

Combined density functional and reverse Monte Carlo simulations of amorphous Ge₁₅Te₈₅

J Kalikka¹, J Akola^{1,2,3}, R O Jones^{3,4}, S Kohara⁵ and T Usuki⁶

¹ Nanoscience Center, Department of Physics, University of Jyväskylä, P.O. Box 35, FI-40014 University of Jyväskylä, Finland

² Department of Physics, Tampere University of Technology, P.O. Box 692, FI-33101 Tampere, Finland

³ Institut für Festkörperforschung, Forschungszentrum Jülich, D-52425 Jülich, Germany

⁴ German Research School for Simulation Studies, FZ Jülich and RWTH Aachen University, D-52425 Jülich, Germany

⁵ Research & Utilization Division, JASRI/SPring-8, 1-1-1 Kouto, Sayo-cho, Sayo-gun, Hyogo 679-5198, Japan

⁶ Graduate School of Science and Engineering, Yamagata University, 1-4-12 Kojirakawa, Yamagata, 990-8560, Japan
E-mail: jaakko.akola@tut.fi

Abstract

The amorphous structure and electronic properties of Ge₁₅Te₈₅ have been studied by combining the results of density functional (DF) simulations and high-energy x-ray diffraction and neutron scattering measurements. Three different atomic models of 560 atoms have been constructed with the aid of reverse Monte Carlo method to satisfy several criteria: Good agreement with the experimental structure factors $S(Q)$, low total energy according to DF, and correct electronic properties (with band gap). The best structure model is based on the melt-quenched DF structure with a small number of Ge-Ge bonds. The atomic structure can be characterized as two interlocked networks of GeTe and pure Te with a considerable amount (22-24%) of free space, cavities. Both tetrahedral and 3+3 defective octahedral configurations are observed for Ge, while Te is slightly overcoordinated in comparison with the 8 - N model. Clusters of $ABAB$ squares ($A=Ge$, $B=Te$) can be observed in the GeTe network. The nearly-covalent bonding of the material is characterized in terms of chemical bond orders.

Introduction

In this work, we have studied the amorphous structure of Ge₁₅Te₈₅ by combining the results of density functional (DF) simulations and high-energy x-ray diffraction (XRD) and neutron scattering (NS) measurements. Three different atomic models of 560 atoms have been constructed: (a) Structure based on DF simulations (melt-quench) and reverse Monte Carlo (RMC) refinement without Ge-Ge bonds, (b) RMC-generated geometry with DF relaxation and without Ge-Ge bonds, and (c) DF-RMC structure with a small number of Ge-Ge bonds as in the base structure. The obtained results are consistent with an earlier DF study with a 216-atom sample [1], while the system size is considerably larger, and the agreement between theory and experiments has improved greatly.

Computational methods

For MD simulations, we apply the PBEsol approximation, the final geometries after MD simulations and RMC refinements were optimized using the Tao-Perdew-Staroverov-Scuseria (TPSS) functional. The atomic coordinates of amorphous Ge₁₅Te₈₅ were generated from the previously reported melt-quenched 216-atom sample[1]. The new unit cell dimension is 27.08 Å, which results in the experimental number density of 0.0282 Å⁻³ for the 560-atom structure. The structure was then heated up to viscous regime at 500 K (below melting point, 680 K) and cooled down in 5 subsequent simulation steps at 500, 450, 400, 350 and 300 K (simulated annealing). Each MD simulation lasted 20 ps, corresponding to a total annealing time of 100 ps. The geometry was then optimized with the TPSS functional prior to the RMC refinement.

We used three different schemes to refine the base structures to produce a close fit to the experimental neutron and XRD structure factors, $S(Q)$, while requesting that the DFT potential

energy of the RMC models had to remain close to the DFT-optimized base energy. The one which gave the best results was based on the annealed DFT structure, refined with short RMC-runs tuned to produce equal quality fits for the NS and XRD data sets and allowed Ge-Ge bonding.

The lengths of the short RMC runs were tuned to produce structures approx. 100 meV/atom higher in DFT energy with respect to the base structure while improving the $S(Q)$ fit with the experimental data. The energy deviation from the target was at most ± 5 meV/atom.

Results and Conclusions

All the structures display semiconductor properties close to the Fermi energy, and the electronic spectra are consistent with the base structures. The structure which had a small number of Ge-Ge bonds was the one that reconciled best with the different criterions: The agreement of $S(Q)$ is good for *both* XRD and neutron scattering, total energy of the base structure (annealed/melt-quenched) is low, and the electronic structure shows a small band gap at the Fermi energy (semiconductor). This finding suggests that Ge-Ge bonds, albeit their small number, should not be excluded from the amorphous structure.

The atomic structure of amorphous $\text{Ge}_{15}\text{Te}_{85}$ can be characterized in terms of local and medium-range order. Although the Ge concentration is small for the 15:85 composition, it affects the properties of Te significantly. Approximately one half of Te atoms are in direct contact with Ge (type I), and forms a GeTe network throughout the sample. This network is interlocked with Te domains (types II and III, which are not in direct contact with Ge) which form a similar network and are not able to grow spatially large locally. Due to the large content of Te, there is also a considerable fraction of cavities present in the material (22-24% of total volume) [2].

The GeTe network itself comprises *ABAB* squares which are the basic structural units of $\text{Ge}_{50}\text{Te}_{50}$, and occasionally, these units combine and form larger fragments, *ABAB* clusters [3, 4]. The Ge coordination displays an interesting co-existence between tetrahedral fourfold coordination and defective octahedral 3+3 coordination as observed for the GeTe and $\text{Ge}_2\text{Sb}_2\text{Te}_5$ alloys previously [3, 5, 6, 7], and both situations are equally likely to occur. The obtained bond orders confirm that there is a difference in chemical bonding between the two types of Ge and illustrate the variation of bond strength as a function of distance. The Ge-Te and Te-Te bonds are nearly-covalent, and a reasonable cutoff distance for counting bonds lies around 3.0-3.2 Å for this class of chalcogenide materials.

References

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