

Local Structural Origin of the Crystallization Tendency of Pure and Alloyed Sb

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Phase change materials are highly important for technological applications in data storage. This work is focused on the family of phase-change materials comprising antimony alloys. The crystallization of amorphous models of Sb, $\text{Ge}_{15}\text{Sb}_{85}$, and $\text{In}_{15}\text{Sb}_{85}$ generated by simulated quenching from the melt is investigated. The structural properties of these alloys are also analyzed and their crystallization kinetics is elucidated in terms of the local structural motifs.

Phase change materials (PCMs)^[1–3] exhibit a remarkable ability to switch rapidly and reversibly between the crystalline and amorphous state under electrical or optical stimulus. Originally employed in rewritable CD's and DVD's that exploited the optical contrast between the two states, PCMs are now used in electronic phase-change memories, which are based on the electrical contrast between the two states. The first PCM memory products entered the market last year.^[4,5] Other promising applications of PCMs include brain-inspired computing^[6] and opto-electronic devices.^[7]

The most important PCMs lie on the ternary Ge-Sb-Te phase diagram and can be roughly divided into three families. The first one consists of pseudo-binary alloys along the $\text{GeTe-Sb}_2\text{Te}_3$ line,^[8–12] for example, $\text{Ge}_2\text{Sb}_2\text{Te}_5$ (GST). The second group comprises alloyed SbTe compounds near the eutectic composition $\text{Sb}_{70}\text{Te}_{30}$,^[13–15] such as $\text{Ag}_4\text{In}_3\text{Sb}_{67}\text{Te}_{26}$ (AIST). The third family encompasses Sb alloys such as $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{In}_{15}\text{Sb}_{85}$.^[16,17] Recently, a new PCM has been designed and synthesized: Sc-alloyed Sb_2Te_3 ($\text{Sc}_{0.2}\text{Sb}_2\text{Te}_3$), which enables sub-nanosecond switching of phase-change memory cells.^[18] Such speed could lead to the development of phase-change DRAM and even SRAM replacements.

Amorphous antimony is known to crystallize very rapidly, even at room temperature. This impedes applications in storage

devices. However, recent work has shown that nanoconfinement combined with ultra-fast quenching can dramatically improve the stability of the monatomic Sb glass.^[19,20] These findings open up the possibility of using pure antimony for memory-mapped storage class memories (SCMs) replacing DRAM in energy-sensitive applications and for other devices which do not require long retention times. Alloying Sb with Ge, In and other elements is known to improve the stability of the amorphous state at room temperature, while maintaining the fast

crystallization speed at elevated temperatures.^[16] This alloying routine can also make antimony suitable for storage-mapped SCMs, which require true non-volatility for long-term storage.

A clear trend in crystallization speed was observed experimentally in these Sb alloys. Both the growth rate and nucleation rate of $\text{In}_{15}\text{Sb}_{85}$ were found to be higher than those of $\text{Ge}_{15}\text{Sb}_{85}$.^[21] Here, information on the kinetics of pure Sb could not be obtained due to its extreme tendency to crystallize. Ab initio molecular dynamics (AIMD) simulations based on density functional theory (DFT) have shown that pure Sb can crystallize very rapidly in the presence of crystalline Sb boundaries, with an extremely high growth velocity of $\approx 36 \text{ m s}^{-1}$ at $T = 600 \text{ K}$.^[22,23] Such a crystallization speed is much greater than that of $\text{Ge}_2\text{Sb}_2\text{Te}_5$.^[24–27] Here, we aim at elucidating the atomic origin of the crystallization tendency of pure and alloyed Sb by AIMD simulations.

To this end, Sb, $\text{In}_{15}\text{Sb}_{85}$, and $\text{Ge}_{15}\text{Sb}_{85}$ were investigated using the second-generation Car–Parrinello scheme^[28] as implemented in the CP2K suite of programs.^[29] The Kohn–Sham wave functions were expanded in a triple-zeta plus polarization Gaussian-type basis set and the charge density was expanded in plane waves with a cutoff 300 Ry. The time step for the integration of the equations of motion was 2 fs. The scalar-relativistic Goedecker pseudopotentials^[30] and the generalized gradient approximation (GGA) for the exchange correlation (XC) potential, as parameterized by Perdew, Bruke, and Ernzerhof (PBE),^[31] were used. The use of PBE functionals for liquid Sb^[32] yields structural features in fair agreement with neutron scattering experiments.^[33] A 360 atoms were placed in an orthorhombic unit cell with $A = 21.77$, $B = 22.62$, and $C = 22.78 \text{ Å}$. The corresponding atomic density of 6.49 g cm^{-3} coincides with the experimental value for liquid Sb at $T = 915 \text{ K}$.^[34] Only the Gamma point of the Brillouin zone was sampled.

