Ab initio simulation of crystallization of amorphous Ge–Te–In system

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Phase change materials are promising candidates for memory materials because their ability to change between amorphous to crystalline state or vice versa with the application of specific profile of heat. Due to fast transition between crystalline and amorphous form, chalcogenide based on Ge-Te has been regarded as potential candidate of phase change materials. Our investigation of amorphous structures of $GeTe_4$ with indium dopant have shown that amorphous Ge–Te–In has a significant number of fourfold rings which are responsible for the rapid crystal growth in crystal-amorphous transition. In the present study, *ab initio* molecular dynamics were used to study crystallization process of $GeTe_4$ with indium dopant (5, 10, 15 and 20 at%). The structural changes in transition process were analyzed by evaluation of ring statistics. Results from *ab initio* simulations show that crystallization of samples with 80–100 atoms occur in hundreds of picoseconds.

Key words: Crystallization, *Ab initio* Molecular Dynamics, Chalcogenide.

INTRODUCTION

Chalcogenide glasses are interesting materials because of their technological applications and commercial importance. Due to their unique properties (low phonon energies, optical transparency in IR region, high index of refraction), chalcogenide glasses have many important applications in optics and optoelectronics. These applications include phase change material [1–4], sensor [5, 6], optical circuits, gratings, waveguides [7–9], and many others.

Phase change materials have been extensively studied by many authors because it is expected to be the future of non-volatile memories [10, 11]. The emerging non-volatile phase change memory holds the potential for the next generation data storage which is faster and more stable than present data storage. Chalcogenide based on Ge–Te has been regarded as a potential candidate of phase change materials due to its fast transition between crystalline and amorphous form. However, very little theoretical guidance is available for chalcogenide materials based on Ge–Te, especially for Ge–Te–In system.

With these motivations, theoretical study of crystallization process in amorphous $GeTe_4$ doped with indium 0, 5, 10, 15, and 20 at% using numerical calculation has been done. Models reported in this work are generated through melt quenching *ab initio* molecular dynamics (AIMD) simulations. This approach, first pioneered by Car and Parrinello, which combines density functional theory (DFT) with molecular dynamics (MD) is a powerful tool for investigating liquid and amorphous structures [12].

CALCULATION DETAILS

Relaxed structure of $(GeTe_4)_{100-x}In_x$ with $x = 0$, 5, 10, 15, 20 were generated by AIMD simulation. The calculations were performed with the SIESTA program [13] using a linear combination of numerical atomic orbitals as the basis set and norm-conserving pseudopotentials. The total energy is approximated in the non-self consistent Harris functional. The SIESTA program was run under periodic boundary conditions and employed one point ($k = 0$) in the Brillouin zone. Mesh Cutoff 30 Ry was used for calculation and temperature was controlled by a Nosé-Hoover thermostat.

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Structures of amorphous $(GeTe_4)_{100-x}In_x$ were investigated using atomic models contain up to 300 atoms. The starting point of these models is model of $GeTe_4$ contains 240 atoms placed randomly inside cubic lattice with periodic boundary condition. The lattice constant of cubic lattice were calculated from mass density of system which is measured from experiment [14]. AIMD was performed to obtain relaxed stucture of $GeTe_4$ system. Indium atoms were then added to relaxed structure of $GeTe_4$ so atomic models of $(GeTe_4)_{100-x}In_x$ with x = 5, 10, 15, 20 contain 300 were obtained. Using relaxed structures, bond angle distributions and ring statistics were calculated and discussed for amorphous state.

Unfortunately up to now there is no standard procedure to model amorphous structure using MD method. Although several amorphous systems were successfully generated from so called "melt quenching" technique, but this technique itself varies in details. Melt quenching can be done using classical MD or AIMD. The "melt and quench" simulation scheme proceeds by carrying out a series of MD simulations. At each step, the structure obtained from the previous MD simulation is used as the starting point for the next one. In this work, process of melt quenching technique contains three AIMD steps, one annealing process and two *NVT* MD processes. First, system is annealed at 1500 K which is higher than melting temperature of system and then system is allowed to reach thermodynamic equilibrium in this temperature using *NVT* MD. The process is then continued with quench of the system to 300 K. Then, the structure is equilibrated at this temperature using *NVT* MD. For each MD step, system is given enough time to reach its thermal equilibrium in order to eliminate its correlation to the previous structure. At each step, system is allowed to run for 10 ps to reach its thermodynamic equilibrium. The time step for the simulations is set to be 2 fs in order to suppress numerical error.

