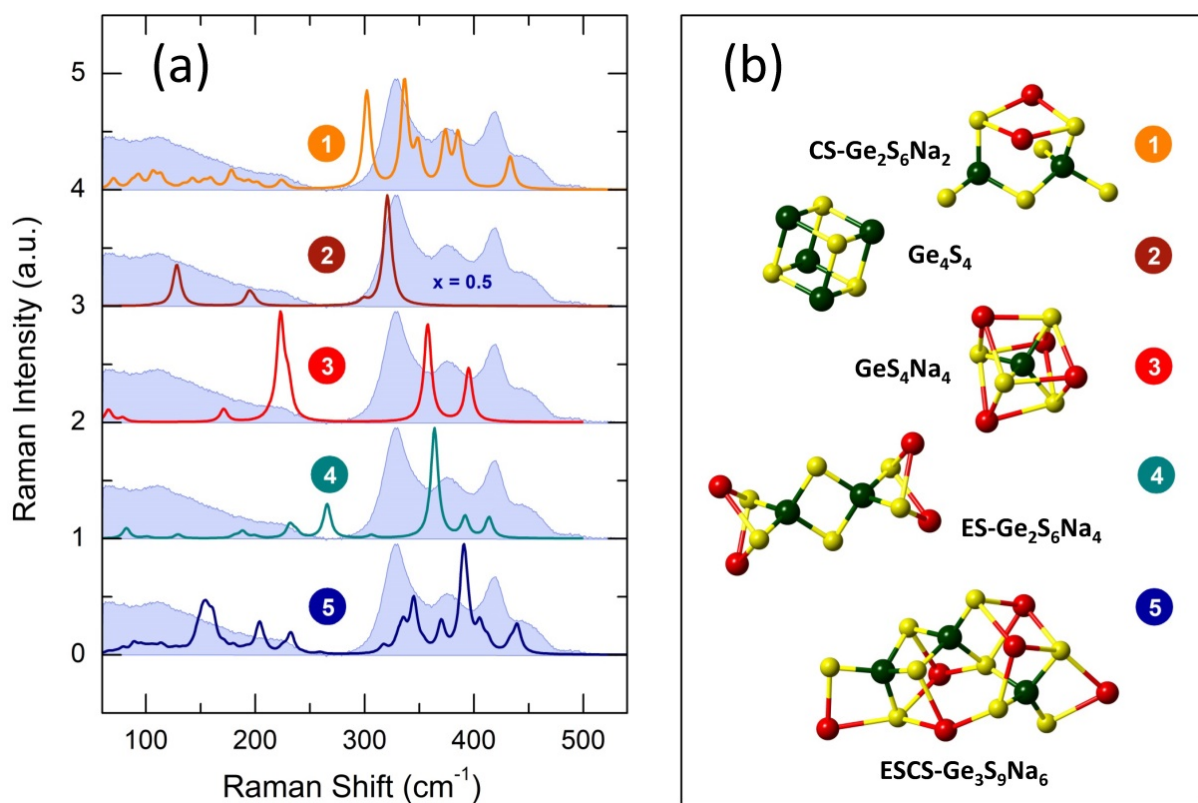


**Figure S6.** Ge-Ge and S-S stretching in Raman spectra of glassy (a)  $(\text{Na}_2\text{S})_{0.1}(\text{GeS}_2)_{0.9}$  and (b)  $\text{GeS}_2$  plotted together with DFT spectra of ethane-like  $\text{ETH-Ge}_2\text{S}_6\text{H}_6$  and  $\text{CS-Ge}_2\text{S}_8\text{H}_6$  clusters (the insets in Figure S6b). Terminal hydrogen species are not shown, and H-related vibrations are removed from the spectra.

The DFT modeling of ethane-like  $\text{ETH-Ge}_2\text{S}_6\text{H}_6$  cluster confirms the Ge-Ge stretching at  $\approx 250 \text{ cm}^{-1}$ , while DFT-optimized  $\text{CS-Ge}_2\text{S}_8\text{H}_6$  cluster, including S-S dimer, shows S-S stretching at  $\approx 490 \text{ cm}^{-1}$ .



