Ab-initio simulation of amorphous $Ge_2Sb_2Te_5$

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ABSTRACT

We perform *ab-initio* molecular dynamics simulations aiming at shading light onto the structure of amorphous $Ge_2Sb_2Te_5$ (GST), the prototypical phase change material. First principles simulations show that amorphous GST obtained by quenching from the liquid phase displays two types of short range order. One third of Ge atoms are in a tetrahedral environment while the remaining Ge, Sb, and Te atoms display a defective octahedral environment, reminiscent of cubic crystalline GST. Secondly, we have simulated the pressure induced amorphization of the cubic crystal of GST. The simulations revealed the role of vacancies in the transformation process and suggested that the amorphization is driven by the higher compressibility of the amorphous phase with respect to the crystal.

Key words: ab-initio molecular dynamics, phase change materials, GST, chalcogenide glasses, pressure-induced amorphization, structural properties.

1. INTRODUCTION

In spite of the great technological importance of chalcogenides alloys as phase change materials for electronic and optical storage, the present microscopic understanding of the properties of materials in this class is still largely unsatisfactory. The atomistic structure of the amorphous phases, the detailed mechanism of the phase change and the microscopic origin of the electronic and optical properties exploited in the storage devices are still largely unknown [1].

For instance, alternative models for amorphous $Ge_2Sb_2Te_5$ (GST), the prototypical compound in this class, have been proposed on the basis of extended x-ray absorption fine structure (EXAFS) and x-ray absorption near-edge structure (XANES) measurements [2] or Reverse Monte Carlo (RMC) based on the total x-ray scattering function [3]. Kolobov *et al.* could interpret their EXAFS/XANES data [2] by assuming that in amorphous GST (*a*-GST), Ge is tetrahedrally coordinated as opposed to its octahedral coordination in the crystalline phases (hexagonal and metastable cubic). Based on *ab-initio* calculations, Wełnic *et al.* [4] proposed a spinel-like geometry for the local structure of *a*-GST with the coexistence of tetrahedral sites for Ge and octahedral sites for Te and Sb. However, the model of *a*-GST proposed by Kolobov *et al.* is in contrast with other interpretation of EXAFS data [5], and with more recent RMC ones [3] which both assume an octahedral geometry of Ge in the amorphous phase. The interpretation of the experimental data is, however, not unique and several different structural models might be compatible with the data.

In this respect, first principles atomistic simulations can provide precious insight. In a recent work we have shed light onto the structure of *a*-GST by providing models generated by quenching from the melt using *ab-initio* molecular dynamics (MD) based on density functional theory [6]. To this aim we have applied a newly developed method for *ab-initio* molecular dynamics [7] which allowed speeding up the simulations by a factor 20 with respect to standard *ab-initio* MD for a supercell size of the order of 300 atoms.

In this paper we briefly review our results on the structural properties of *a*-GST [6] and we report on the simulation of pressure induced amorphization of GST recently discovered experimentally [8].

2. COMPUTATIONAL DETAILS

Ab-initio molecular dynamics simulations have been performed using the scheme of Kühne *et al.* [7] In the spirit of the Car-Parrinello (CP) approach, the wavefunction is not selfconsistently optimized during the dynamics. However, in contrast to CP, large integration time steps can be used in the simulation. This scheme leads to a slightly dissipative dynamics of the type $-\gamma d\mathbf{R}_I/dt$, where $\mathbf{R}_I$ are the ionic coordinates. In Ref. [7], it is shown how to compensate for this dissipation and obtain a correct canonical sampling. This scheme has been implemented in the CP2K suite of programs (http://cp2k.berlios.de). We use the Perdew-Becke-Ernzerhof gradient corrected exchange correlation functional and Goedecker-type pseudopotentials. The Kohn-Sham orbitals are expanded in a valence triple-zeta plus polarization (TZVP) Gaussian-type basis set, and the charge density is expanded in a planewave basis set with a cutoff of 100 Ry to solve efficiently the Poisson equation.

