Supporting Information for:
A multi-technique approach to unravel the (dis)order in amorphous materials
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S1. Ge-Se system preparation
The Vahishta Force Field has the generic form:
\[ \phi(r) = \frac{Z_i Z_j}{r} - \frac{1}{r^4} \left( \frac{1}{2} \alpha_i Z_i^2 + \alpha_j Z_j^2 \right) \frac{e}{r_{4s}} + \frac{H_{ij}}{r^{\eta_{ij}}} \] (1)

The first term represents the Coulombic interaction between charged atoms with \( Z_i \) the charge of the \( i \)th particle. The second term is the charge-dipole potential due to the high polarizability of large ions (Se). \( \sigma_i \) is the polarizability of the \( i \)-th particle and \( r_{4s} = 4.43 \text{Å} \) is a decay length, chosen to screen the charge-dipole interaction. The polarizability \( \alpha_i \) of Ge\(^{4+} \) is set to 0 due to the smaller size with respect to Se\(^{2-} \), while the polarizability of Se\(^{2-} \) is \( 7 \text{Å}^1 \). The third term takes into account for the steric repulsion where \( H_{ij} \) is the strength of the repulsion and \( \eta_{ij} \) depends on the interatomic interaction: 11 for Ge-Ge, 9 for Ge-Se and 7 for Se-Se interactions\(^1\). The form of \( H_{ij} \) factor is
\[ H_{ij} = A_{ij} (\sigma_i + \sigma_j)^{\eta_{ij}} \] (2)
where \( \sigma_i \) is the ionic radius of the of the \( i \)-th ions and \( A_{ij} \) is the repulsion strength of 249.7 meV.
S2. Structural analysis tools.

S2.1 Radial distribution function

Figure S1. Sketch of the construction of the g(r) for a central atom. Atoms in the first neighbor shell are represented in solid colors, those in the second shell and those far away in transparent colors.

S2.2 Bond-angle-decomposition

Figure S2. a-c) Representative FOLDS with the corresponding $q$-value. Se atoms are colored in yellow and Ge atoms in pink.
S2.3 Voronoi tessellation

Figure S3. Voronoi tessellation procedure from a) the starting system expressed in cartesian coordinates (x, y, z), to b) Voronoi polyhedron, and c) VP probability. The representation of the most probable structure is shown in panel d).

S2.4 Persistent homology diagram

Figure S4. Homology analysis and persistence diagram construction. a) Sketch of atoms represented by cartesian coordinates with an increasing radius $\varepsilon$. b) Simplified example of a persistence diagram, where points are colored according to the formation of loops in panel a). c) Persistence diagram in the case of the Ge$_{0.4}$Se$_{0.6}$ system (4480 atoms).
S3 Analysis of Ge\textsubscript{x}Se\textsubscript{1-x} systems

S3.1 Bond angle decomposition

![Figure S5](image)

**Figure S5.** Bond-angle distributions (BAD) for the Ge\textsubscript{x}Se\textsubscript{1-x} systems: a) Ge-Se-Ge, b) Se-Ge-Se angles. In purple, green and blue corresponds to Ge\textsubscript{0.4}Se\textsubscript{0.6}, Ge\textsubscript{0.5}Se\textsubscript{0.5} and Ge\textsubscript{0.6}Se\textsubscript{0.4}, respectively.

For the Se-rich system, the decomposition of the BAD on the most abundant 2-FOLD atoms shows that the Se-centered atoms span a wide range of values from 80 to 180° with a peak centered at 90°. The Ge-centered atoms have a higher probability at 90°, as reported in **Figure S5**. Increasing the Ge-content, the contribution of homopolar angles becomes more relevant, even though heteropolar angles are the most relevant ones. In the Ge-rich system, a peak at 60° appears for the Ge-Ge-Se (or Se-Ge-Ge) and Se-Ge-Se angles.
Figure S6. BAD decomposition as a function of the folding of each central atom, expressed in percentage to find single angle type. Panels (a-c) correspond to the 2-FOLD, panels (d-f) to the 3-FOLD, and panels (g-i) to the 4-FOLD central atoms. Color legend is reported below the graphs.
Figure S7. Bond-angle distributions (BAD) for the (Ge_{0.75}Se_{0.25})_{0.85}Te_{0.15} system. Each plot reports different BAD as shown in the legend. The atom in the middle is the central atom in the angle calculation.
S4. Steinhardt parameters and X-ray diffraction

The VP analysis shows a different behavior for the Ge$_{0.4}$Se$_{0.6}$ system, with respect to the other stoichiometries. To clarify this point, we computed the so-called Steinhardt parameters to understand the similarities between structures and the X-ray diffraction spectra. These are based on spherical harmonics notation and are able to distinguish between liquid and solids or to identify structural defects since they measure the order degree of the first coordination shell of a given atom. The calculation of the 3$^{\text{rd}}$ ($q_3$), 4$^{\text{th}}$ ($q_4$) and 6$^{\text{th}}$ ($q_6$) order of Steinhardt parameters is also employed in Metadynamics simulations to discriminate two different states. For a central atom, the general form of the Steinhardt parameter is:

$$q_{nm}(i) = \frac{\sum_j \sigma(r_{ij}) Y_{nm}(r_{ij})}{\sum_j \sigma(r_{ij})},$$

where $Y_{nm}(r_{ij})$ is one of the $n$-th order spherical harmonics with $m$ going from $-n$ to $n$ and $\sigma(r_{ij})$ is a switching function that depends on the distance between atoms $i$ and $j$.