**Figure S7.** (a) Experimental Raman spectrum of glassy (Na<sub>2</sub>S)<sub>0.6</sub>(GeS<sub>2</sub>)<sub>0.4</sub> (highlighted in magenta) and calculated spectrum of DFT-optimized S<sub>2</sub>Na<sub>3</sub> cluster (the red line) revealing Na-S and S-S stretching vibrations between  $224 \leq \omega_{\text{Na-S}} \leq 242 \text{ cm}^{-1}$  and at  $\omega_{\text{S-S}} \approx 489 \text{ cm}^{-1}$ , respectively; (b) structural motifs in  $\alpha$ - and  $\beta$ -polymorphs of Na<sub>2</sub>S<sub>2</sub>.<sup>S4</sup> The S<sub>2</sub>Na<sub>3</sub> cluster is also shown in (a).



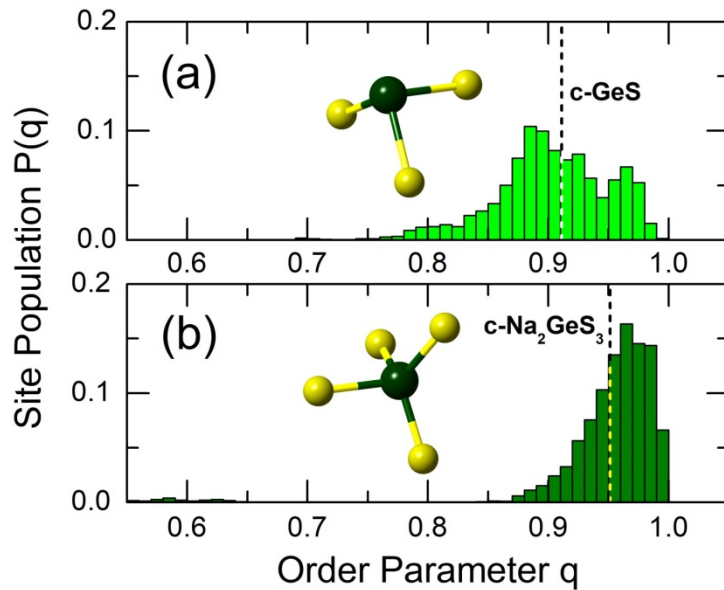
**Figure S8.** (a) DFT Raman spectra of size-limited Ge-S and Na-Ge-S clusters in comparison with experimental data for glassy equimolar  $(\text{Na}_2\text{S})_{0.6}(\text{GeS}_2)_{0.4}$ , highlighted in light blue; (b) schematic representation of optimized clusters: (1) corner-sharing  $\text{CS-Ge}_2\text{S}_6\text{H}_3$  (the terminal hydrogen species are not shown, the H-related vibrations are removed from the calculated spectrum), (2)  $\text{Ge}_4\text{S}_4$ , (3)  $\text{GeS}_4\text{Na}_4$ , (4) edge-sharing  $\text{ES-Ge}_2\text{S}_6\text{Na}_4$ , (5)  $\text{ES/CS-Ge}_3\text{S}_9\text{Na}_6$ .

