Atomic mobility and fast crystallization of the phase change compound GeTe

G. C. Sosso[1,2], Jörg Behler[3],M. Bernasconi[1,*]

[1]Department of Materials Science, University of Milano-Bicocca, Via R. Cozzi 53,
I-20125 Milano, Italy
[2]Department of Chemistry and Applied Biosciences, ETH Zurich, and Facoltà di Informatica,
Istituto di Scienze Computazionali, Università della Svizzera Italiana, Via G. Buffi 13,
CH-6900 Lugano, Switzerland
[3]Lehrstuhl für Theoretische Chemie, Ruhr-Universität Bochum, Universitätsstrasse 150,
D-44780 Bochum, Germany
*e-mail:marco.bernasconi@unimib.it

ABSTRACT

The application of amorphous chalcogenide alloys as phase change materials in data-storage media rests on their ability to undergo an extremely fast (10-100 ns) crystallization upon heating. What makes these materials so special in this respect is, however, still a matter of debate. By means of large scale molecular dynamics simulations, we demonstrate that the phase change compound GeTe shows a high atomic mobility in the amorphous phase overheated just above the glass transition temperature. This behavior leads to a breakdown of the Stokes-Einstein relation between the self-diffusion coefficient and the viscosity which is one of the keys to understand the fast crystallization of materials in this class.

Key words: molecular dynamics simulations, supercooled liquids, crystallization

1. INTRODUCTION

Phase-change materials based on chalcogenide alloys are of great interest due to their ability to undergo reversible and fast transitions between the amorphous and crystalline phases upon heating. This property is exploited in rewriteable optical disks (DVD) and phase change non volatile memories (PCM) [1]. What makes these materials so special in this respect is, however, still a matter of debate. The fast crystallization of the prototypical GeTe and $Ge_2Sb_2Te_5$ (GST) phase change compounds has been ascribed to the similarity of the bonding topology in the amorphous/liquid and crystalline phases [2]. In fact, the must abundant rings in amorphous GST and GeTe are the four-membered ABAB rings (A=Ge/Sb and B=Te) which are also the building blocks of the cubic crystalline phase. The presence of nanocavities [3] in the amorphous/liquid phase has also been proposed as a structural feature that aids the alignment of the four-membered rings during crystallization. More recently, it has been proposed [4,5] that another feature boosting the crystallization speed is actually the fragility of the supercooled liquid phase which allows a high atomic mobility down to temperatures very close to the the glass transition temperature T_g. Experimental evidences came from ultrafast differential scanning calorimetry [4] that allowed measuring the crystallization speed of GST in the range 450-650 K of interest for PCM operation. The temperature dependence of the crystallization speed suggested the occurrence of a breakdown of the Stokes-Einstein relation $D \propto T/\eta$ (SER) between the self-diffusion coefficient D and the viscosity η at temperature T close T_g, which is a typical feature of fragile liquids [6]. In a fragile liquid, the viscosity follows an Arrhenius behavior only above a cross-over temperature T^* below which a super-Arrhenius function $\eta=\eta_o \ exp(E/(T-T_o))$ is customarily used to reproduce the data [6]. On the contrary, an ideal strong liquid shows an Arrhenius behavior of η from the melting temperature T_m down to T_g. The diffusion coefficient D actually controls the kinetic prefactor of both the nucleation rate I_{ss} and the speed of crystal growth u. The thermodynamic factors

in I_{ss} and u are instead controlled by the difference in free energy between the crystal and the liquid ($\Delta\mu$) which is the driving force for crystallization. In phase change materials, due to fragility and the breakdown of SER, the diffusivity in the supercooled liquid is very high just above T_g in spite of a large viscosity. Consequently D can reach high values at temperatures much lower than T_m which assures a large driving force for crystallization.

