Comment to "New Structural Picture of the Ge2Sb2Te5 Phase-Change Alloy"

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In their Letter, Liu et al.[1] introduced a new structural model for the metastable crystalline (MC) state of the phase change material Ge2Sb2Te5. Such compounds are characterized by a pronounced difference of optical and electrical properties between the amorphous and MC phase. Hence an understanding of the atomic arrangement and the resulting properties could facilitate the design and optimization of phase change materials. Liu et al. claim that large clusters of tetrahedrally bonded Ge atoms (t-Ge) exist in the MC state of Ge2Sb2Te5 (called VtGC in Ref.[1]).They support this conclusion through DFT calculations and HRTEM measurements. Their finding is in contrast to previous experimental studies, which determine a rock-salt (RS) structure[2] with some disorder on the Ge/Sb/Vacancies sublattice, while the Te fcc sublattice is regular[3]. Liu et al. claim the existence of structural motifs, consisting of Ge atoms tetrahedrally bonded to four Te atoms and surrounded by four vacancies (i.e. n=4, called V4tG defect in Ref.[1]). We have reproduced Liu's calculations and also find that the cost of formation for such defects is lower than that of other VntG defects (n=0-3 vacancies)[4]. However, the RS structure is always lower in energy than the proposed VtGC model, independently of the Ge/Sb/Vacancy sublattice configuration, and of the number of t-Ge atoms in the VtGC structure. This agrees with previous DFT calculations[5], which have revealed that if similar tetrahedrally bonded Ge atoms are present in the Ge1Sb2Te4 spinel phase, then the energy is 36 meV/atom higher than the RS phase. The occupation of tetrahedral sites by Ge atoms also leads to a larger unit cell size, deviating further from the experimental value of 6.0293(1) Å^2.

Nevertheless, as we are dealing with metastable phases, these findings do not yet completely rule out the possibility for the VtGC structure to be formed. However, a simple relaxation of this structure shows that it is unstable, rather than metastable, against amorphization and/or locally switching back to RS sites of the t-Ge subregion of the crystal (see Supp. Info.). This is actually already visible in Ref.[1] Fig S3a, as Ge atoms have obviously moved off their initial tetrahedral sites, sometimes by a large extent. Our results are in line with data by[6] which confirm that the configurations obtained by displacing Ge atoms from octahedral sites to tetrahedral sites near intrinsic vacancy sites in cubic Ge2Sb2Te5 are unstable and relax into disordered structures. We have obtained further confirmation of this via MD simulations[4] (longer than the one reported in Ref.[1]). The tetrahedral Ge atoms (see Fig..1), deviate from their initial undistorted high symmetry sites by a few Angstroms: this is incompatible with the reported Debye-Waller factors of Ge2Sb2Te5. On the contrary,

the displacements in the RS structure are in agreement with the experimentally observed DWF's[7]. This simulation confirms the tendency to recrystallize in the RS structure or locally amorphize the structure as some Te atoms are also driven out of their initial fcc lattice positions (see Fig. 1) . In conclusion, DFT calculations reveal that the metastable crystalline phase of Ge2Sb2Te5 is characterized exclusively by a distorted octahedral atomic arrangement of atoms in contrast to the conclusion of Ref.[1] and that another interpretation of the HRTEM measurement should be invoked.

[1] X.Q.Liu *et al.* Phys. Rev. Lett. **106** (2011) 025501.

[2] T. Matsunaga, N. Yamada and Y. Kubota, Acta. Cryst. B **60** (2004) 685.

[3] M. Wuttig *et al.* Nature Mater. **6** (2007) 122.

[4] See supplementary information.

[5] W. Welnic *et al.* Nature Mater. **5** (2006) 56

[6] J. L. F. Da Silva *et al.*, J. Appl. Phys. **106**, (2009) 113509.

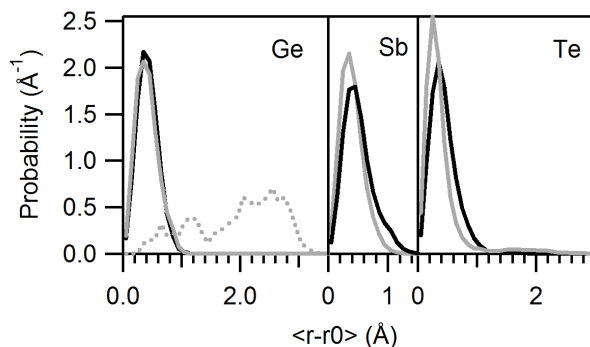[7] T. Matsunaga et al., Adv. Funct. Mater. **21**, 2232 (2011).

FIG. 1: Distributions of the atoms displacements respective to their initial positions (r0), for the different species, averaged over the last 5ps of an MD simulation at 300K, for the RS structure (black curves) and the VtGC model proposed by Liu et al. (full grey curve: octahedral sites, grey dashed curve: tetrahedral Ge sites). In the VtGC case the germanium atoms that were originally on tetrahedral sites move up to 3Å away from the tetrahedral r0 position. This value corresponds to the distance between the tetrahedral r0 position and a neighboring octahedral (RS) site.