



Defect and phase stability of solid solutions of Mg_2X with an antiferroite structure: An ab initio study

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ABSTRACT

First principles calculations are done for Mg_2X ($X=Si, Ge$ or Sn) antiferroite compounds and their solid solutions in order to investigate their pseudo-binary phase diagram. The formation energies of the end-member compounds agree qualitatively with the experiments. For $X=Si$ and Ge , there is a complete solubility, but we observe a miscibility gap in the pseudo-binary phase diagram Mg_2Si-Mg_2Sn . This agrees with the most recent experiments and phase diagram assessments. Calculated electronic properties of $Mg_2Si_{1-x}Sn_x$ alloys qualitatively agree with experiments and in particular the energy bandgap decreases when Si is substituted by Sn . Supercell calculations are also done in order to determine the most stable defects and the doping induced by these defects in the three end-member compounds. We find that the intrinsic n-doping in pure Mg_2Si can be attributed to the presence of magnesium atoms in interstitial positions. In Mg_2Ge and Mg_2Sn , since other defects are stable, they can be also of p-type.

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1. Introduction

In the search of new green energy sources, thermoelectric conversion has recently attracted the attention, notably due to the progress in the search of new thermoelectric materials since the middle of the nineties. However, one important aspect for the sustainability of an energy source is to use non toxic, recyclable and abundant elements. Therefore, in the case of thermoelectric materials, some materials, such as the semiconducting silicides [1,2] moderately studied during the sixties and seventies, have recently been the subject of an intense research. Among these materials, the alloys based on the antiferroite compound, Mg_2Si , are very promising, more specifically for the n-type conductors. The Mg_2X compounds of this family are semiconductors with an energy bandgap of about 0.75–0.8, 0.7–0.75 and 0.3–0.4 eV for, respectively $X=Si, Ge$ and Sn [2]. The $Mg_2Si_{1-x}Sn_x$ alloys were found to have the best dimensionless figure of Merit ZT (about 1.1) close to 800 K [3]. However, a recent study of the phase diagram of the $Mg_2Si_{1-x}Sn_x$ solid solution questions us about the stability of these alloys [4]. Indeed, contrary to a previous work indicating that the alloys investigated in [3] have a single-phase composition [5], this work indicates that this is not the case and that these compounds are two-phase compounds with compositions inside a miscibility gap [4]. Conversely, in the

case of $Mg_2Si_{1-x}Ge_x$, a complete solid solution seems to exist [6], making these compounds more attractive, but the cost of Ge is an obstacle in this case. In addition, these alloys have the advantage to be stable until much higher temperatures than the tin-based alloys. Thus, we can see the importance to have a better knowledge of the phase diagram of solid solutions of Mg_2Si with Mg_2Ge and Mg_2Sn for the evaluation of these alloys for future applications in thermoelectric generation at high temperature. Also, because of the importance of finding an optimal doping of these alloys, it is important to study the native point defects of these materials in order to understand how these defects can influence the doping of these materials and therefore their thermoelectric properties. Because Mg_2Si is highly covalent [7], it is not possible to conclude using too simplistic ionic models. It is necessary to make an ab initio study of the stability of the solid solutions, the point defects and of their electronic structure. This is the aim of the present work.

2. Computational details

First-principles calculations are performed using the scalar relativistic all-electron Blöchl's projector augmented-wave (PAW) method within the generalized gradient approximation (GGA), as implemented in the highly-efficient Vienna Ab initio Simulation Package (VASP) [8–10]. For the GGA exchange–correlation function, the Perdew–Berke–Erzenhof parametrization (PBE) [11] is employed for the calculations of the solid solutions with a plane-wave cut-off

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energy of 500 eV. Brillouin zone integrations are performed using the tetrahedron method for relaxation and electronic density of states calculations for the Ge-based alloys with a k -point sampling of $21 \times 21 \times 21$. In the case of the alloys, we use the simple cubic cell containing 4 formula-units of Mg_2X . The total energy is converged numerically to less than 1×10^{-6} eV/unit. In the case of Sn-based alloys, relaxation calculations are done with both the Tetrahedron method and the Monkhorst–Pack k -point meshes [12] and the Methfessel–Paxton technique [13] with a smearing parameter of 0.2 eV. Indeed, as we cannot find an energy bandgap for pure Mg_2Sn , it is better to use the second method in that case, but for the alloys, we need to use both methods as we do not know by advance if the ab initio calculations give a bandgap or not. In the present case, the difference between the two methods is negligible for the formation energy and very small for the structural parameters. In the case of defect calculations and in the case of $Mg_{64}X_{31}Y$ (with $X, Y = Si, Ge$ or Sn) alloys, we also use the second method [12], with a k -point sampling of $3 \times 3 \times 3$ in a supercell containing 32 formula-units of Mg_2X . The interstitial atom is added at the center of the supercell which is an empty site in the pure compound. In that case the total energy is converged numerically to less than 1×10^{-4} eV/(unit cell). After structural optimization, calculated forces are converged to less than 0.1 eV/Å. To test the robustness of the tendencies observed for the defect formation energy calculations, we have also made calculations using another exchange–correlation functional, the Perdew–Wang 91 (PW91) parameterization [13]. The electronic structure is calculated using the Tetrahedron technique in order to determine the effect of the native defects on the electronic structure. Indeed, as mentioned in the introduction, these compounds (at least Mg_2Si) are highly covalent semiconductors [7].