The melt-quench procedure employed in this work consisted of a randomization at very high temperature (above 2000 K) and subsequent equilibration for more than 40 ps at temperatures

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(900–930 K) close to the experimental melting temperature of Sb^[34] (903 K). Then, two different quenching rates were implemented for all of the three compounds, namely $\approx 30 \text{ K ps}^{-1}$ (fast quenching) and $\approx 3 \text{ K ps}^{-1}$ (slow quenching). Finally, all the models were annealed at 300 K over 450 ps. It is noted that even the slower quenching protocol considered here is still much faster than the experimental one. It is not feasible to further reduce the quench rate, due to the heavy computational load. Nevertheless, the current simulations are already sufficient to shed light on the crystallization tendency of these alloys.

The evolution of the potential energy of the three materials during the quenching and annealing processes is plotted in **Figure 1**. Clearly, some models crystallized completely during the simulation, as shown by the significant drop in the potential energy. To monitor the crystallization process more closely, a

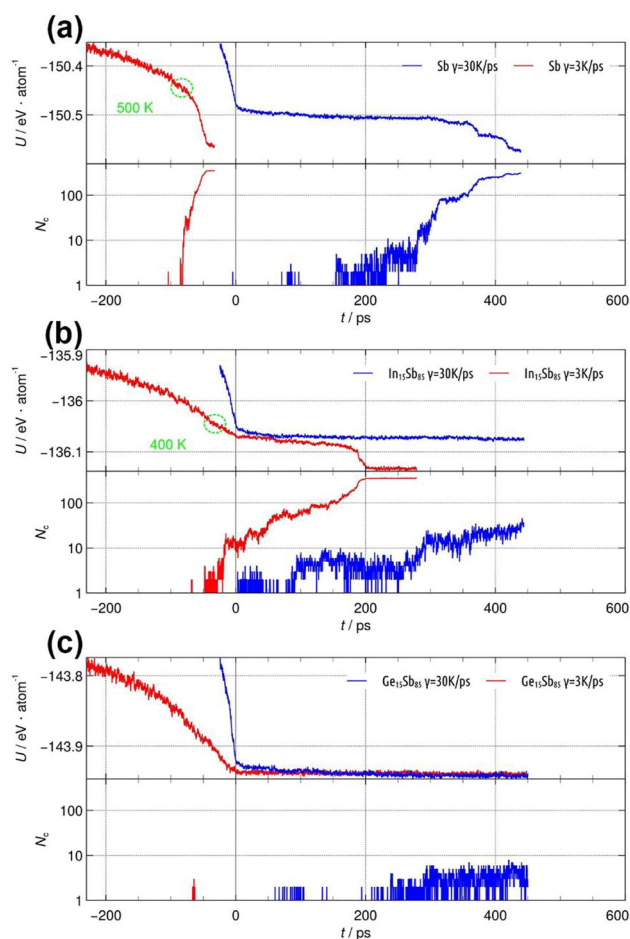


Figure 1. Evolution of the potential energy U and the number of crystalline-like atoms N_c during the ab initio molecular dynamics simulations of (a) Sb, (b) $\text{In}_{15}\text{Sb}_{85}$, and (c) $\text{Ge}_{15}\text{Sb}_{85}$. Red and blue curves correspond to the two quenching rates of 3 and 30 K ps^{-1} , respectively. The target temperature of 300 K is reached at time $t = 0$; thus, the quenching region corresponds to negative times. Crystallization occurs for both models of unalloyed Sb in (a), albeit at different times. The slowly quenched model of $\text{In}_{15}\text{Sb}_{85}$ crystallizes quickly as well, whereas the rapidly quenched one exhibits a slow increase in N_c at $T = 300 \text{ K}$. Both amorphous models of $\text{Ge}_{15}\text{Sb}_{85}$ remain stable on a time scale of 450 ps.

bond order correlation parameter “dot-product” $q_4^{\text{dot}[35]}$ was employed to distinguish the crystalline-like atoms from the amorphous-like or liquid-like atoms.^[19]

For unalloyed Sb, crystallization already occurred during the slow quenching process. The onset of crystallization was found at $\approx 500 \text{ K}$, which was followed by a rapid increase in the fraction of crystalline atoms (Figure 1a left). Fast quenching extended the lifetime of our Sb model by a few hundreds of ps. Crystallization started after about 200 ps annealing at 300 K, and almost completed after 450 ps (Figure 1a right). These results are in line with the simulations presented in ref. [19].