In a recent work [5], we have indeed demonstrated the breakdown of SER in the supercooled liquid phase of GeTe by means of large scale molecular dynamics (MD) simulations. From the independent calculation of D and η we have shown that GeTe is a highly fragile liquid (fragility index $m\sim100$) with a self-diffusion coefficient as high as $D\sim10^{-6}$ cm^2/s down to 505 K which is just above the crystallization temperature of 450 K [7].

Actually in PCM operation the crystallization would occur from the supercooled liquid or from the overheated amorphous phase depending on the details of the programming current in the set operation. Since a hysteresis is expected across the glass transition, also due to the high heating rate experienced in the device, it is important to assess whether a large D and a breakdown of SER is present in the overheated amorphous phase as well. To this end, in the present paper we report on large scale MD simulation of the diffusivity and viscosity of the overheated amorphous phase of GeTe. As in our previous work on the supercooled phase, we used an interatomic potential [8] generated by fitting a large database of density functional energies by means of a Neural Network (NN) method.

2. COMPUTATIONAL DETAILS

The NN interatomic potential of GeTe was obtained in [8] by fitting a huge database by means of the method introduced by Behler and Parrinello [9]. The database consists of the total energies of about 30000 configurations of 64-, 96-, and 216-atom supercells computed within density functional theory (DFT) with the Perdew-Burke-Ernzerhof (PBE) exchange and correlation functional and norm conserving pseudopotentials. The NN potential displays an accuracy close to that of the underlying DFT-PBE framework whose reliability in describing structural and dynamical properties of GeTe and other phase change materials has been validated in several previous works [3,8,10].

We used a 4096-atom cubic cell and a time step of 2 fs. The amorphous phase was generated by quenching the melt from 1150 K to 300 K in 100 ps at the fixed density of 0.0334 atoms/Å^3 very close to the experimental one for the amorphous phase. By increasing the quenching time up to 2.1 ns the structure of the amorphous phase does not change sizably as shown in Fig.1a. The volume of the first amorphous model (quenched in 100 ps) was then increased according to the calculated linear thermal expansion coefficient at 300 K. We increased the temperature from 300 K to 700 K in 5 steps. At each step the system is equilibrated for 25 ps at fixed temperature with a stochastic thermostat. Overall the system is thus heated from 300 K to 700 K in 125 ps. At each temperature statistical averages are then collected on longer microcanonical simulations.