3. RESULTS

A model of *a*-GST has been generated by quenching from the melt. We started our simulations from a 270-atoms supercell of metastable cubic GST, where Te occupies one sublattice of the rocksalt crystal, and Ge, Sb, and vacancies are randomly placed in the other sublattice. The atomic density is chosen equal to 0.030 at./Å^3 close to the experimental value for *a*-GST. The system has then been heated at 2300 K and then quenched and further equilibrated at 990 K. In order to generate a model of *a*-GST, the liquid has been brought to 300 K in 18 ps. The calculated neutron scattering function $S(Q)$ of *a*-GST reported in Fig. 1 is in good agreement with neutron scattering experimental data [9], especially considering that the latter are recorded on the as-deposited amorphous film which might be structurally slightly different from *a*-GST quenched from the melt as suggested by their different optical reflectivity.
In our *a*-GST model [6], most of Ge and Sb atoms in *a*-GST are 4-coordinated while Te is mostly 3-coordinated in defective octahedral-like sites which recall the local environment of cubic crystalline GST (inset in Fig. 1). However, as much as one third of Ge atoms are in a tetrahedral geometry as suggested by EXAFS/XANES measurements. This configuration is absent in the crystalline phase, and favoured in *a*-GST by the presence of homopolar (Ge-Ge and Ge-Sb) bonds. Namely, 38% of Ge are bonded with at least another Ge or Sb, a percentage which is raised to 52% for Ge atoms four-coordinated. The fraction of Sb bonded to another Sb or Ge is instead 59%. Our results thus reconcile EXAFS and x-ray diffraction data. In contrast to common beliefs on the structure of chalcogenide glasses, we have not found long chains of Te, but only Te dimers and trimers. Our conclusions on the structural properties of GST have then been fortified by analogous results from conventional *ab-initio* simulations on GST and other systems along the pseudobinary line $(GeTe)_x(Sb_2Te_3)_y$ [10, 11].

The absence of long chains of Te atoms is probably also at the origin of the absence in our model of Valence Alternation Pairs (VAPs) which are defects often suggested to be present in chalcogenide glasses including GST [12]. To identify the possible presence of charged defects, we have computed the Bader ionic charges from the total electronic charge density by using the scheme of Ref. [13]. In Fig. 2 the calculated Bader ionic charges of the cubic rocksalt crystal and of *a*-GST are compared. In *a*-GST the ionic charges distribution tails toward zero due to the presence of homopolar bonds. No highly charged defects such as VAPs are found. We should also mention that in our *a*-GST model the precursors of VAPs in the form of one-coordinated Te or three-coordinated Ge and Sb are absent as well. Similar structural properties with the coexistence of defective octahedral sites (for Te and Ge) and tetrahedral sites (Ge only) have been found for the related GeTe binary compound which has been simulated as well. For this latter system we have generated a 216-atoms model by quenching from the melt within spin-unrestricted simulations which might allow for the appearance of radicals species as possible VAPs precursors. The resulting amorphous model does not present, however, radical species nor VAPs precursors.
The absence of VAPs species might still be due to the small size of our simulation cell whenever the expected density of VAPs would be lower than 1/270 atoms. However, we have also to consider that the fast quenching protocol used here usually largely overestimate the concentration of the most prominent defects.

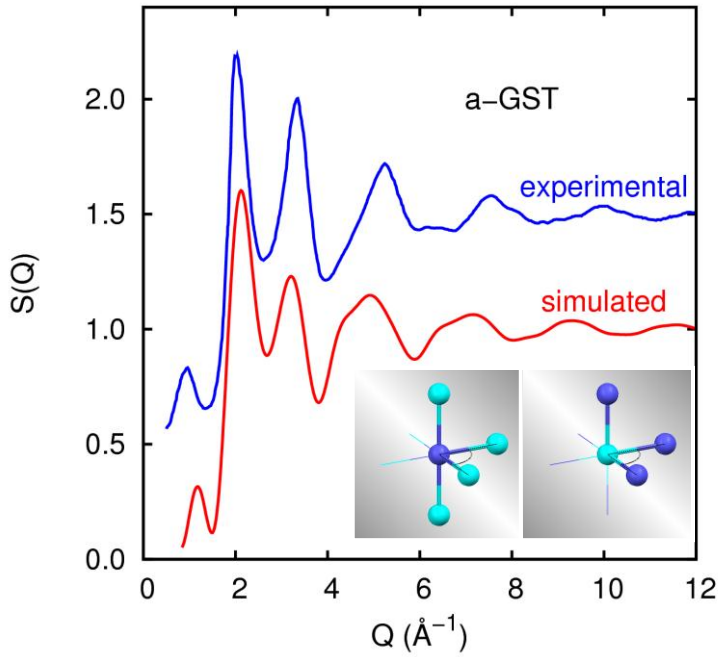

Fig. 1. Calculated and experimental [9] neutron scattering factor $S(Q)$ of *a*-GST. Inset: a sketch of the geometry of defective octahedral sites of four-coordinated Ge and three-coordinated Te.