As regards $\text{In}_{15}\text{Sb}_{85}$, crystallization started at $\approx 400 \text{ K}$ during the slow quench and completed after 200 ps annealing at 300 K. In contrast, fast quenching made this model stable over 450 ps at 300 K, with a slow increase in the number of crystalline atoms starting from $\approx 300 \text{ ps}$ (see Figure 1b). Crystallization was not observed during both slow- and fast-quenches of $\text{Ge}_{15}\text{Sb}_{85}$ (Figure 1c). The two latter models were also shown to be robust in the amorphous form, as no obvious change in potential energy could be observed after the short equilibration period at 300 K. The number of crystalline-like atoms fluctuated, but remained below 10, corresponding to only $\approx 3\%$ of the total volume. It must be stressed that nucleation is a stochastic process and, thus, a large number of independent simulations should be carried out to improve the statistics and extract quantitative information. Furthermore, our models are not immune to finite-size effects. Nevertheless, the observed crystallization trends are fully in line with the experimental observations reported in ref. [21] and can be rationalized in terms of the structural properties of the three compounds, as discussed below.

The similarity of the local structural motifs of the amorphous and the crystalline phase has been demonstrated to strongly affect the crystallization kinetics of PCMs. For instance, upon fast crystallization, GST forms a rocksalt phase, which consists of octahedral units and fourfold ABAB rings (where A = Ge or Sb, B = Te). We consider (defective-) octahedral units and ABAB rings in amorphous GST to be crystalline precursors. The abundance of these precursors was proposed to be the essential ingredient for the fast nucleation of GST.^[36–40] Recent work has demonstrated that the dynamical stability of these precursors is a second key parameter to tune the nucleation rate of PCMs.^[18] To gain further understanding of the crystallization trend in Sb, $\text{In}_{15}\text{Sb}_{85}$, and $\text{Ge}_{15}\text{Sb}_{85}$, we thus investigated the structural features of their amorphous phases. All the data regarding the amorphous phase shown below were obtained from the room-temperature trajectories of the fast quenched models shown in Figure 1, between 50 and 100 ps. The first 50 ps of the trajectories were omitted, for equilibration.

The total and partial pair correlation functions (PCFs) of the three amorphous models are plotted in **Figure 2**. In amorphous Sb, the first peak and valley appear at 2.97 and $\approx 3.5 \text{ \AA}$ (Figure 2a). Upon alloying with Indium, the total PCF only shifts slightly toward larger distance values. The Sb–Sb PCF looks identical to that of pure amorphous Sb, while both the In–Sb and the In–In PCFs are shifted, with the first peak at 3.11 and 3.25 Å (Figure 2b), respectively. The decrease of the In–In PCF after the first maximum is not as sharp, compared to the other two PCFs, but this does not greatly alter the total PCF curve, owing to the

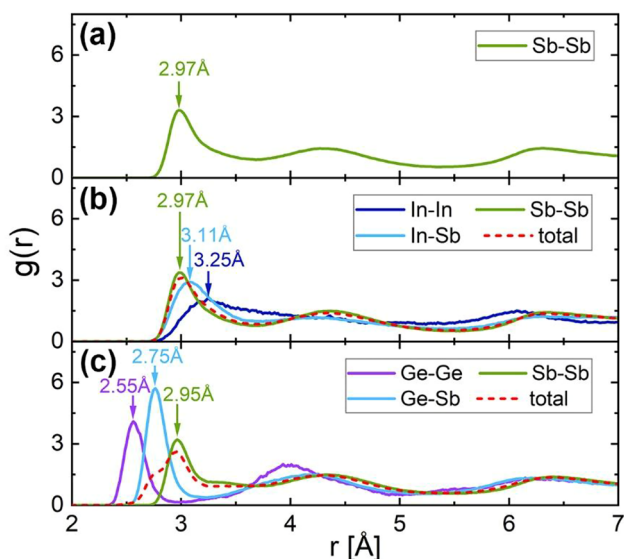


Figure 2. Total and partial pair correlation functions (PCFs) of (a) Sb, (b) $\text{In}_{15}\text{Sb}_{85}$, and (c) $\text{Ge}_{15}\text{Sb}_{85}$. The r values corresponding to the maxima of the PCFs are indicated explicitly.

