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Amorphous magnesium silicide

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ABSTRACT

A first principles molecular dynamics technique is employed to generate an amorphous magnesium silicide (Mg_2Si) model from its liquid state and its structural, electrical and mechanical features are disclosed for the first time. Si atoms form predominantly the standard square dodecahedron-like and the tri-capped trigonal prism-like configurations while Mg atoms arrange themselves primarily in higher coordinated crystal-like and icosahedral-like polyhedrons. The mean coordination number of Mg and Si is estimated to be ~12.84 and ~8.2, respectively. Si−Si homopolar bonds are also presented in the amorphous network, in contrast to the crystal. Based on our findings, we propose that the amorphous model has a short-range order, quite different than that of the anti-fluorite Mg_2Si crystal but similar to that of metallic glasses. The different local structure of the amorphous state yields distinct electronic and mechanical properties, relative to the crystal. Within the known limitation of DFT-GGA simulations, the amorphous Mg_2Si is found to be semimetal though the anti-fluorite structure is semiconductor. Furthermore, amorphous Mg_2Si is predicted to be less brittle than the crystal structure. Since the potential use of the Mg_2Si crystal as a biodegradable implant material is hindered because of its brittle behavior, here we propose that amorphous or nanoglass forms might eliminate this limitation of Mg_2Si and hence it can serve as an implant material in near future.

1. I. Introduction

Magnesium silicide (Mg_2Si) is an important narrow gap semiconductor (an indirect band gap of about 0.6 eV [1]) of considerable current interest due to its unique physical properties. Mg_2Si is expected to a wide variety of high technological applications. A large Seebeck coefficient, low electrical resistivity, and low thermal conductivity are a few exceptional characteristics of Mg_2Si [2–8], which make it a promising candidate for thermoelectric materials. Since Mg_2Si is an environmentally friendly material [9], it might replace lead-based thermoelectric materials as well. Due to its small band gap, it is also a suitable candidate for an infrared detector [10]. Furthermore, the studies have revealed that Mg_2Si can be used as a new implant material if its brittle character is enhanced [11].

The ground state of Mg_2Si is a face-centered cubic lattice having the anti-fluorite structure ($Fm\bar{3}m$) [12]. Amorphous form of Mg_2Si was also prepared using pulsed laser deposition and rf magnetron sputtering techniques [13]. It was reported that amorphous Mg_2Si could be an anode material in rechargeable lithium batteries since it showed superior cyclability over 200 cycles. Yet to our knowledge, there has not been any attempt to investigate this material in details. In this work, we execute ab initio molecular dynamics (MD) simulations to produce an amorphous Mg_2Si model using the rapid solidification process and expose its local structure, and its electronic and mechanical properties for the first time.

2. Method

Simulations were done using the ab initio density functional theory (DFT) code SIESTA [14]. To estimate the exchange correlation potential, we selected the generalized gradient approximation (GGA) of PBE [15]. To create pseudopotentials, we used the Troullier–Martins method [16]. A numerical basis set with polarization (DZP) was used for the valence electrons. A uniform mesh cutoff of 120 Ry, a finite 3D grid for the calculation of electron density and potentials, was selected for the simulations. One femtosecond was chosen for each MD step. We adopted the isothermal–isobaric ensemble in which temperature and pressure were controlled using velocity scaling and Parrinello-Rahman techniques [17], respectively. No shear deformations were allowed during the thermalization and quenching. The anti-fluorite structure, illustrated in Fig. 1, having 216 atoms (arranged as a 2x3x3 block and 144 Mg and 72 Si atoms) with periodic boundary conditions was used as a starting structure. The initial supercell lengths were L_1 = 12.782 Å and $L_2 = L_3$ = 19.173 Å. This crystalline phase was subjected to 1800 K for 3.0 ps and then the external temperate was reduced to 1400 K in 2.0 ps. At this temperature the configuration was equilibrated for 25 ps. Then the temperature applied was decreased to 300 K in 75 ps. The supercell lengths of the amorphous model at 300 K, given in Fig. 1, were

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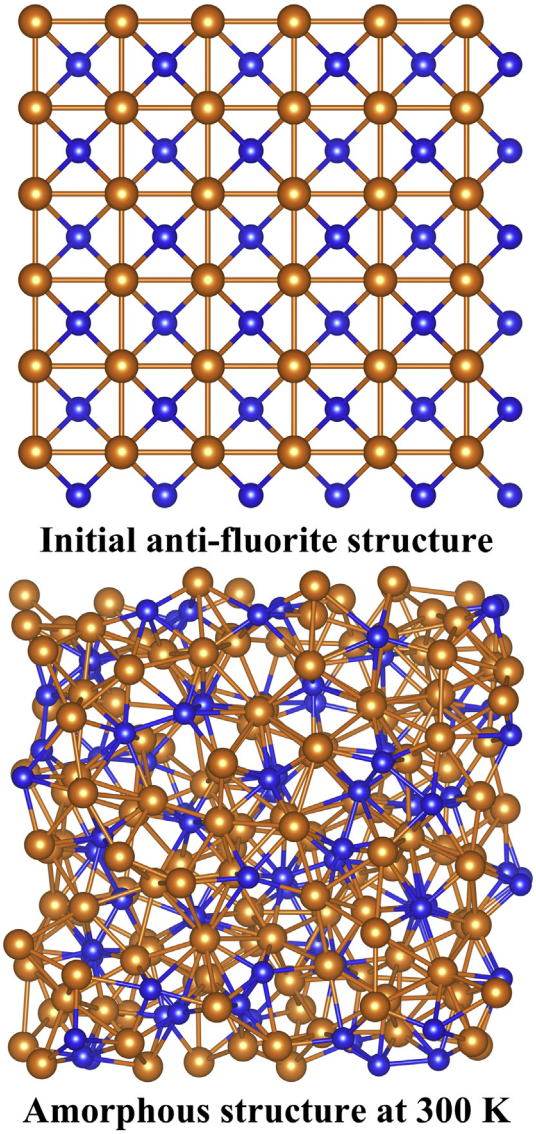

Fig. 1. Ball stick representation of the initial anti-fluorite crystal and the amorphous model at 300 K. Mg and Si atoms are symbolized by large and small spheres, respectively.

