
Effect of dopant size and dopant concentration on the crystallization pressure of phase change materials: The role of local order and non-local interactions

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Abstract. - $\text{Ge}_{0.15}\text{Sb}_{0.85}$ is a phase change material that undergoes a transition from a semi-conducting glass to a crystalline metal when being densified. In this work, we investigate some parameters controlling the crystallization pressure P_c in related compounds by conducting high-pressure experiments on initially amorphous, germanium and silicon-doped antimony. We find that the amorphous phase is stabilized to higher pressures when the dopant size is decreased. This result can be easily rationalized under the assumption that in the glass, Ge and Si atoms occupy tetrahedral or related small coordination shells. When pressure increases, the larger Ge atoms move earlier into the larger octahedral shells, which are characteristic for the crystal, than the smaller Si atoms. We also find that P_c increases quickly with Ge and Si concentrations. This observation implies that the pressure-induced change of local coordination cannot be a local, elementary event, but that the four coordination of the group 14 atoms is stabilized by the presence of other four-coordinated atoms.

Introduction. – Many properties of electronic phase change materials (PCMs), such as electrical conductivity, light reflectivity, and density, differ distinctly depending on whether the PCMs are in a metastable amorphous or a crystalline phase. [1] The possibility of switching PCMs reversibly between these two phases with the help of suitably designed heating or laser radiation treatments is used in optical storage media as well as in other non-volatile memory and makes PCMs attractive candidates for further electronic applications. [2] Popular PCM compositions are $\text{Ge}_1\text{Sb}_2\text{Te}_4$, $\text{Ge}_2\text{Sb}_2\text{Te}_5$, and $\text{Ge}_{0.15}\text{Sb}_{0.85}$. [3]

The first convincing explanation as to why the properties of amorphous and ordered PCMs differ significantly was given when they had already long been used commercially. Kolobov et al. [4] found that the coordination of many Ge atoms is tetrahedron like in disordered PCMs, whereas their first shell in crystals is a (distorted) octahedron. This quite dramatic difference in local order distinguishes PCMs from most other materials, which tend to have similar local order in their metastable glassy and crystalline phases despite differences in their long-range order.

The Kolobov model has spurred many activities in which various groups investigated if tetrahedral coordination of Ge atoms is present and potentially induces local hybridization changes, [5–11] thereby opening an electronic gap or reducing conductivity by other means. Although a significant effect of sp^3 hybridization onto the electronic gap could not yet be established with certainty, see in particular the recent discussions in Refs. [11, 12], ab-initio studies of disordered PCM glasses support the idea that the majority of Ge atoms is four-coordinated in the glass and often even tetrahedrally-coordinated. Estimates obtained in DFT-based calculations include 21% tetrahedral coordination in amorphous $\text{Ge}_1\text{Sb}_2\text{Te}_4$ [11], 50% four-coordination in amorphous $\text{Ge}_2\text{Sb}_2\text{Te}_2$ out of which one third is tetrahedrally bonded [7, 8], and 50% four-coordination in liquid $\text{Ge}_{0.15}\text{Sb}_{0.85}$, which increases to 70% in the glass [13]. The trends conveyed in these numbers agree with those obtained in EXAFS and XRD experiments [4, 10, 14, 15]. Lastly, Raman peaks observed experimentally above 190 cm^{-1} [16] could be linked to the vibrations of tetrahedrally coordinated Ge atoms in first-principle simulations [12].

It was recently argued that the existence of tetrahedral coordination of Ge atoms in the glass can be exploited to switch PCMs reversibly by stress [10,13] rather than by energy intensive heating or radiation pulses. The underlying picture is that the free volume associated with the tetrahedral shell (or that produced by other four-coordination) is smaller than that of the (distorted) octahedral shell. This is why the local glass structure becomes unstable under high pressure and more favorable under low or negative pressure. In fact, diamond anvil cell experiments revealed that amorphous $\text{Ge}_{0.15}\text{Sb}_{0.85}$ became crystalline at about 2 GPa. DFT-based simulations found that the transition could be reversed: crystalline $\text{Ge}_{0.15}\text{Sb}_{0.85}$ changes its local order at negative pressures so that it becomes similar to that of quenched glasses. [10]