Crystallization process was investigated by carried out AIMD simulations on $(GeTe_4)_{100-x}In_x$ with x = 5, 10, 15, 20 using models contain 80–100 atoms. Each model was first equilibrated at 1500 K followed by a thermal quenching to 900 K slightly above melting points. Then model was quenched with slow cooling rate (dT/dt = −0.75 K ps⁻¹) for 400 ps. In this step, structural changes in transition process are analyzed by evaluation of ring statistics.

RESULTS AND DISCUSSION

Bond angle distribution between first neighbor atoms can give information about structural nature of system. As member of group IV chalcogenide we expect that $GeTe_4$ has tetrahedral nature as $GeSe_4$.

The average Ge coordination number in the amorphous models is around 4, but this does not prove that amorphous models only have tetrahedral coordination. Bond angle distributions of Te–Ge–Te for amorphous $(GeTe_4)_{100-x}In_x$ in Figure 1 gives us information that prepared models have maximum angle distribution at around 88–100° and a contribution lower than 180° in amorphous state. The presence of a small peak at around 60° in the angle distribution function is due to a very small fraction of three membered rings. This result indicates that tellurium atoms can lay either in equatorial plane (90°) of a Ge atom or at its vertices (180°). It also shows that amorphous structure doesn't display a full tetrahe-
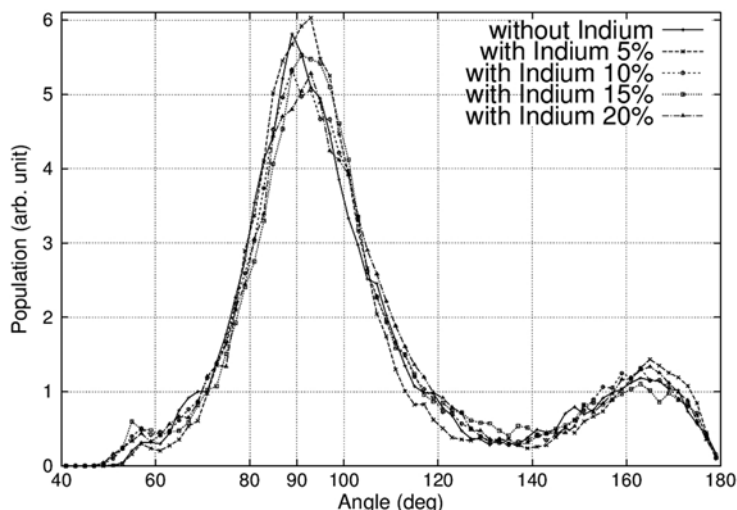

Fig. 1. Bond angle distributions of amorphous state of system $(GeTe_4)_{100-x}In_x$

dral character which should show by max at 109° like in system $GeSe_4$.

With max angle distribution found between 88 and 109° prepared amorphous structures should be made of 4-fold which is partially tetrahedral and defective octahedral-like environment. Structure of $GeTe_4$ show that the distribution peak is around 90° which indicates defective octahedral structure. With indium atom addition, distribution peak shifts to tetrahedral characteristic. It looks like that Ge atom can be bonded as tetrahedral and octahedral structure. Atoms participating in Ge–Te bond favour octahedral coordination and the presence of homopolar Ge–Ge and Ge–In bonds favors the tetrahedral coordination.

Beside bond angle distribution structural information can be gathered from ring statistics. Topology analysis of amorphous, liquid or crystalline systems is often based on part of structural information which can be represented in the graph theory using nodes for the atoms and links for the bonds. A series of nodes and links connected sequentially without overlap is called a path. Following this definition a ring is therefore simply a closed path.

The ring statistics is an important structural parameter to investigate crystal growth in amorphous-crystal transition. Ring calculation in present study uses the definition of ring which was proposed by Guttman [15], who defines a ring as the shortest path which comes back to a given node (or atom) from one of its nearest neighbors.

Bond angle distribution analysis suggests that $(GeTe_4)_{100-x}In_x$ structure should be made from 4-fold rings. 4-fold rings are the basic structural elements of rocksalt crystal. Therefore it is important to investigate their distribution in amorphous state and during crystallization processes.

Result of ring statistics calculation is shown in Figure 2. As expected, ring statistics have good agreement with bond angle distribution analysis. $(GeTe_4)_{100-x}In_x$ structure shows that amorphous $(GeTe_4)_{100-x}In_x$ has a significant number of 4-fold rings with most of them being in the form ABAB (A=Ge, In; B=Te). In 2008, Hegedus and Elliot showed that rapid phase transitions in phase change material GST due to the presence of crystal-nuclei seeds (fragments of octahedral rocksalt structure which is 4-fold rings) in amorphous states [16]. From bond angle distribution and rings statistics result, it looks that Ge-Te-In system has similar characteristics with GST. So it is plausible to assume that 4-fold rings can be responsible to the rapid crystal growth in crystal-amorphous transition in Ge–Te–In system.