low concentration of In–In pairs. As regards $\text{Ge}_{15}\text{Sb}_{85}$, the amorphous topology is changed significantly, as seen in the total PCF (Figure 2c). In addition to the main peak at 2.94 Å, a pre-peak appears at ≈ 2.7 Å and the first valley is shifted to ≈ 3.2 Å. This is due to the fact that the alloyed Ge atoms can form much shorter chemical bonds, namely the first peak of the Ge–Ge and Ge–Sb PCFs are found at 2.55 and 2.75 Å. These peak values are in line with extended X-ray absorption fine structure (EXAFS) measurements,^[17] where Ge–Ge and Ge–Sb bond lengths were determined to be 2.46(2) and 2.66(1) Å, respectively. The

presence of germanium also influences the Sb–Sb pairs, leading to a dip in the PCF at 3.2 Å. Clearly, Ge atoms are more effective than In atoms in altering the local structure of the amorphous network of Sb.

Now, we turn to the discussion of local structural motifs. The angular distribution functions (ADFs) and the coordination number (CN) profiles are plotted in Figure 3. The average and the distribution of the CNs are similar with and without In alloying. Most Sb and In atoms have 4, 5, or 6 neighbors. Taking into account the fact that a primary peak and a secondary peak are found at $\approx 90^\circ$ and $\approx 165^\circ$ in the ADF curves, we can conclude that both amorphous Sb and $\text{In}_{15}\text{Sb}_{85}$ are primarily comprised of (defective-) octahedral units. This is supported by more careful analyses using bond order parameters,^[40] see Table 1. Almost all the Sb atoms are octahedrally coordinated in both Sb and $\text{In}_{15}\text{Sb}_{85}$, while only a small fraction of In atoms ($\approx 9\%$) in $\text{In}_{15}\text{Sb}_{85}$ show tetrahedral coordination. In contrast, the majority of Ge atoms in $\text{Ge}_{15}\text{Sb}_{85}$ are found to be tetrahedrally coordinated ($\approx 74\%$), while the rest of the Ge atoms display defective octahedral coordination with the average CN being 4.0. Most Sb atoms in amorphous $\text{Ge}_{15}\text{Sb}_{85}$ are found in (defective-) octahedral units with the average CN being 4.5. The average CN of Ge is in good agreement with the extended X-Ray absorption fine structure (EXAFS) experiments reported in ref. [17], whereas the theoretical CN of Sb is larger than the experimental estimate (3.2) provided in the latter work. However, the CNs depend sensitively upon the choice of the cutoff. In particular, for Sb atoms having three short bonds and up to three elongated ones, changing the cutoff across the region that separates short and long bonds can result in large changes in the CN. In fact, using a cutoff of 3.2 Å for Sb–Sb (corresponding to the dip in the respective PCF of $\text{Ge}_{15}\text{Sb}_{85}$) yields an average CN of 3.2, which coincides with the experimental value.

From the ADF curve of $\text{Ge}_{15}\text{Sb}_{85}$, a primary peak around $\approx 109^\circ$ is found near Ge atoms, supporting the conclusion that the majority of Ge atoms are in tetrahedral coordination. Two snapshots of amorphous $\text{In}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$ are presented in Figure 4a,b, in which the major structural motifs around In and Ge atoms are also highlighted as insets. In summary, these findings clearly show that the presence of Ge atoms significantly alters the local bonding environment of amorphous Sb, whereas In atoms only lead to slight changes.