When replacing Ge with the smaller group 14 element Si, the relative stability of the glass phase of that PCM alloy should be increased, in particular under compression. Thus reducing the size of the group 14 element in PCM alloys should move the amorphous \leftrightarrow crystal transitions to higher pressures. In this work, we investigate this train of thought by compressing and decompressing various $\text{Ge}_x\text{Sb}_{1-x}$ and $\text{Si}_x\text{Sb}_{1-x}$ alloys. Note that reversible pressure switching in PCMs can only be achieved for those alloys that are free of stoichiometric vacancies in their crystalline reference phases, because such vacancies cannot sustain pressure and will be squeezed out before the tetrahedral coordination becomes unstable. Indeed, when such crystals are compressed, the metallic crystals amorphize into a metallic glass [6, 13, 17]. Thus, compression of $\text{Ge}_1\text{Sb}_2\text{Te}_4$ or $\text{Ge}_2\text{Sb}_2\text{Te}_5$, which contain roughly 10% vacancies in their relevant crystalline phases, are not candidates of interest for the current investigation.

Experimental Details. – Our samples were prepared with the Edwards Auto 500 sputter deposition system at the Nanofabrication Facility of the University of Western Ontario. The chamber was first sputtered with a chromium target to ensure low oxygen contamination and then purged with argon under 3×10^{-3} mbar. Sputtering of Ge and Sb (or Si and Sb) was done at a constant r.f. power of 100 W. Different stoichiometries were produced by controlling and changing the respective sputtering rates of Ge and Sb (or Si and Sb). The NaCl substrates were dissolved in water immediately after sputtering. The films were lifted off the NaCl-water solution, washed in distilled water, and dried.

The samples were placed into a diamond anvil cell (DAC), which was equipped with $400\mu\text{m}$ culet diamond anvils. A few ruby (Cr^{+3} doped $\alpha\text{-Al}_2\text{O}_3$) chips were placed inside the gasket sample chamber, which allowed us to determine the pressure within ± 0.05 GPa accuracy under quasi-hydrostatic conditions by using the pressure shift of the R_1 ruby fluorescence line (at 694.2 nm under ambient conditions). [18] In some cases, NaCl single crystals were placed into the sample chamber and the equation of state reported in Ref. [19] was used to obtain pressure

values from the unit cell dimensions.

Angle-dispersive powder x-ray diffraction (ADXRD) measurements were carried out at room temperature under compression up to 30 GPa. Binary GeSb alloys were measured under isotropic compression at the high-energy, high-intensity superconducting-wiggler X-ray beam line X17C (at 30.55 keV; $\lambda = 0.4066$ nm) of the National Synchrotron Light Source at Brookhaven National Laboratory. Binary SiSb alloys were measured at the 16-IDB station of the High Pressure Collaborative Access Team (HPCAT)-Advanced Photon Source (APS), at 33.69 keV; $\lambda = 0.368018$ nm. The monochromatic x-ray beam was focused down to $10 \times 10 \mu\text{m}^2$ using Kickpatrick-Baez mirrors. The images were collected using a MAR345 image plate located around 350 mm away from the sample. The collected images were integrated using FIT2D.

Results. – XRD spectra showing how $\text{Ge}_{0.15}\text{Sb}_{0.85}$ transforms under pressure from amorphous to the rhombohedral A7 had already been shown in Fig. 1C of Ref. [10]. In Fig. 1 of this work, we show equivalent spectra on $\text{Si}_{0.08}\text{Sb}_{0.92}$. Initially there are broad features in the spectra, which are indicative of an amorphous structure. At 0.9 GPa a sharp peak, suggestive of crystalline order, coexists with the one associated with the amorphous phase. At higher pressures as well as during decompression, the broad peaks disappear and only sharp peaks remain that can be associated with the rhombohedral A7 phase. Some peaks have very small intensity, such as the (0,0,3) reflection. This and related peaks would be symmetry forbidden in the simple cubic phase towards which the A7 structure would be moving if the pressure were increased further.

Not all amorphous alloys investigated in this work crystallize into the A7 structure upon densification. Depending on which dopant is used at what concentration, other crystalline structures can be obtained. For example, germanium concentrations exceeding 0.25 lead to Bragg reflections that are better described by the α -uranium A20 crystal system than by rhombohedral A7. Along similar lines, higher silicon concentrations lead to an apparently direct transformation from the glass to the intertwined tetragonal host-guest structure, [20] which Ge-Sb mixtures only acquire when the pressure is increased another few GPa beyond the initial crystallization pressure. However, all the observed high-pressure crystalline phases, (except for the most highly Si-doped alloy) can be derived from simple cubic through displacive modes via a second-order (or at most weak first-order [21]) phase transformation without requiring lattice reconstruction [22], including the incommensurate host guest structure [23]. This is why all structures can be seen as similar and thus we do not expect the instability point of the amorphous phase to depend much on the precise nature of the final crystal structure. Details on the high-pressure phases for values of x exceeding 0.3 will be reported separately.

