Hybrid functional study on liquid and amorphous structures of $Ge_2Sb_2Te_5$

Kyeyeop Kim, Bora Lee, and Sohee Park, and Seungwu Han*
Department of Materials Science and Engineering, Seoul National University, Seoul, Korea, 151-744
Fax: +82-(2)-883-8197- E-mail address: hansw@snu.ac.kr

ABSTRACT

We perform molecular dynamics simulations on the liquid and amorphous structures of $Ge_2Sb_2Te_5$ using hybrid functionals (HSE06) for exchange-correlation energies between electrons. The results are compared with those from other exchange-correlation functionals such as GGA and BLYP. We pay attention to the fact that the conventional GGA functional produces results that are at variance with the experimental data. In particular, Ge-Te distances are significantly longer than experimental data. This is due to the fact that octahedral Ge atoms are prevalent in the simulation. In contrast, the hybrid functionals significantly increase the population of tetrahedral Ge atoms and the liquid and amorphous structures are in much better agreement with experiment compared to results with semilocal functionals. This implies that the chemistry-based functionals such as hybrid functionals might better describe the disordered systems than GGA.

Key words: hybrid functional, MD simulations, $Ge_2Sb_2Te_5$, disordered system

1. INTRODUCTION

$Ge_2Sb_2Te_5$ (GST) is a popular phase-change material that is applied to the rewritable phase change optical memories and the phase change random access memory (PRAM). The fundamental understanding of phase change materials is important to resolve many technological issues. In particular, the liquid structure of GST is important because the amorphous state is made through the melt-quench process of GST. The high ionic mobility in liquid phase implies that the liquid state is critical for device reliability. The simulations for liquid and amorphous structures of GST, however, have failed to reproduce experimental data when semilocal functionals are used. This motivated us to carry out molecular dynamics simulation using hybrid functionals.

2. COMPUTATIONAL METHOD

We use VASP. The electron-ion interaction is described by projected-augmented-wave potential. We use various exchange-correlation functionals such as GGA, BLYP and HSE schemes to describe electron-electron interaction. In the HSE functional, the screening parameter to cut off the long-range Fock potential is set to 0.2 eV/Å (called HSE06 scheme) and the mixing coefficients, or α, are defined to 0.25 and 0.5.

We prepare initial structures by randomly dispersing atoms into a given cubic cell. The initial structure includes 72 atoms (Ge:16, Sb:16, Te:40) with density set to experimental liquid data (0.030 atoms/$Å^3$ [1]). The unit cell is pre-melted at 2000 K for 12 ps. The liquid is then cooled to 900 K and melted until energy, pressure and atomic structure properties are equilibriated. Subsequently, the liquid structure is quenched from 900 K to 300 K with a cooling rate of -15 K ps^{-1}. Finally, the quenched structure is fully relaxed at 0 K including cell shape.

3. RESULTS & DISCUSSION

To study structural properties with respect to functionals, we first investigate radial distribution function (RDF). The averaged bond length is obtained by reading the position of the first peak in the corresponding partial RDFs. In particular, Ge-Te distances of liquid are 2.82, 2.77, 2.74 and 2.66 Å for GGA, BLYP, HSE06 (α=0.25) and HSE06

(α=0.5). The amorphous data are 2.82, 2.75, 2.67 and 2.63 Å. HSE06 (α=0.5) data is much better in agreement with experimental data (2.64 Å (liquid)[2] and 2.60-2.63 Å (amorphous)[3]).

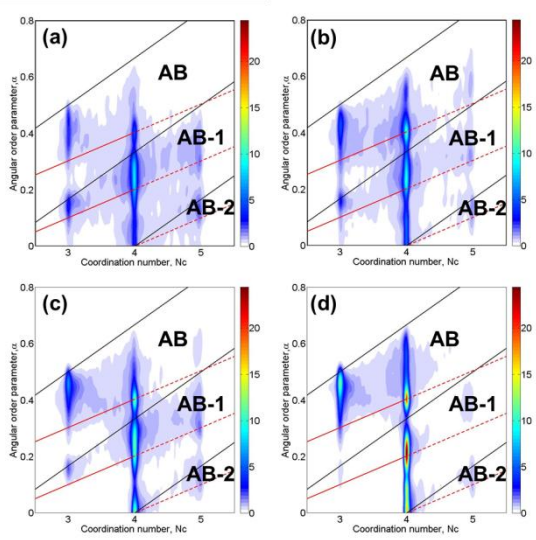

Figure 1. Topology map of Ge bonding in liquid $Ge_2Sb_2Te_5$ depending on functionals
(a) GGA (b) BLYP (c) HSE06 (α=0.25) (d) HSE06 (α=0.50)

To reveal the microscopic origin of dependence of functionals, we examined the atomic bonding around Ge in detail. In the liquid, we calculated the angular order parameter according to coordination numbers.[Ref. 4] Black lines mark ideal octahedral site and red line indicates the ideal tetrahedral site for different degrees of AB ordering (AB, AB-1, AB-2). In Fig. 1, Ge atoms in liquid GST show more tetrahedral bonding as the Hartree-Fock contribution increases in the functional. A similar trend is confirmed in the amorphous structure by examining the angular distribution function around Ge atoms. Therefore, the liquid and amorphous structures within the hybrid functional is similar to the ideal glass structure of GST.[Ref. 5]

4. CONCLUSION

The hybrid functional significantly increases the population of tetrahedral Ge atoms in liquid and amorphous GST in contrast with the conventional functional such as GGA. This results in a significantly shorter Ge-Te distances which is in good agreement with experimental data.

REFERENCES

1. M. Wuttig et al: “Characteristic Ordering in Liquid Phase-Change Materials”, Adv. Mater. (2008) 20, 4535-4540
2. J. Tominaga et al: “Liquid Ge2Sb2Te5 studied by extended x-ray absorption”, Appl. Phys. Lett. (2009) 95, 241902
3. A. V. Kolobov et al: “Understanding the phase-change mechanism of rewritable optical media”, Nat. Mater. (2004) 3, 703
4. J. Akola et al: “Density functional study of amorphous, liquid and crystalline Ge2Sb2Te5:homopolar bonds and/or AB alternation?”, J. Phys.: Condens. Matter (2008) 20, 465103
5. S. Han et al: “Atomic and electronic structures of amorphous Ge2Sb2Te5; melt-quenched versus ideal glasses”, J. Phys.: Condens. Matter (2010) 22, 205504

Biographies

Professor Seungwu Han received B.S. (1993), M.S. (1995), and Ph.D. (2000) degrees from department of physics at Seoul National University in Korea. He spent the postdoctoral period in 2001-2004 at Princeton Materials Institute in Princeton University. Between 2004-2009, He worked as a professor in department of physics at Ewha Womans University. He then moved to Materials Science and Engineering at Seoul National University and is holding an associate professor position. His research interests are integrated materials modeling of phase-change materials, oxide semiconductors, and energy materials.