## The tetrahedral shape and orientational order parameter $q$

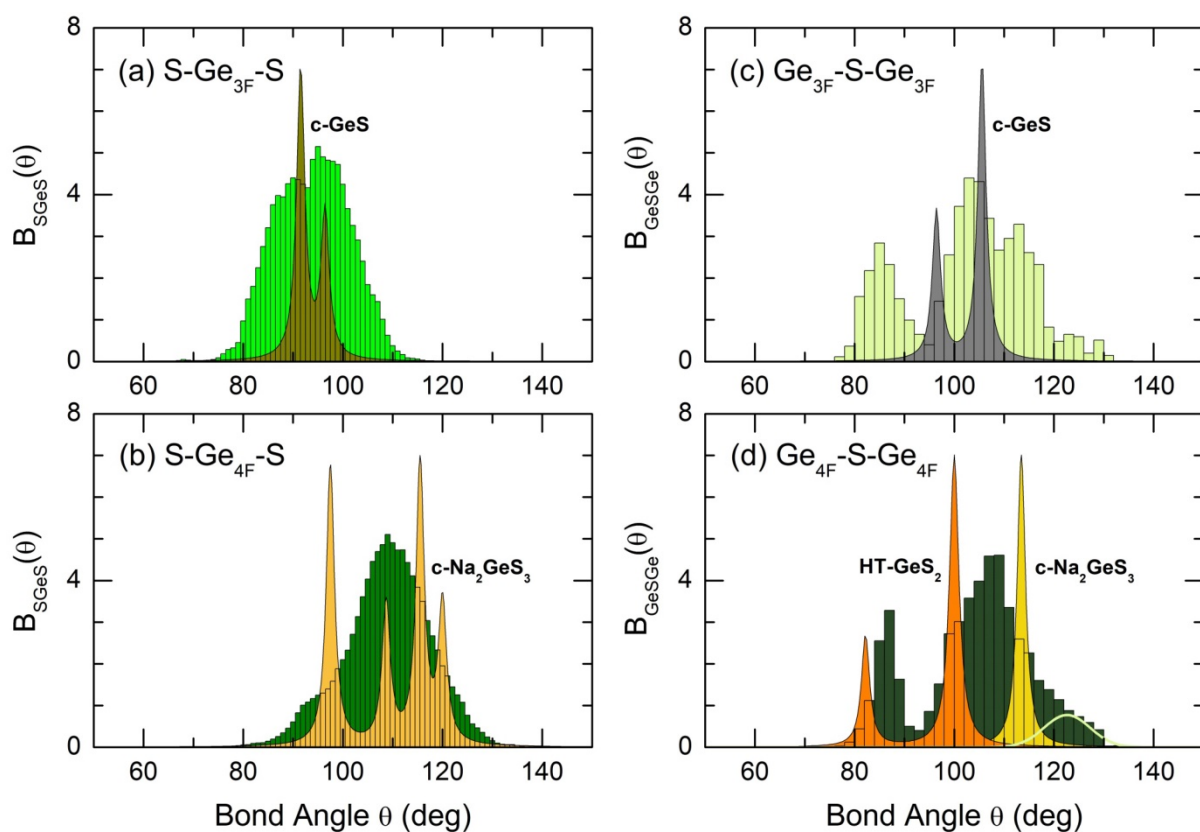
The tetrahedral shape of  $\text{GeX}_4$  entities clearly shows the orientational order parameter  $q$ ,<sup>S5,S6</sup> extended beyond the tetrahedral geometry<sup>S7</sup>

$$q = 1 - \frac{3}{8} \sum_{j=1}^{n-1} \sum_{k=j+1}^n \left( \cos \psi_{jk} + \frac{1}{3} \right)^2, \quad (\text{S4})$$

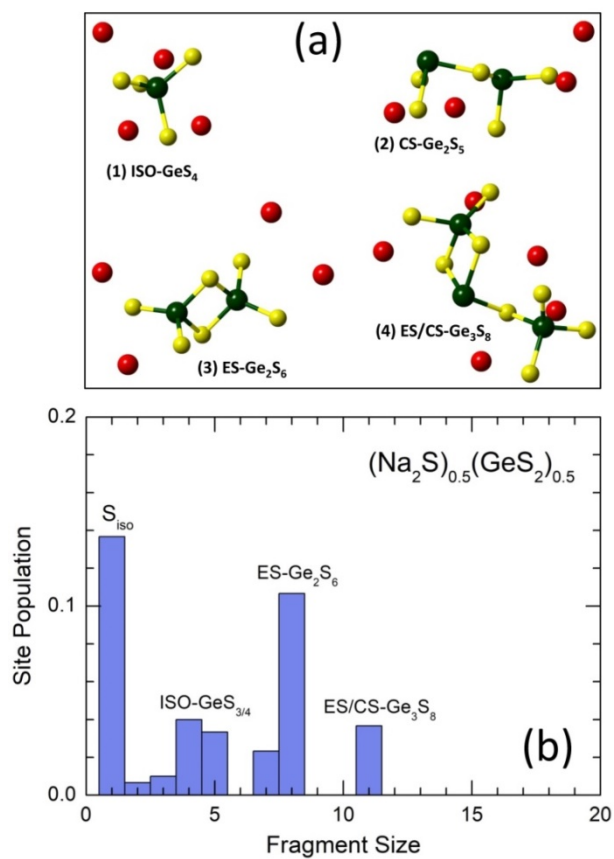
where  $\psi_{jk}$  is the X-Ge-X angle of a given  $\text{GeX}_n$  unit. The average  $q$ -value changes between 0 for an ideal gas and  $q = 1$  for a regular tetrahedral network ( $n = 4$ ). The distorted tetrahedral geometry is characterized by  $0.8 \lesssim q < 1$ .<sup>S7-S10</sup> The probability distribution  $P(q)$  for  $\text{GeX}_4$  entities is peaked at  $q = 0.96$  with a low- $q$  tail mostly expanding up to  $q = 0.86$ , Figure S9b. The non-tetrahedral fraction, centered at  $q \approx 0.60 \pm 0.05$  and corresponding to defect octahedral species,  $q_{\text{O}_h} = 5/8$ , is negligible, 2.6%. Basically, the  $\text{GeX}_4$  tetrahedra are slightly more distorted than those in monoclinic  $\text{Na}_2\text{GeS}_3$ ,  $q = 0.9514$ , confirmed also by the S-Ge<sub>4F</sub>-S bond angle distribution  $B_{\text{SGeS}}(\theta)$ , Figure S10b. We note however a low- $\theta$  shoulder at  $92^\circ$  in addition to the  $B_{\text{SGeS}}(\theta)$  maximum at  $109.9^\circ$ , indicating the presence of ES- $\text{GeS}_4$  entities, similar to those in monoclinic HT- $\text{GeS}_2$ .<sup>S11</sup> In contrast to tetrahedral germanium, the  $\text{GeX}_3$  trigonal pyramids are highly distorted in comparison with orthorhombic GeS evidenced by  $P(q)$ , Figure S9a, and  $B_{\text{SGeS}}(\theta)$ , Figure S10a.