Long-range order is associated with a small width $\Delta\theta$ of the maxima in elastic XRD spectra. The longer-ranged

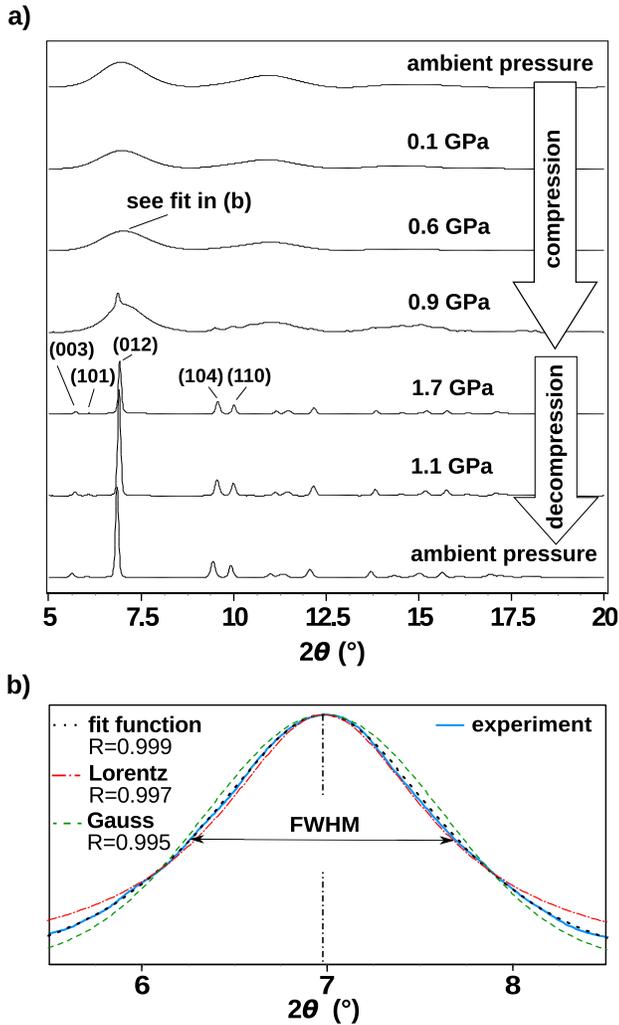


Fig. 1: a) Selective XRD spectra of $\text{Si}_{0.08}\text{Sb}_{0.92}$ under compression and decompression. The maximum achieved pressure was 1.7 GPa. Coexistence of crystal and glass can be recognized at $p = 0.9$ GPa. Some selected peaks are indexed with respect to the A7 structure. Peaks with small intensity are symmetry-forbidden in the simple cubic phase and increase in intensity as pressure is lowered. The wavelength was $\lambda = 0.368 \text{ \AA}$. b) Fits to a line shape based on a Gaussian, a Lorentzian, and an intermediate fit function defined in the text. A linear background is considered each time. FWHM indicates the full width at half maximum.

the order, the smaller is the peak width. In order to quantify the degree of order in the system, we determine $\Delta\theta$ through fitting the peaks lying near $2\theta = 7^\circ$, i.e., in the vicinity of the (012) peak of the A7 structure. These peaks turned out to be half way between a Gaussian and a Lorentzian, which motivated us to use the square root of these fitting functions, i.e., we fitted individual peaks to $A \cdot \sqrt{\exp\{-(\theta_0 - \theta)^2/2\Delta\theta^2\} / \{1 + (\theta_0 - \theta)^2/\Delta\theta^2\}}$ plus a linear background, see also the lower part of Fig. 1. (Fitting the line shapes with the better justified Voigt profile, which one obtains by folding a Lorentzian with a Gaussian, would not have produced better fits.) The