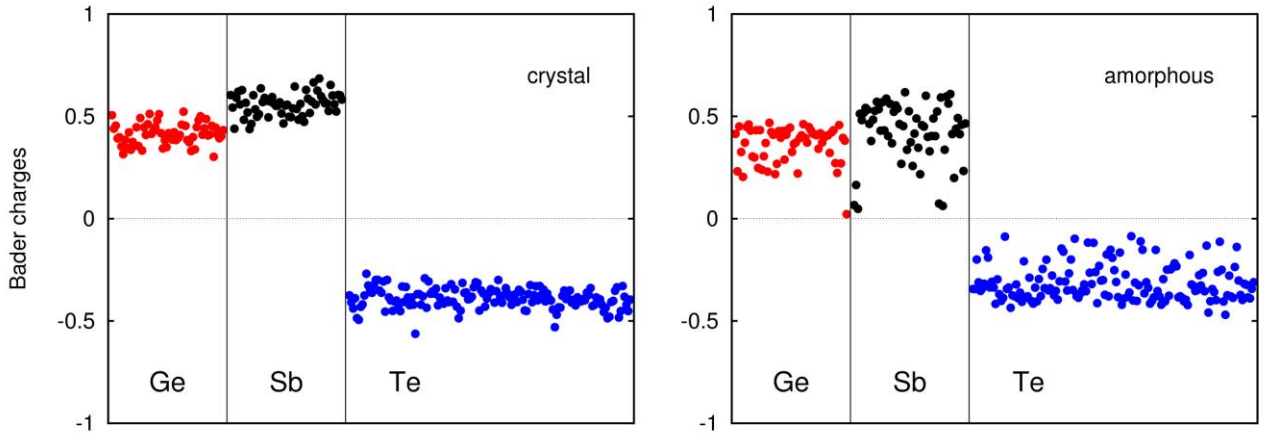

Fig. 2. Bader ionic charges (atomic units) of our models of cubic GST and of *a*-GST. Each point corresponds to an individual atom in the 270-atoms supercell.

As a second example of simulations of *a*-GST, we now turn to the discussion of our recent results on pressure induced amorphization of the cubic phase. Our work has been stimulated by recent experiments which show that cubic crystalline GST turns into an amorphous phase when submitted to a pressure of 20 GPa at room temperature [8]. The amorphous phase can be recovered upon decompression at normal conditions. EXAFS and XANES data on pressure amorphized GST are very similar to those of *a*-GST generated by quenching from the melt [2]. Other cubic crystals along the pseudobinary lines $(GeTe)_x(Sb_2Te_3)_y$ similarly undergo amorphization above a threshold pressure which, however, depends on the concentration of vacancy on the Ge/Sb sublattice of the cubic rocksalt phase [14], the higher the concentration of vacancy the lower the transition pressure. In particular, the binary GeTe compound which adopts a rocksalt geometry without vacancies does not amorphize up to the highest pressure (~25 GPa) reached in experiments [8, 14].

To shed light onto the role of vacancies in the amorphization process, we have performed *ab-initio* MD simulations of GST at increasing pressure by using the scheme outlined in Sec. 2. We started from the same 270-atoms supercell of cubic GST discussed above, Te occupying one sublattice of the rocksalt crystal, and Ge, Sb, and vacancies randomly placed in the other sublattice at the density of cubic GST at normal conditions. We have

then submitted the model to increasing pressure by reducing isotropically the volume in 12 steps up to the pressure of 31 GPa, each simulation at fixed volume lasting on average 8 ps. The ionic temperature is set at 300 K by a Langevin thermostat.