L_1 = 10.671386 Å, L_2 = 20.387108 Å and L_3 = 20.972086 Å. Fig. 2 shows the variation of volume per unit formula as a function of temperature. The volume curve decreases gradually and below 700 K it exhibits a change in slope, suggesting the glass-transition temperature (T_g) between 700 and 800 K.

3. Results

3.1. Structural properties

In order to identify the structural features of the amorphous network and compare them with those of the anti-fluorite Mg_2Si phase, we first probe their partial pair distribution functions (PPDFs) and show them in Fig. 3. It can be seen that the peak position of the Mg—Mg, Mg—Si and Si—Si (the second peak) correlations of both structures fairly overlaps each other. Yet the most obvious distinction between these two structures is the presence of Si—Si homopolar bonds as indicated by the peak located at around 2.5 Å in the Si—Si correlation function.

To have a clear description about the short-range order, the partial coordination numbers and the chemical identities around Mg and Si are

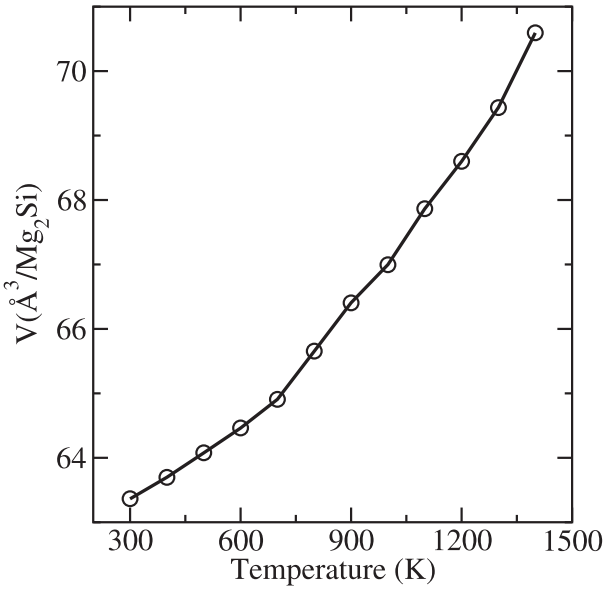

Fig. 2. Variation of volume per unit formula as a function of temperature.

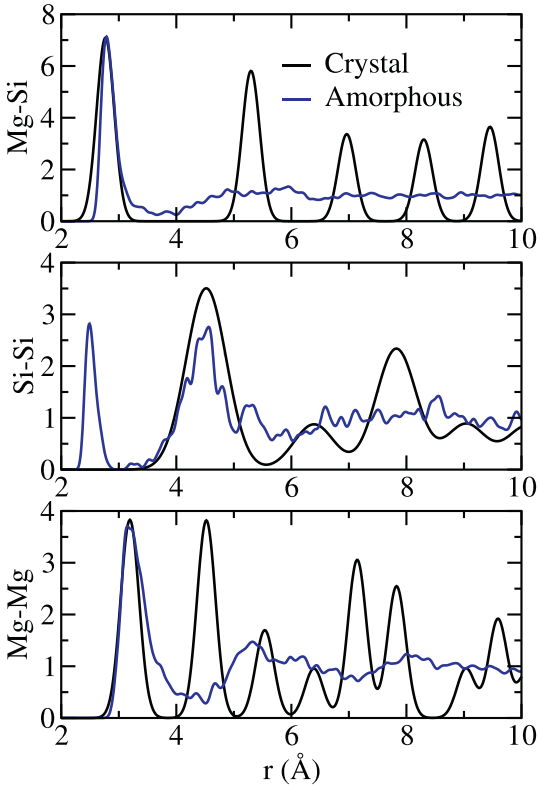

Fig. 3. Partial-pair distribution functions of amorphous and anti-fluorite Mg_2Si. For clarity, the peaks' intensity of the anti-fluorite crystal is reduced.

projected using the Voronoi tessellation technique. The first minimum of the PPDFs is used as the cutoffs that are ~4.0, 3.3, 3.0 Å for Mg—Mg and Mg—Si and Si—Si correlations, respectively. The analysis leads the mean Mg—Mg, Mg—Si, Si—Mg and Si—Si coordination numbers to be ~9, 3.5, 7.1, and 0.86, correspondingly. The average coordination number of Mg and Si atoms is ~12.84 and ~8.2, respectively, which are higher than those of the crystalline phase in which each Mg atom is tenfold coordinated and six of which are Mg atoms ($Mg\text{-}Mg_6Si_4$) while each Si atom is eightfold coordinated and its all neighbors are Mg atoms ($Si—Mg_8$). We also study the statistical distribution of the clusters