**Figure S9.** Orientational order parameter  $q$  for (a) three-fold  $\text{Ge}_{3F}$  and (b) four-fold coordinated  $\text{Ge}_{4F}$  germanium species. The  $q$ -parameters for crystalline GeS and  $\text{Na}_2\text{GeS}_3$  are also shown.

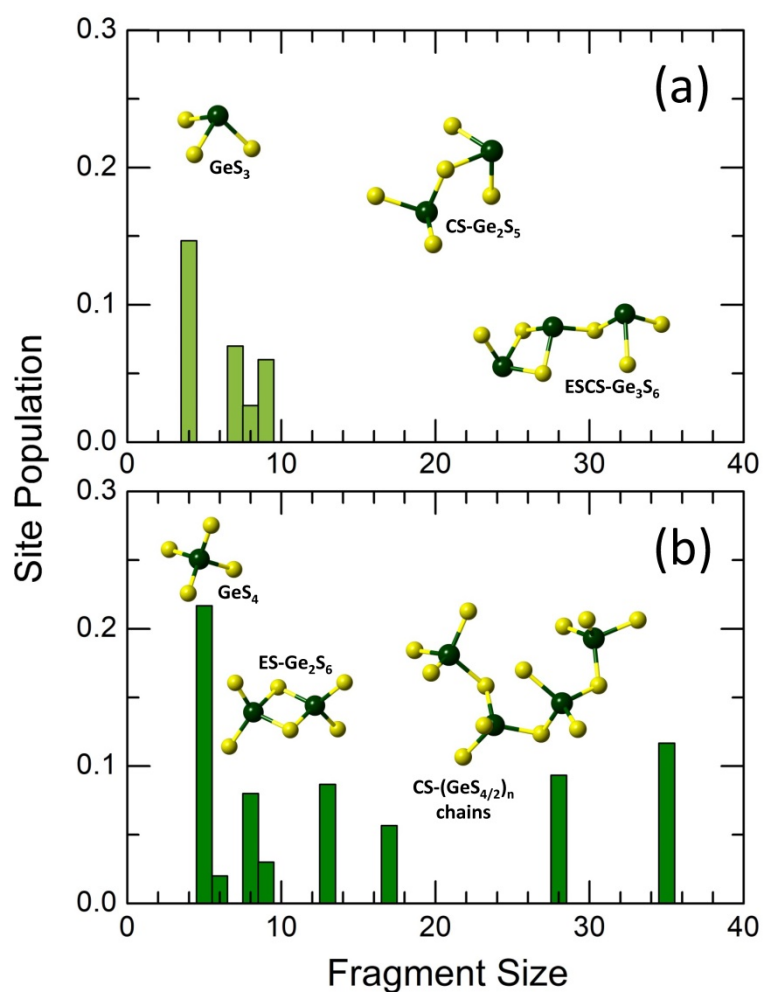


**Figure S10.** Bond angle distributions  $B_{S\text{Ge}_3\text{F}}(\theta)$  and  $B_{\text{Ge}_3\text{F}\text{S}\text{Ge}_3\text{F}}(\theta)$  for trigonal  $\text{Ge}_{3\text{F}}$  and tetrahedral  $\text{Ge}_{4\text{F}}$  species: (a)  $\text{S-Ge}_{3\text{F}}\text{-S}$ , (b)  $\text{S-Ge}_{4\text{F}}\text{-S}$ , (c)  $\text{Ge}_{3\text{F}}\text{-S-Ge}_{3\text{F}}$ , and (d)  $\text{Ge}_{4\text{F}}\text{-S-Ge}_{4\text{F}}$ . The angular distributions for crystalline references are also shown: orthorhombic  $\text{GeS}$ ,<sup>S12</sup> monoclinic  $\text{Na}_2\text{GeS}_3$ ,<sup>S13</sup> and high-temperature  $\text{HT-GeS}_2$ .<sup>S11</sup>