The vast majority of tetrahedral Ge and In units in amorphous $\text{Ge}_{15}\text{Sb}_{85}$ and $\text{In}_{15}\text{Sb}_{85}$ have heteropolar configuration with four Ge–Sb (respectively, In–Sb) bonds, indicating that homopolar Ge–Ge/In–In bonds do not drive the formation of tetrahedral units in these alloys, contrary to the case of amorphous GeTe and GST.^[37,40–43] This can be qualitatively understood by considering that there exist Ge–Sb and In–Sb crystals with tetrahedral Ge [Ge_0Sb_4] (respectively, In [In_0Sb_4]) units, while no such structural motifs can be found in Ge–Te crystals.^[44,45] This could lead to potentially different aging

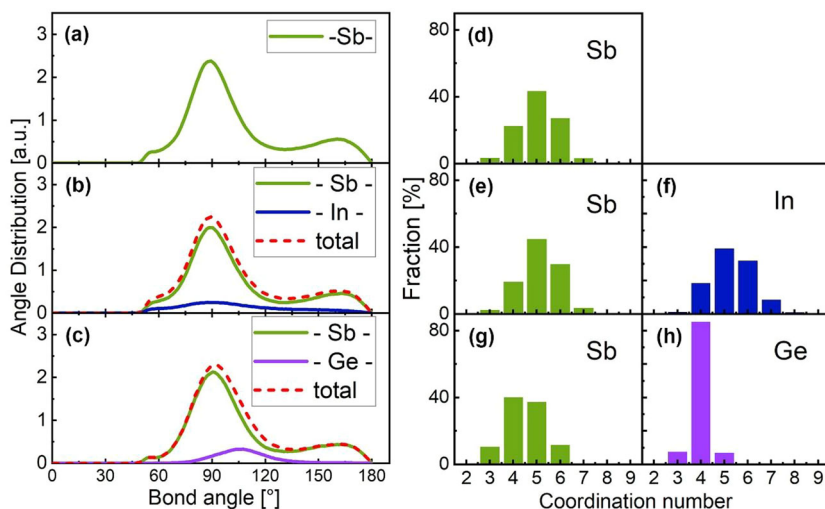


Figure 3. (a–c) Angular distribution functions and (d–h) distributions of the coordination numbers of the three compounds. Cutoffs are set to 3.5 Å for amorphous Sb and $\text{In}_{15}\text{Sb}_{85}$, whereas, for $\text{Ge}_{15}\text{Sb}_{85}$, different cutoffs are selected for different bonds: 2.9 Å for Ge–Ge, 3.1 Å for Ge–Sb, and 3.5 Å for Sb–Sb. The cutoff values for Ge–Ge and Ge–Sb correspond to the first valley of the respective partial PCFs.

Table 1. The local structural motifs in amorphous Sb, $\text{In}_{15}\text{Sb}_{85}$, and $\text{Ge}_{15}\text{Sb}_{85}$. Data were obtained by averaging the trajectories at 300 K for 50 ps.

Amorphous	Sb	$\text{In}_{15}\text{Sb}_{85}$		$\text{Ge}_{15}\text{Sb}_{85}$	
Center atom	Sb	In	Sb	Ge [%]	Sb
Def. Octa.	93%	82%	96%	26	99%
Tetra.	4%	9%	/	74	/
Tetra. $[\text{X}_0\text{Sb}_4]$	100%	92%	/	70	/
Tetra. $[\text{X}_1\text{Sb}_3]$	/	8%	/	24	/
Tetra. $[\text{X}_2\text{Sb}_2]$	/	/	/	6	/

paths as compared to GeTe/GST ,^[45–51] since the driving force to remove tetrahedral units should be smaller in Sb and alloyed Sb compounds. Nevertheless, the reinforcement of Peierls distortion observed in GeTe upon aging could be relevant to Sb alloys as well.^[45]

Independent crystallization simulations were also carried out for $\text{In}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$ at high temperature (500 K) to determine the impact of In and Ge on the crystalline structure of Sb. The trajectories were branched off at 500 K from the

simulations with high quenching rates (30 K ps^{-1}). At this temperature, $\text{In}_{15}\text{Sb}_{85}$ started to nucleate after 70 ps and crystallized in about 40 ps, whereas, in $\text{Ge}_{15}\text{Sb}_{85}$, nucleation started after about 200 ps and the system crystallized within 100 ps. The recrystallized phase of both compounds is found to be cubic and to contain hardly any tetrahedral motifs, as shown in Figure 4c,d.

As far as bonding properties are concerned, it is well known that crystalline Sb is characterized by meta-valent (resonant) bonding,^[52] while the amorphous state exhibits covalent bonding due to the directional disorder and the strong Peierls-like distortions. Upon alloying Sb with Ge and In, the covalent bonding character remains unchanged in the amorphous state.