In Fig. 3 we report the evolution of the main peaks in the structure factor S(Q) which correspond to the order parameters of the crystalline phase. Crystalline order clearly disappears above 20 GPa in agreement with experiments [8]. The <200> peak which gives a measure of the alignment of the squared rings along <100> directions is the last to disappear. By progressively increasing the volume of the supercell (in 12 steps lasting 7 ps each) the amorphous phase has been recovered at normal conditions. The structure of the amorphous phase turns out to be very similar to that of melt-quenched *a*-GST discussed previously and reported in Ref. [6].

In particular, the fraction of homopolar Ge/Sb and Te/Te bonds is the same as in melt-quenched *a*-GST. Again, most of Sb and Ge are 4-coordinated in defective octahedral sites, while a fraction of Ge atoms are in tetrahedral geometry. Actually, the conversion from octahedral to tetrahedral coordination of Ge takes place during decompression, since the coordination number of Ge at 20 GPa is as large as 6-7. The fraction of tetrahedral Ge atoms is now 17 %, a value lower than that found in melt-quenched *a*-GST (33 %). However, we must consider that, due to the short time span of the simulation, the system faces more difficulties to reach a fully relaxed low-energy structure in the decompression run at 300 K.

By inspecting the atomic trajectories during pressurization, we have identified the role of vacancies. In the crystalline phase, the system can increase the density upon compression by filling the vacancy voids without reducing too much the nearest neighbours distances. This is achieved by a displacement of Te atoms toward the nearest vacancy as sketched in the inset of Fig. 3. The movement of Te atom induces the breaking of Te-X bond opposite to the vacancy and the formation of new homopolar Ge/Sb bonds. This process gives rise to squared rings rotated by 45^{o} with respect to the crystalline axis (inset of Fig. 3). Snapshots of the rotated rings at two different pressures are showed in Fig. 4.

We speculate that the role of vacancies is twofold. They increase the compressibility of the crystal and allow reaching a higher density at lower pressure; secondly, they contribute to destabilize the system once the concentration of rotated rings becomes too high.

The formation of rotated rings can actually accommodate the density increase without compressing the Te-X bonds, but only up to a certain extent. When pressure is too high, Te-X bonds become too compressed and the system transforms into an amorphous phase. The amorphization transition is actually driven by a higher compressibility of the amorphous phase with respect to the crystal. In fact, although at normal conditions the average coordination number of atoms in *a*-GST is lower than in the crystal (Ge/Sb are mainly 4-coordinated in *a*-GST but 6-coordinated in the crystal at normal conditions) the opposite is true at high pressure.