3. RESULTS & DISCUSSION

We first computed D from the atomic mean square displacement on the time scale of 50 ps. The values of D as a function of temperature are reported in Fig. 2 and compared with the corresponding values in the supercooled liquid phase obtained in our previous work [5]. The ratio between the self-diffusion coefficient of Ge and Te decreases by increasing temperature as shown in Fig. 3a. We remark that the temperature in the supercooled liquid is changed in time along the curve in Fig. 2 following a protocol similar to that used to generate the amorphous model. In fact, the liquid was quenched from 1000 K to 500 K in 250 ps while the amorphous models were generated by quenching from 1150 K to 300 K in either 100 ps or 2.1 ns with similar results. Clearly a hysteresis is present, as the values of D are lower in the amorphous phase than in the supercooled liquid it originates from.
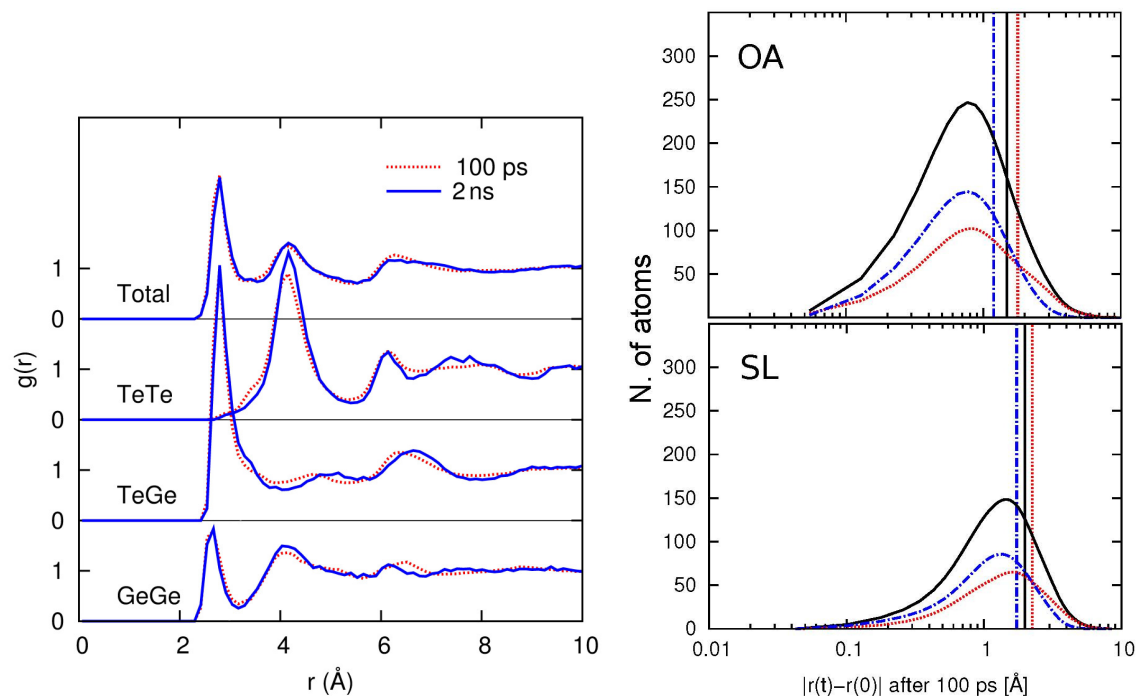
Fig. 1.a) (Left panel) Total and partial pair correlation functions (300 K) of two 4096-atom models of amorphous GeTe generated by quenching from the melt in 100 ps (dashed line) or 2.1 ns (continuous line). b) (Right panel) Distribution of the displacement | r(t) - r(0) | of individual Ge atoms (dotted line), Te atoms (dotted-dashed line) and their sum (total, continuous line) at t=100 and at 500 K in the overheated amorphous GeTe (OA, upper panel) and in the supercooled liquid phase (SL, lower panel). The values of the average (over atoms) mean displacement are displayed by vertical lines.
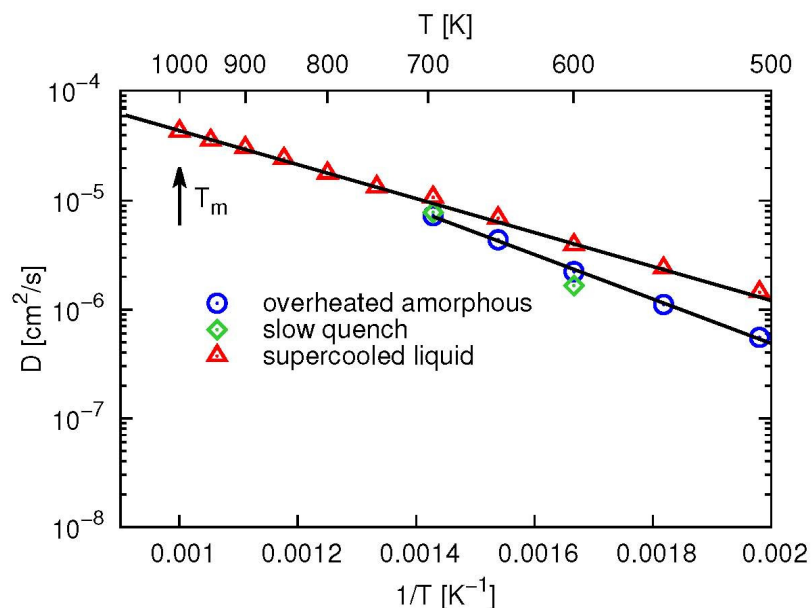

Fig. 2. Self-diffusion coefficient D as a function of temperature calculated from the mean square displacement in the overheated amorphous phase (open circle) and in the supercooled liquid phase (triangles from [5]). The diamonds refer to a second amorphous model quenched from the melt in 2.1 ns. The straight lines are Arrhenius fits of the data that give an activation energy of 0.417 eV for the overheated amorphous phase and 0.296 eV for the supercooled liquid.