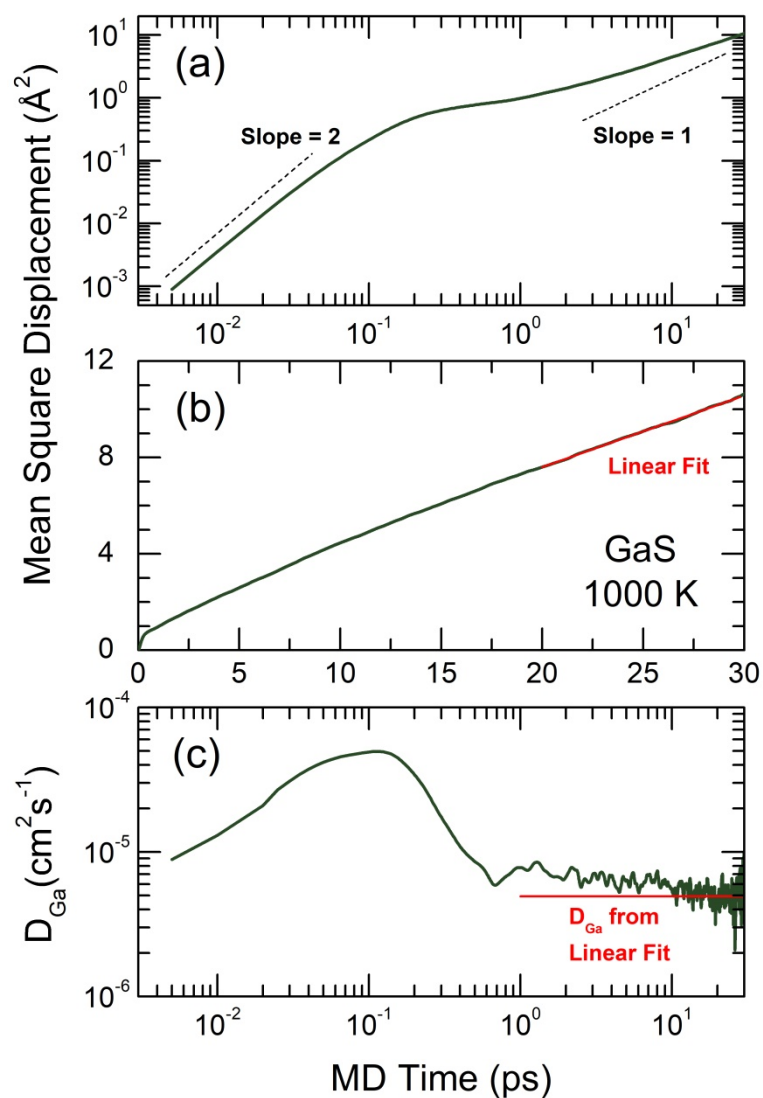
**Figure S11.** Small Ge-S fragments forming a disconnected Ge-S subnetwork in glassy (Na<sub>2</sub>S)<sub>0.5</sub>(GeS<sub>2</sub>)<sub>0.5</sub>: (a) typical examples present in FPMD simulation boxes, (b) statistics of small isolated Ge-S units.





**Figure S12.** Connectivity of (a) Ge<sub>3F</sub>-S and (b) Ge<sub>4F</sub>-S subsets. The insets show typical Ge<sub>3F</sub>-S and Ge<sub>4F</sub>-S entities.

The three-fold coordinated germanium species are distributed rather randomly in the glass network mostly existing as isolated or connected GeS<sub>3</sub> pyramids and CS-Ge<sub>2</sub>S<sub>5</sub> dimers ( $\approx 71\%$  of the entire Ge<sub>3F</sub> population), Figure S12a, with the average Ge<sub>3F</sub>-Ge<sub>3F</sub> separation distance of  $5.7 \pm 0.5$  Å. In contrast, the Ge<sub>4F</sub>-centered units are forming complex  $n$ -membered chains,  $n \leq 35$ . The fraction of small entities, isolated or connected GeS<sub>4</sub> or ES-Ge<sub>2</sub>S<sub>6</sub>, is below 45%, Figure S12b.