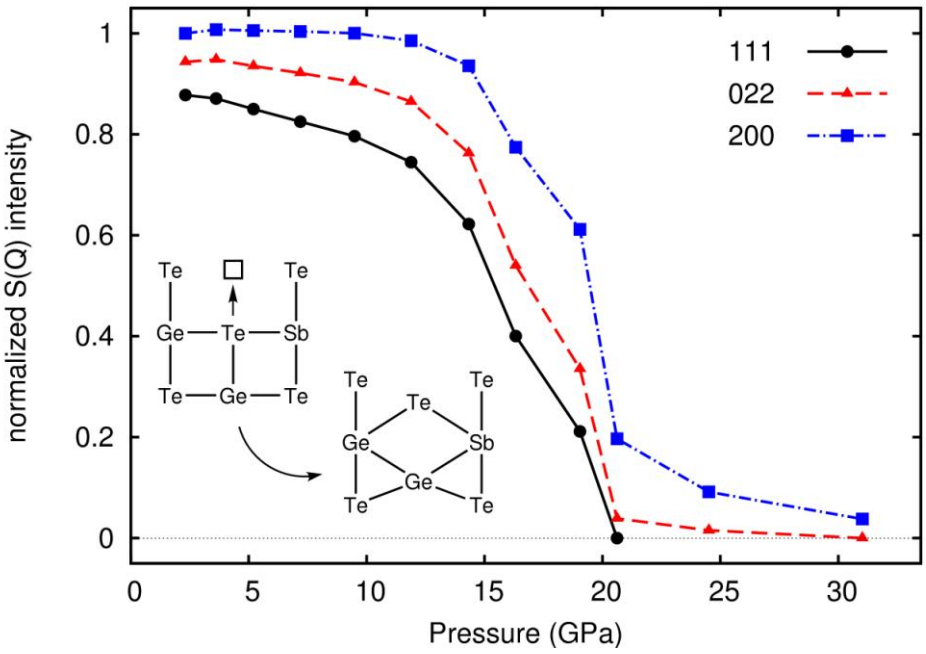

Fig. 3. Evolution with pressure of the intensity of the main peaks of the structure factor S(Q) normalized to the intensity of the <200> peak at zero pressure. Inset: sketch of the displacement of Te atom toward the vacancy giving rise to a rotated square ring with homopolar bonds.

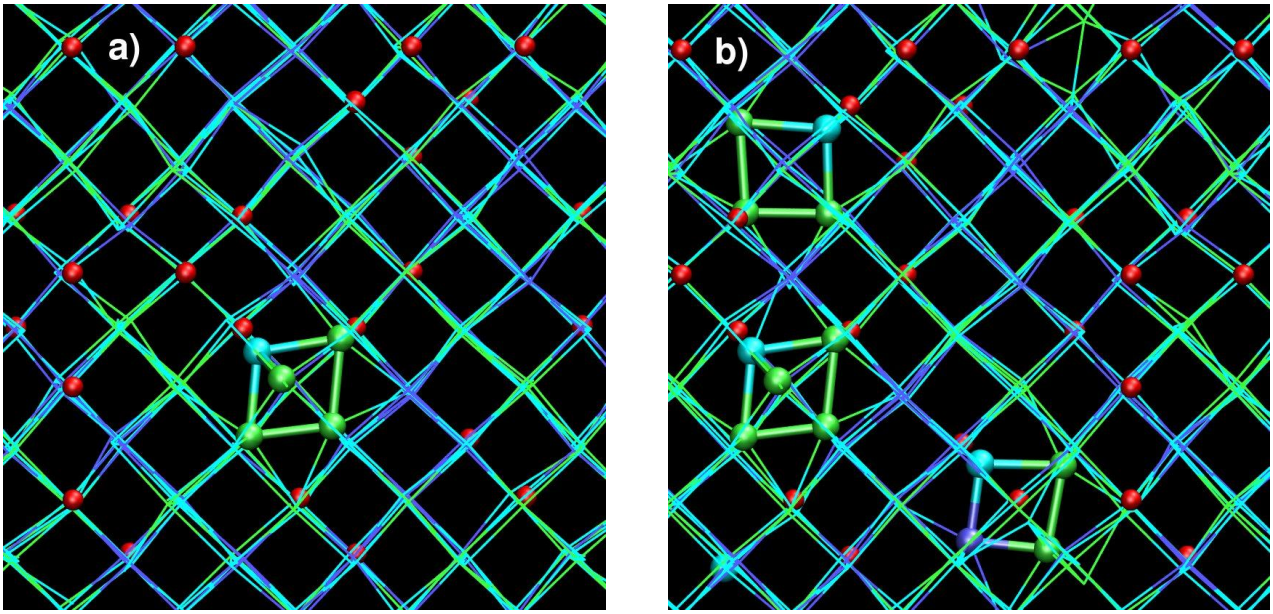

Fig. 4. Snapshots of the simulation at a) 12 GPa and b) 14 GPa showing the appearance of squared rings formed by homopolar Ge/Sb bonds rotated by 45^{o} with respect to the crystalline axis.

The distribution of coordination numbers in the crystal and *a*-GST both at 21 GPa are compared in the inset of Fig. 5. In the high pressure amorphous phase, atoms are clearly more coordinated than in the crystal at the same pressure. As a result, in the amorphous phase, density has increased via an increase in the coordination numbers with a lower compression of Te-X bonds than occurring in the crystal.
In other words, the amorphous is more compressible than the crystal as shown by the equation of state (at zero temperature) reported in Fig. 5. By fitting the energy versus volume points with a Murnaghan function we obtain a bulk modulus of 27 GPa for the crystal and 11 GPa for the amorphous phase. These values could be compared with the bulk modulus of rombohedral GeTe which is 51 GPa [15].