Crystallization is very fast in prepared models. Figure 3 shows snapshots of atomic configuration of 80 atoms of $GeTe_4$ in amorphous state and partially crystals form produced by slow cooling of the melt. Crystallization event is starting to occur only after 150 ps. It can be seen that crystals have the rocksalt-like structure characteristic similar with phase change GST materials [16, 17].

The time evolution of 4-fold rings that are crystal-nuclei seeds and the building blocks of the rocksalt structure are presented in Figure 4. Beside Hegedus [16], the significance of four-fold rings to phase transition in phase change materials GST also has been investigated by Kohara [18] using reverse Monte
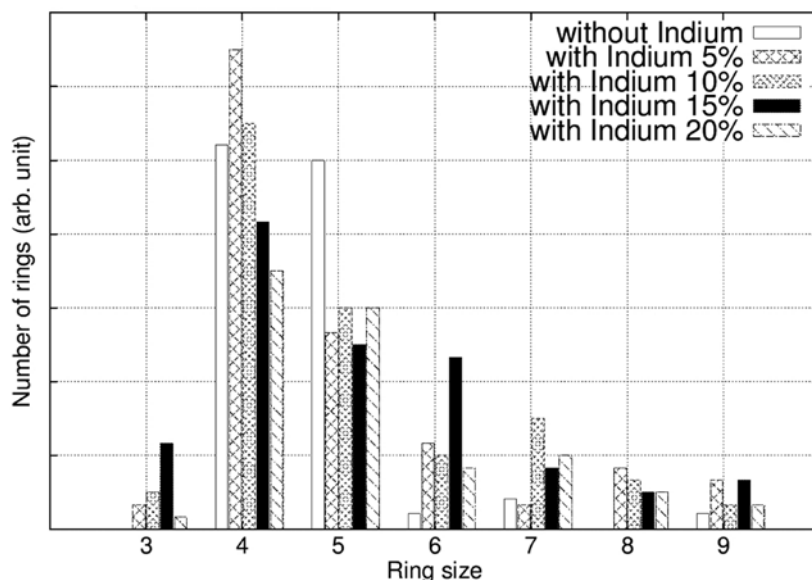