**Figure S13.** Gallium mean-square displacements in GaS at 1000 K:<sup>S14</sup> (a) log-log scale, (b) linear scale; (c) Ga diffusion coefficients obtained by differentiation. A ballistic regime is observed below 30 fs, a diffusive motion above 20 ps. Gallium diffusion coefficient  $D_{\text{Ga}}$ , obtained by a least-square fitting between 20 and 30 ps is shown in (c) by the red solid line.

**Table S1. Interatomic Distances and Bond Angles in Optimized DFT Clusters and Crystalline References**

Ge-S

Cluster/Reference	Ge-S (Å)	S-Ge-S (deg)	Ge-S-Ge (deg)
Ge <sub>4</sub> S <sub>4</sub>	2.460(1)	91.8(1)	88.2(1)
GeS <sup>S12</sup>	2.441(1)	93(2)	96.4 105.6

Na-S

Cluster/Reference	Na-S (Å)	S-S (Å)	S-Na-S (deg)	Na-S-Na (deg)
S <sub>2</sub> Na <sub>2</sub>	2.810(5)	2.10(1)	45.9	134(1)
S <sub>2</sub> Na <sub>3</sub>	2.809	2.15	45.0	106.3
α-Na <sub>2</sub> S <sub>2</sub> <sup>S4</sup>	2.818(15)	2.128	44.2(2)	106.6(1)
β-Na <sub>2</sub> S <sub>2</sub> <sup>S4</sup>	2.90(12)	2.158	45.2 106.2	106.2

Na-Ge-S

Cluster	Ge-S (Å)	Na-S (Å)	S-Ge-S (deg)	Ge-S-Ge (deg)	S-Na-S (deg)	Na-S-Na (deg)
Ge <sub>4</sub> S <sub>10</sub> Na <sub>4</sub>	2.151* 2.28(2)**	2.75(4)	109(2)	111(1)	85	–
CS-Ge <sub>3</sub> S <sub>10</sub> Na <sub>4</sub> H <sub>2</sub>	2.18(2)* 2.298(4)**	2.78(7)	109(6)	114.4	80.3 151.5	143(16)
CS-Ge <sub>2</sub> S <sub>7</sub> Na <sub>6</sub>	2.215(1)* 2.298(1)**	2.79(5)	109(4)	116.3	85(6) 144.7	94(20) 142(10)
ES-Ge <sub>2</sub> S <sub>6</sub> Na <sub>4</sub>	2.224* 2.275**	2.81	109(7)	83.6	81.9	81.3
CS/ES-Ge <sub>3</sub> S <sub>9</sub> Na <sub>6</sub>	2.19(2)* 2.269(9)**	2.83(8)	109(10)	86.0 114.5	81(3) 112(25)	90(3) 131(9)
GeS <sub>4</sub> Na <sub>4</sub>	2.239*	2.906	109.47	–	77.96	100.86
CS-Ge <sub>2</sub> S <sub>6</sub> Na <sub>2</sub> H <sub>3</sub>	2.25(2)* 2.27(3)**	2.78(1)	109(5)	103.5	94.6(2)	84.0(4)

**Table S2. Interatomic Distances and Bond Angles in Crystalline Na-Ge-S References**

Reference	Ge-S (Å)	Na-S (Å)	S-Ge-S (deg)	Ge-S-Ge (deg)	S-Na-S (deg)	Na-S-Na (deg)
Na <sub>4</sub> Ge <sub>4</sub> S <sub>10</sub> <sup>S15</sup>	2.139(3)*	2.88-3.34	109(2)	106.7(5)	89(14)	88(19)
	2.225(21)**				137(5)	148(12)
Na <sub>2</sub> GeS <sub>3</sub> <sup>S13</sup>	2.16(3)*	2.88-3.09	Figure S10			Figure 9
	2.24(2)**					
Na <sub>6</sub> Ge <sub>2</sub> S <sub>7</sub> <sup>S16</sup>	2.192(10)*	2.71-3.35	109(6)	113.1(2)	89(11)	86(8)
	2.262**				152(23)	163(12)

\* Ge-S(*t*)

\*\* Ge-S(*b*)

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