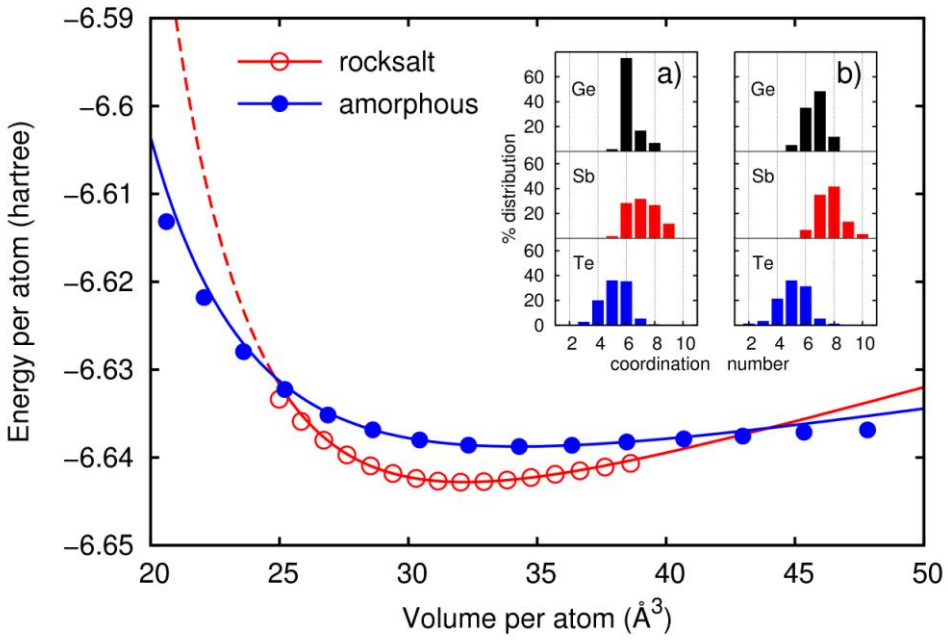

Fig. 5. Equation of state of the crystalline cubic GST and of *a*-GST obtained from decompression of the pressure-amorphized system. Inset: distribution of coordination numbers for crystalline GST and *a*-GST at 21 GPa.

4. CONCLUSIONS

In summary, *ab-initio* molecular dynamics simulations have shed light on the microscopic structure of amorphous GST quenched from melt. Most of the Ge and Sb atoms in *a*-GST are four-coordinated, while Te is mostly three-coordinated in defective octahedral-like sites which recall the local environment of cubic crystalline GST. However, as many as 33% of Ge atoms are in a tetrahedral geometry, absent in the crystalline phase, and favored by the presence of homopolar (Ge–Ge and Ge–Sb) bonds. The coexistence of the two types of local environment might be the key to understand the two apparently contradictory and peculiar features of GST exploited in the devices, namely, the strong optical (and perhaps electronic) contrast between the amorphous and crystalline structures, and the high speed of phase change.
Moreover, the simulations have revealed the microscopic mechanism behind the pressure induced amorphization of GST. By pressurizing the cubic crystalline form of GST, firstly Te atoms move to fill the vacancy voids giving rise to topological defects in the rocksalt crystal made of homopolar Ge/Sb bonds in squared rings rotated by 45º with respect to the crystalline axis. By further increasing pressure the concentration of these topological defects increase up to 20 GPa at which the system transforms into an amorphous phase. The amorphization occurs on the time scale of few picoseconds and it is driven by the higher compressibility of the amorphous phase with respect to the crystal.

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Biography

Marco Bernasconi received the undergraduate degree in Physics at the University of Milano in 1988 and the Phd in Theoretical Condensed Matter Physics at Sissa (Trieste) in 1993. He spent two years as a postdoc at the Max-Planck-Institut fuer Festkoerperforschung (Stuttgart, Germany) in the group of Prof. M. Parrinello and then joined the Department of Materials Science of the University of Milano-Bicocca (Milano, Italy) where he currently holds the position of associate professor in Condensed Matter Physics. His research activity is devoted to the ab-initio modelling of materials ranging from crystalline and amorphous semiconductors and insulators for applications in microelectronic and photonics to superionic conductors and low-Z superconductors. He is author of over 80 articles in international journals with peer review.