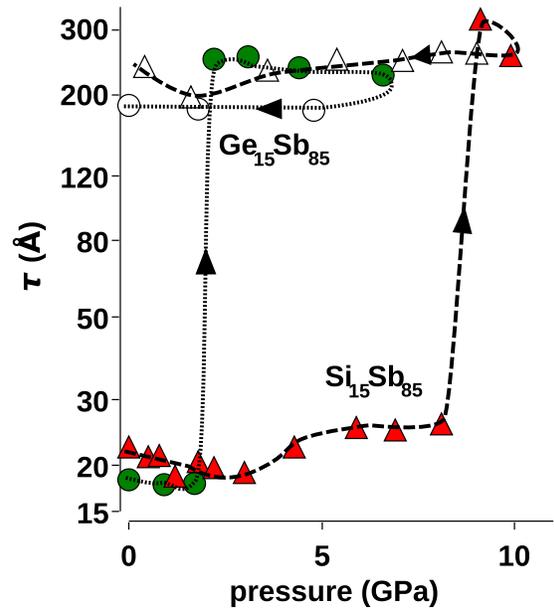


Fig. 2: Correlation length or typical domain size τ as a function of pressure for $\text{Si}_{0.15}\text{Sb}_{0.85}$ and $\text{Ge}_{0.15}\text{Sb}_{0.85}$ during compression.

widths of the peak $\Delta\theta$ provide a lower bound for the size of correlated (crystalline) order, τ , through the equation $\tau \gtrsim \lambda/\Delta\theta \cos\theta$ [24]. The resulting correlation lengths τ for $\text{Ge}_{0.15}\text{Sb}_{0.85}$ and $\text{Si}_{0.15}\text{Sb}_{0.85}$ are reported in Fig. 2 as a function of pressure.

There is a discontinuity in the half width for the $\text{Ge}_{0.15}\text{Sb}_{0.85}$ alloy at roughly 2 GPa, which is identical to the crystallization pressure identified earlier. From the width of the diffraction peaks shown in Fig. 2 one may conclude that the crystallites are at least 200 \AA large, in particular given the unavoidable distortions that the dopants must induce in the crystalline lattice. The smoothness of the diffraction rings observed experimentally are consistent with nanocrystallinity. The correlation length in the disordered systems is found to be 20 \AA , which is roughly twice as large as what one would estimate from looking at molecular snapshots of a quenched melt. However, the $S(Q)$ -peaks at $2\theta = 7^\circ$ computed from simulations of a quenched glass are about twice as broad as those measured experimentally, see, for example Fig. S5 in the supplementary material of Ref. [10].

The smaller Si dopants stabilize the amorphous phase to distinctly higher pressures, however, this stabilization is not sufficient to make the transition reversible when the alloy is decompressed back to ambient conditions. Interestingly, the values for $\Delta\theta$ and thus τ are insensitive to the choice of dopant in either phase. This is why we believe that the local structures show much similarity between freshly sputtered, amorphous Si and Ge doped antimony.

Analysis like the ones shown in Fig. 2 were conducted for a variety of dopant concentrations x , all the way up to $x = 0.5$. The resulting values of P_c are shown in Fig. 3.

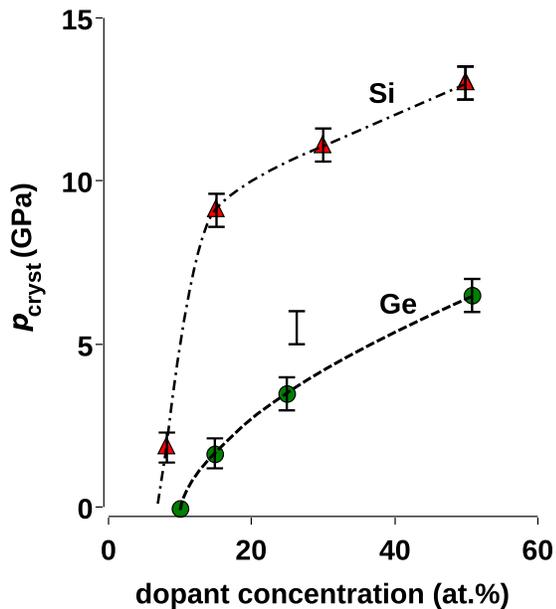


Fig. 3: Crystallization pressures for $\text{Ge}_x\text{Sb}_{1-x}$ and $\text{Si}_x\text{Sb}_{1-x}$ as a function of the dopant concentration x .

While one usually may no longer talk about a dopant when it reaches concentrations of 50%, we feel it is appropriate to do so here, because the crystalline high-pressure phases are similar to those of pure antimony rather than of group 14 elements, again with the exception of $\text{Si}_{0.5}\text{Sb}_{0.5}$.