Fig. 2. Ring statistics of amorphous state of system $(GeTe_4)_{100-x}In_x$

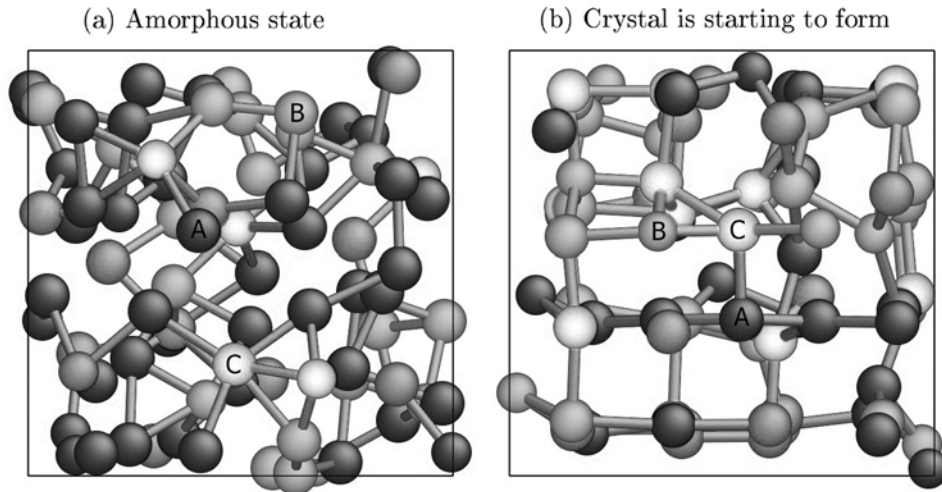(a) Amorphous state

(b) Crystal is starting to form

Fig. 3. Snapshots of atomic configuration of (a) amorphous $GeTe_4$ (b) crystallization event that is starting to occur after 150 ps (A: atom with coordination number 3, B: atom with coordination number 4, C: atom with coordination number 5)
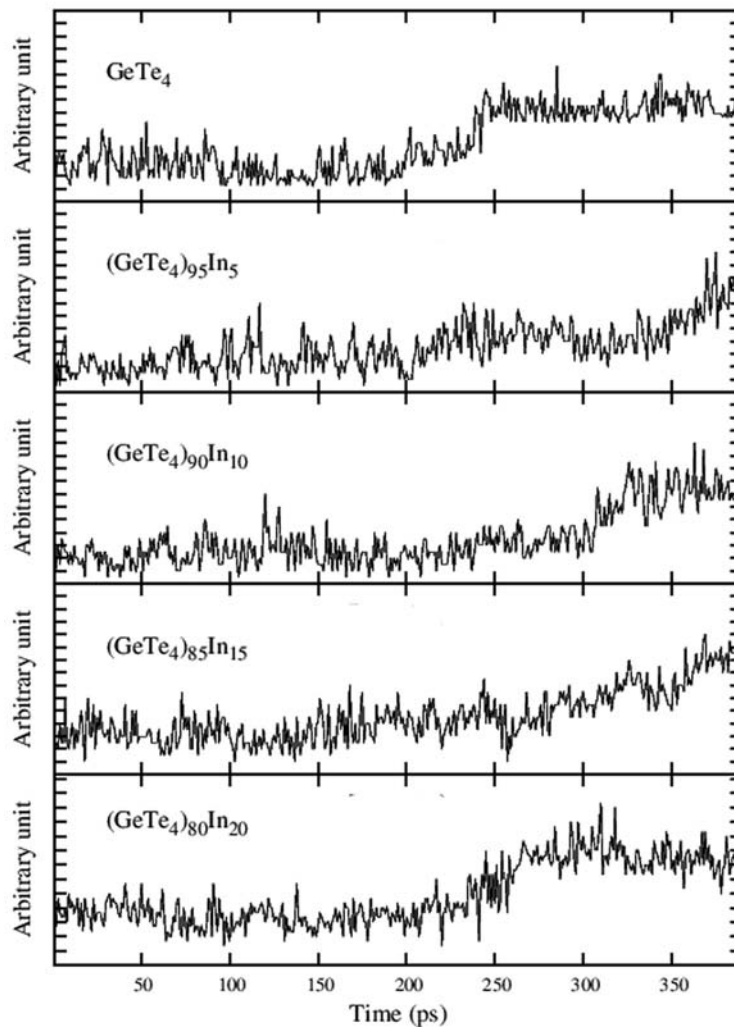

Fig. 4. Number of four-fold rings evolution of system $(GeTe_4)_{100-x}In_x$ with $x = 0, 5, 10, 15, 20$ during 400 ps quench

Carlo simulations and by Akola [20]. Figure 4 shows that crystalline fraction of prepared samples increase after 200 ps. The binary $GeTe_4$ system goes through rapid crystallization between 200–250 ps and for ternary $(GeTe_4)_{100-x}In_x$ rapid crystallization occur after 250 ps. This result is expected because model for binary system has fewer atoms than model for ternary system. For all prepared samples, crystallization occurs in hundreds of picoseconds.

CONCLUSSION

Models of $(GeTe_4)_{100-x}In_x$ with x = 0, 5, 10, 15, 20 have been made using melt quenching AIMD. Calculation results of bond angle distributions suggest that the structure of prepared amorphous system should be made of 4-fold coordinated structure which is partially tetrahedral and defective octahedral-like environment. Ring statistics investigation of amorphous $(GeTe_4)_{100-x}In_x$ suggest that structure of $(GeTe_4)_{100-x}In_x$ with x = 0, 5, 10, 15, 20 have a significant number of 4-fold rings which responsible to the rapid crystal growth in crystal-amorphous transition. Results of time evolution of 4-fold rings investigation show that crystallization of samples with 80–100 atoms occur in hundreds of picoseconds. All these results show promising properties as candidates of phase change material. With further development, Ge-Te-In system has potential to be applied as new phase change materials.

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AB INITIO СИМУЛАЦИЯ НА КРИСТАЛИЗАЦИЯТА НА АМОРФНИ ОБРАЗЦИ ОТ СИСТЕМАТА Ge–Te–In

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(Резюме)

Материалите с промяна на фазата са многообещаващи кандидати за изработване на памети, поради способността им да преминават от аморфно в кристално състояние, или обратното, при прилагане на топлина. Поради бързия преход между кристалната и аморфната форма, халкогенидните материали на базата на Ge–Te се разглеждат като потенциален кандидат за материали с промяна на фазата. Изследването на аморфни структури GeTe$_4$, дотирани с индий показва, че аморфната система Ge–Te–In съдържа значителен брой четворни пръстени, които са отговорни за бързия растеж на кристалите при прехода кристал–аморфно състояние. В настоящото проучване е използвана *ab initio* молекулярна динамика за изучаване на процеса на кристализация в GeTe$_4$ при дотиране с индий (5, 10, 15 и 20%). Структурните промени в процеса на прехода са анализирани чрез статистическа оценка на пръстените. Резултатите от *ab initio* симулациите показват, че кристализацията на образци с 80–100 атоми протича за няколко стотин пикосекунди.