3. Results and discussion

3.1. Alloys Mg_2Si – Mg_2Y ($X = Ge, Sn$)

We find that the calculated volume is 2% larger than the experimental volume for Mg_2Ge (65.07 \AA^3), slightly larger than the experimental volume for Mg_2Sn (76.89 – 77.57 \AA^3) [2] and inside the experimental range for Mg_2Si (63.65 – 65.23 \AA^3) [2]. Our results indicate that the formation energy increases linearly with the Ge concentration in the $Mg_2Si_{1-x}Ge_x$ alloys (see Fig. 1), indicating that these alloys form a solid solution whereas this is not the case for the $Mg_2Si_{1-x}Sn_x$ alloys (see Fig. 2). In this last case, the formation energy is clearly above the line joining the two end members which is the indication of the presence of a

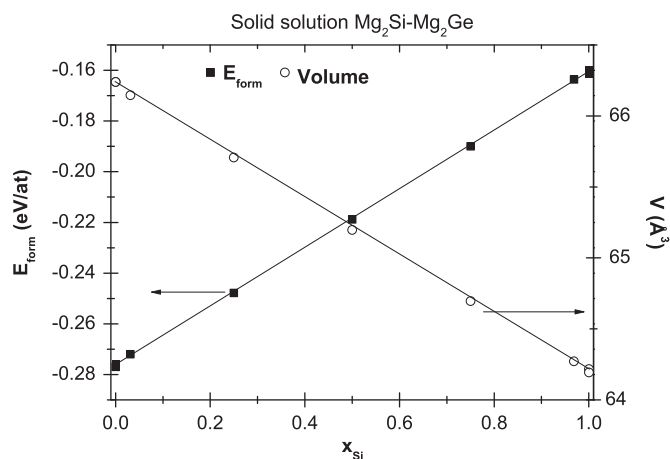


Fig. 1. Formation energy and volume vs x_{Si} silicon content for the solid solutions Mg_2Si – Mg_2Ge .

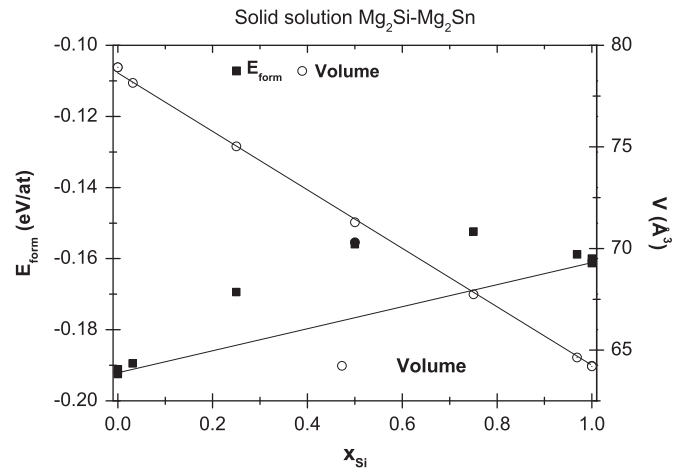


Fig. 2. Formation energy and volume vs x_{Si} silicon content for the solid solutions Mg_2Si – Mg_2Sn .

miscibility gap. We note that the formation energy of Mg_2Sn is smaller in absolute value than that of Mg_2Ge but larger than that of Mg_2Si in absolute value. This tendency agrees with the experimental data where it is found that the formation energy of Mg_2Si is about -0.22 to -0.31 eV/at. [14–16] and is much smaller than that of Mg_2Ge (-0.355 to -0.4 eV/at.) in absolute value [16,17] and close to that of Mg_2Sn (-0.213 to -0.278 eV/at.) [5,16,18]. Note that the above calculations have been performed using the PBE parameterization. We confirm this tendency using the PW 91 parameterization, although Zhang et al. [16] do not find results following the experimental tendency, contrary to us. Very recently, another group has calculated the formation energy of the end-member compounds Mg_2X ($X = Si, Ge$ and Sn) using the PBE exchange–correlation functional [19] and found structural parameters in very good agreement with us and also formation energies in much better agreement with our values than those of Zhang et al. [16].

As the calculations are done at 0 K, we have to compare our results with the low temperature part of the assessed phase diagrams. Clearly, our results for the $Mg_2Si_{1-x}Sn_x$ alloys agree well with the new pseudo-binary phase diagram Mg_2Si – Mg_2Sn determined by Kozlov et al. [4] and disagree with the previous one proposed by Jung et al. [5]. We find systematically small displacements of the Mg atoms from their position in the parent compounds. Note also that for the two series of alloys, we find that the Vegard's law is verified, even for the tin-based metastable alloys. From our results and the phase diagram proposed by Kozlov et al. [4], we propose that the presence of the miscibility gap and therefore the metastability of these alloys could simply explain the anomalous bulk modulus values computed by Pulikotil et al. [20] using the equation of states found in the case of the tin-based alloys with the coherent potential approximation (CPA). However, we note that they have used a less accurate approximation in their calculations: the Atomic Sphere Approximation. Our above findings have been independently confirmed by an ab initio study of the $Mg_2Si_{1-x}Ge_x$ and $Mg_2Si_{1-x}Sn_x$ alloys done by Tobola and coworkers using also the CPA technique [21]. They have also found that the formation energy deviates from the linear behavior only for the $Mg_2Si_{1-x}Sn_x$ alloys.

We have calculated the electronic structure of these materials and we do not find any bandgap for the $Mg_2Si_{1-x}Sn_x$ alloys except for pure Mg_2Si , while for all compounds of the $Mg_2Si_{1-x}Ge_x$ solid solutions, we find a small bandgap between 0.05 and 0.23 eV (see Fig. 3). Clearly, the absence of an energy bandgap in the alloys containing tin as well as the small values of the bandgap for the other compounds compared to experiments are due to the usual

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