Whether it is necessary or not to distinguish between the two phases and to take into account the hysteresis in the glass transition depends on the details of the programming current in the set operation which controls the rate of temperature increase and the value of the intermediate temperature between T_g and T_m reached during the recrystallization process. As a typical feature of fragile liquids, we observed heterogeneities in the dynamical properties [6], a sizable fraction of atoms diffusing much faster than the average as shown in Fig. 1b.

To assess the validity of the SER, the viscosity in the overheated amorphous phase as a function of temperature should be computed. However, as discussed in [5] a direct calculation of the viscosity is possible only for temperatures at which the system does not crystallize on the time scale needed to define/compute the viscosity. The customarily used Green-Kubo (GK) formula for the viscosity [5], which involves a time integral of the stress-stress correlation function, requires simulation time longer than the correlation time of the stress tensor. In the supercooled liquid phase and in overheated amorphous phase at and above 700 K, it was possible to reach a converged value of η from the GK formula by averaging the stress-stress correlation function over simulations up to 1 ns long. Longer simulation times should, however, be necessary at lower temperatures as the correlation time of the stress tensor increases by decreasing temperature. Unfortunately, at low temperature the amorphous and liquid phases start to crystallize in few hundreds ps which prevented us to obtain a reliable value for η below 700 K. Improving the statistics by using ten different independent models generated by quenching from the melt with the same protocol does not help to reach convergence in the values of η at lower temperatures. Still the unconverged results strongly suggested the fragility of the supercooled liquid and the breakdown of SER below 700 K as η is one order of magnitude larger than the values obtained from D and the application of SER, i.e by setting $\eta = k_B T/(6 \pi R_v D)$ where R_v is the average van der Waals radius of the two species.
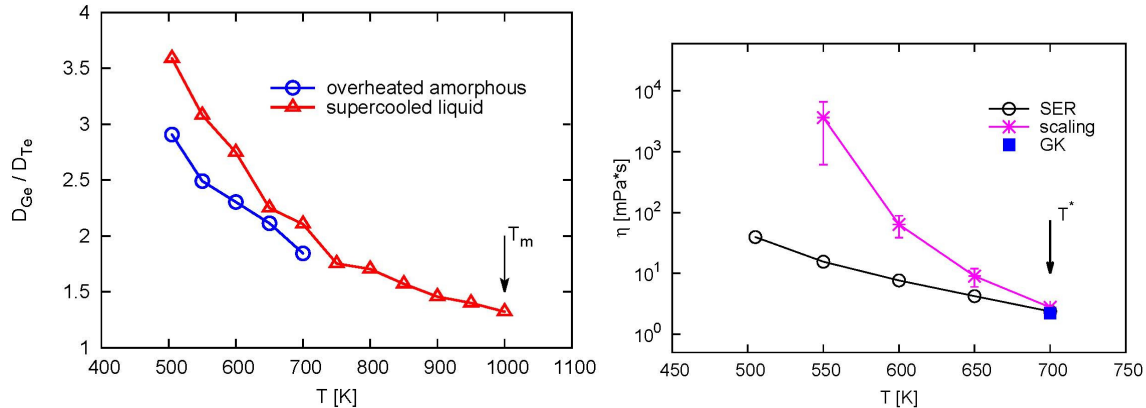

Fig. 3.a) (Right panel) Ratio of the self-diffusion coefficients of the two species as a function of temperature in the overheated amorphous GeTe (open circles) and in the supercooled liquid phase (triangles, from [5]). b) (Left panel) Viscosity computed from the scaling of the diffusion coefficient with the simulation cell size (stars, see text), and from the self diffusion coefficient of the 4096-atom cell and the application of the SER (open circles) in the overheated amorphous phase. The square at 700 K is obtained from the GK formula.