The results shown in Fig. 3 reveal that silicon distinctly enhances the stability of the amorphous phase towards higher pressure when it substitutes germanium not only for $x = 0.15$ but also at larger values of x . In the range $0.15 \leq x \leq 0.5$, the stability range of the glass seems to be about 7 ± 1 GPa higher for the silicon than for the germanium compounds. At smaller values of x , the samples have a faster tendency to be in an initial crystallized state.

It is remarkable how quickly P_c increases with dopant concentration x , i.e., at large values of x we find $\partial P_c / \partial x \approx 20$ GPa for both investigated types of mixture. For smaller concentrations, the increase is even larger. This increase of P_c with x is indicative of some cooperativity, i.e., the group 14 element atoms “feel” when adjacent atoms are also four-fold coordinated and have a stronger tendency to remain therein. If such non locality did not exist, transition pressures would not be so sensitive to the dopant concentration. Instead, the occurrence of a local squeeze-out transition would solely depend on local geometry and local pressure. Our data does not provide evidence for such local squeeze-out events.

Conclusions. – In this paper, we have presented x-ray diffraction data revealing that amorphous silicon-doped antimony crystallizes at roughly 7 GPa higher pressure than germanium-doped antimony at a given dopant concentration. This observation can be interpreted in a straightforward fashion within a simple free volume picture arising from Kolobov’s hypothesis that element 14

atoms in PCMs acquire tetrahedral coordination in their disordered but not in their crystalline phases: Because the associated free volume of the tetrahedral site is smaller than the octahedral site in the crystal, the pressure (or density) where the tetrahedral site is favorable is shifted to higher pressures for smaller atoms. This paper therefore compliments previous studies of ours, in which we showed that the germanium atoms in PCMs (that are vacancy-free in their relevant crystalline phases) can be squeezed from tetrahedral to octahedral using pressure and moved back (in first-principle simulations) to the tetrahedral site through tensile loads. [10, 13] This work thus adds to the already existing evidence that tetrahedral coordination of element 14 atoms in PCMs exists and plays an important role in the structural motifs of amorphous PCMs. [4, 5, 7, 8, 11, 12, 14–17]

The crystallization pressure of glassy PCMs grows quickly with increasing concentration of group 14 atoms. As argued in the result section, this observation is indicative of non-local interactions, or in other words, it is indicative of a feedback mechanism by which the presence of tetrahedrally coordinated Si or Ge atoms stabilizes other tetrahedrally coordinated atoms to higher pressures. This argument is consistent with the observation that the presence of four coordinated germanium atoms in quenched $\text{Ge}_{0.15}\text{Sb}_{0.85}$ speeds up the conversion of other germanium atoms to also acquire four coordination. [13] Specifically, when a system is quenched from the liquid to the glass the number of tetrahedrally coordinated Ge atoms increases during relaxation so that the glass has less similarity with the crystal than the liquid phase from which it had been obtained, i.e., the glass relaxes away from the crystal.

What could be the nature of the feedback leading to this unusual behavior? It cannot be linked to stoichiometric vacancies in the crystal or the loss of resonant bonding in the glass, because crystalline $\text{Ge}_{0.15}\text{Sb}_{0.85}$ is not a resonant structure but Peierls distorted and moreover does not contain stoichiometric vacancies. A non-local mechanism would be that the alloys are trying to open up a band gap through structural relaxation [10, 11, 13] by using a mechanism that is roughly similar to a Peierls distortion, i.e., electronic energy is decreased at the expense of increasing repulsion between the remaining ions.

The way in which the competition between electrons and ions affects the local structure may well be at the origin of the phase change behavior investigated here. What seems particularly important, at least for mechanically induced phase changes, is that the Ge or Si atoms can change their coordination through local, non-cooperative moves from tetrahedral bonding (or other local order exclusively found in the glass) to octahedral provided the pressure exceeds a threshold value. Yet, sufficiently far away from the transition points there is a feedback - or cooperativity - that stabilizes the respective phases. It remains yet to be explained why some alloys show the typical PCM behavior, although they do not contain any group 14 element, [25, 26] which would provide this local switch be-

tween tetrahedral and octahedral. It may be worth investigating if structural motifs can also be as distinct between amorphous and crystalline as they are in the much better characterized Ge-Sb-Te based compounds.

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