In conclusion, our AIMD simulations on pure and alloyed Sb compounds show that Sb crystallizes faster than $\text{In}_{15}\text{Sb}_{85}$, while no obvious sign of crystallization can be observed for $\text{Ge}_{15}\text{Sb}_{85}$ during the quenching simulations and at room temperature. Structural analysis of the amorphous phase provides an explanation for this observation. Upon alloying In atoms, the amorphous network of Sb is not strongly affected, and both the bond lengths and bond angles do not change markedly. By contrast, the presence of Ge atoms alters the

overall amorphous network significantly by leading to the formation of much shorter chemical bonds and tetrahedral structures. However, long annealing simulations at elevated temperatures show that both $\text{In}_{15}\text{Sb}_{85}$ and $\text{Ge}_{15}\text{Sb}_{85}$ crystallize into the cubic phase with very few tetrahedral Ge units. The increasing dissimilarity in local motifs between the amorphous and the crystalline state of $\text{Ge}_{15}\text{Sb}_{85}$ hinders the crystallization kinetics during quenching and stabilizes the amorphous phase at room temperature. Interestingly, it has been shown that the flexibility of chemical bonds is reduced by alloying Ge into amorphous Sb.^[53,54] This increased bond rigidity may also contribute to the stabilization of the amorphous network of $\text{Ge}_{15}\text{Sb}_{85}$, in combination with the tetrahedral motifs discussed here. Our work thus elucidates the atomic origin of the crystallization tendency in the third family of PCMs.

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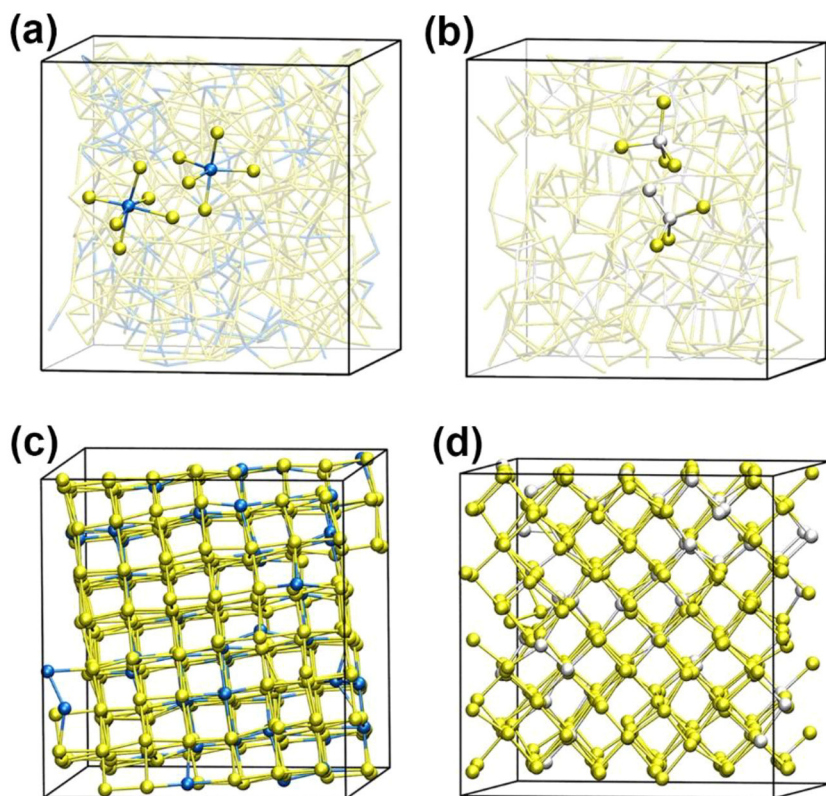


Figure 4. a,b) Snapshots of amorphous (a) $\text{In}_{15}\text{Sb}_{85}$ and (b) $\text{Ge}_{15}\text{Sb}_{85}$ at 300 K. The major structural motifs around In atoms (octahedral structures) and Ge atoms (tetrahedral structures) in the amorphous phase are highlighted. c,d) Snapshots of recrystallized (c) $\text{In}_{15}\text{Sb}_{85}$ and (d) $\text{Ge}_{15}\text{Sb}_{85}$ at 500 K. Both recrystallized states are cubic and contain very few tetrahedral structures. Sb, In, and Ge atoms are rendered with yellow, blue, and gray spheres, respectively.

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Conflict of Interest

The authors declare no conflict of interest.

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