However, a more compelling evidence of the breakdown of SER comes from the finite size scaling of the self-diffusion coefficient on the shorter time scale of 50 ps on which our models never crystallize. In fact, in the hydrodynamic regime where the SER holds it is actually possible to estimate the viscosity from the scaling of D with the edge L of the cubic simulation cell as $D(L) = D_\infty - 2.387\ k_B T/(6 \pi \eta L)$ [11]. The viscosity is in fact much less dependent on the system size than D actually is. This relation, initially developed for polymers [11], was then applied to study inorganic liquids. We considered three models with 512, 1728 and 4096 atoms at the same atomic density. As shown in our

previous work [5] by applying this scaling relation in the supercooled liquid above 700 K we obtained values for η very close to that computed directly from the Green-Kubo formula and consistent with the SER. The same is true for the overheated amorphous phase. Note that η from the GK formula at 700 K is 2.2 mPa s in the overheated amorphous phase and 2.4 mPa s in the supercooled liquid [5]. However, when the scaling relation is applied below 700 K in the supercooled liquid [5] and in the overheated amorphous phase one obtains values of η that are three orders of magnitude larger than those obtained from D and the application of the SER. This inconsistency, shown in Fig. 3b for the overheated amorphous phase, demonstrates that the SER indeed breaks down in the overheated amorphous phase as well. We remark that the numerical values of η reported in Fig. 3b below 700 K are not reliable since they are obtained from the scaling relation which is not applicable when the SER breaks down.

By means of NN simulations of 4096-atom cells lasting 2 ns at different temperatures, it has also been possible to investigate the crystallization process in the supercooled liquid and overheated amorphous phases. We have demonstrated that the formation of supercritical crystalline nuclei is not rate limiting in the temperature range 500-675 K investigated here and of interest for PCM operation. The crystallization rate is controlled by the speed of crystal growth whose temperature dependence is well described by the expression $u = \gamma 6D/\lambda\ (1-exp(-\Delta\mu/k_BT))$ from classical nucleation theory. By plugging our computed values of u (0.5-6 m/s in the range 500-675 K) and D (Fig. 2) and by setting $\lambda \sim 3$ Å as a typical interatomic distance, we indeed obtain values of γ in the range 0.25-0.65 for the supercooled liquid, consistently with classical nucleation theory. The speed of crystal growth u has been computed from the linear dependence of the radius R of the crystalline nucleus as a function of time. In turn R is defined by $R=\sqrt{(3V/4\pi)}$ where V is the volume of crystalline atoms identified by the crystalline order parameter by Steinhardt et al. [12]. This outcome demonstrates that the high crystallization speed in the supercooled liquid/overheated amorphous phases is actually due to a large self diffusion coefficient D down to temperatures very close to T_g.

4. CONCLUSION

The fast crystallization of GeTe and GeSbTe alloys has been ascribed to the similarity of the bonding topology in the amorphous and crystalline phases. The results presented here suggest that the crystallization is promoted also by a high atomic mobility just above T_g where, due to high supercooling, a large driving force ($\Delta\mu$) boosts the crystallization speed. A large atomic diffusivity coexists with a large viscosity due to the breakdown of SER. Therefore the diffusion coefficient to be used in the modeling of the crystallization process can not be inferred from the expected viscosity and the SER, nor the crystallization speed can be extrapolated from measurements below T_g. Indeed the crystallization of the amorphous phase at low temperatures of interest for data retention might take place in a different manner with respect to the crystallization of the highly mobile overheated amorphous and supercooled liquid phases above T_g.

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Biographies

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 für Festkörperforschung (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 holds the position of associate professor in Condensed Matter Physics since 2001. His research activity is devoted to the ab-initio modelling of materials ranging from amorphous semiconductors and insulators for applications in microelectronic and photonics to fast ion conductors and low-Z superconductors. He is author of 117 articles on international journals among which 17 deal with phase change materials.