To measure the order of the whole system, the norm of $q_{nm}(i)$ is defined as:

$$Q_n(i) = \sqrt{\sum_{m=-n}^{n} q_{nm}(i)}.$$

This value is small when the local environment of the system is ordered, and it becomes larger for disordered systems. The Steinhardt parameters are strongly related to the selected system and are not transferable to other systems, containing different atomic types. Calculations of the Steinhardt parameters have been performed using the Plumed package.

The calculation of the 3$^{\text{rd}}$ ($q_3$), 4$^{\text{th}}$ ($q_4$) and 6$^{\text{th}}$ ($q_6$) order of Steinhardt parameters reported in Figure S8a shows that Ge$_{0.5}$Se$_{0.5}$ and Ge$_{0.6}$Se$_{0.4}$ are very similar, while they are both different from Ge$_{0.4}$Se$_{0.6}$, supporting the previous results from VP analysis. Distance between points reported in Figure S8a indicates that Ge$_{0.5}$Se$_{0.5}$ is the most similar to the cubic crystal, followed by Ge$_{0.6}$Se$_{0.4}$, while the Ge$_{0.4}$Se$_{0.6}$ is more similar to the orthorhombic structure. All structures are more similar to the cubic respect to the orthorhombic phase. All $q_n$ parameters discriminate not only the crystal from the amorphous phases, but also the different stoichiometries. Figure S8b shows that the main peak for Ge$_{0.4}$Se$_{0.6}$ is located at 20=30°, while the peak is at 20=34° and 20=36° for the Ge$_{0.5}$Se$_{0.5}$ and the Ge$_{0.6}$Se$_{0.4}$ system, respectively, reported in Figure S8b.

The X-ray diffraction (XRD) analysis is a powerful experimental technique to analyze the crystallinity of a material and can reveal information of the chemical composition. This technique is based on the measurement of the diffraction intensity as a function of the outgoing direction ($\theta$). The XRD intensity at the scattering vector $Q$ is computed using the Debye formula:

$$I(Q) = \frac{1}{N} \sum_{j=1}^{N} \sum_{i=1}^{N} f_i(Q) f_j(Q) \frac{\sin (Q \cdot r_{ij})}{Q \cdot r_{ij}} W(r_{ij})$$

where $N$ is the total number of atoms, $f_i(Q)$ and $f_j(Q)$ are the atomic scattering form factors, $r_{ij}$ is the distance vector between atoms $i$ and $j$ with a length of $r_{ij} = |r_{ij}|$, $W(r_{ij}) = \frac{\sin(\pi r_{ij} / R)}{\pi r_{ij} / R}$ is the Lorch function used to overcome the artifacts due to the finite simulation box, and $R_c$ is the upper limit for
To compute the XRD intensity we employed a plugin developed by Lodesani et al.\textsuperscript{4} and coupled with Plumed.\textsuperscript{5} This method is based on the chemistry of the system due to the atomic scattering factors that are characteristic of the element and it is able to localize the presence of crystalline surfaces, such as the (100) or the (200), and to discriminate between different phases of the system.\textsuperscript{7} However, the XRD technique is not able to go deeper inside the atomistic arrangement because it averages over the whole simulation box, losing information about peculiar structures.

The XRD patterns for the crystal structures are not as accurate as the experimental one, but the main peak at $2\theta=32$ is very similar to that obtained by Ren et al.\textsuperscript{8} for GeSe orthorhombic system. The main peak of the cubic crystal obtained from our simulations is comparable with the well-known peak of the perfect cubic crystal as reported in of the MaterialsProject database (https://materialsproject.org/, ID mp-10759) and on http://www.hqgraphene.com/GeSe.php.

From this analysis we can obtain an order classification: $\text{Ge}_{0.5}\text{Se}_{0.5} \approx \text{Ge}_{0.6}\text{Se}_{0.4} > \text{Ge}_{0.4}\text{Se}_{0.6}$.

![Figure S8](image)

**Figure S8.** a) Steinhardt parameters $q_3$, $q_4$ and $q_6$ and b) the XRD pattern computed for the Ge$_x$Se$_{1-x}$ compounds as a function of the Ge-content $x$ (purple, green and blue). The cubic and orthorhombic crystal values (black and blue, respectively) are included for comparison. In panel a) lines and respective values represent the distance between points.
S5. Homology analysis for the three stoichiometries

**Figure S9.** Persistence diagrams for the three systems at increasing Ge-content. a) to c) report the liquid phase and d) to f) the amorphous phase. Numbers in the top panels of each graph represent the surface of the PD expressed in Å².
S6. Correlation between Persistent homology and g(r)

Figure S10. Projection of the Homology on the Birth axis and comparison with the total and partial g(r) for a) Ge$_{0.4}$Se$_{0.6}$ and b) Ge$_{0.6}$Se$_{0.4}$ amorphous systems.

**Strength and weakness points of each technique**

| Technique | Strength | Weakness |
|-----------|----------|----------|
| g(r)      | • Easy to interpret  
           • Partially describe the order to a reference system, e.g. a crystal | • Too many data for systems with 3 or more elements  
• No information on the MRO |
| BELLO     | • Accurate description of the atomic local environment  
           • Order parameter | • Too many data for systems with 3 or more elements  
• No information on the MRO |
| Voronoi   | • Independent on the atomic species  
           • Connection between the SRO and MRO | • No information on the chemistry of the system  
• Shannon entropy, Diversity index and Voronoi probabilities strongly dependent on the number of atoms in the system |
| Homology  | • Independent on the atomic species  
           • Comparison of the MRO of different systems | • No information on the chemistry of the system  
• Persistent entropy and Persistence diagram strongly dependent on the number of atoms in the system |

**References**

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