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A comparison of the mixing thermodynamics of the antifluorite-structured $Mg_2Si_{1-x}Ge_x$, $Mg_2Sn_{1-x}Ge_x$ and $Mg_2Si_{1-x}Sn_x$ alloys from first principles

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The mixing thermodynamics of the antifluorite-structured $Mg_2Si_{1-x}Ge_x$ is investigated using the first-principles calculations. We find that Mg_2Si and Mg_2Ge readily mix with each other leading to formation of a single-phase random solid solutions of $Mg_2Si_{1-x}Ge_x$ across the entire composition range from the temperature of about 50 K and above. At 0 K, $Mg_2Si_{1-x}Ge_x$ exhibits a weak energy preference toward local phase segregation into Mg_2Si and Mg_2Ge without forming any ordered patterns of Si and Ge atoms. Through a comparison with the mixing thermodynamics of Mg_2Sn with Mg_2Si or Mg_2Ge , a small lattice misfit between Mg_2Si and Mg_2Ge of less than 1 % is responsible for the formation of stable $Mg_2Si_{1-x}Ge_x$ random solid solutions, such as lattice parameters and elastic moduli, are found to suitably follow the Vegard's law. Besides their thermodynamic stability, our prediction reveals that the random solid solutions of $Mg_2Si_{1-x}Ge_x$ are dynamically and mechanically stable. These findings justify the uses of structural models of $Mg_2Si_{1-x}Ge_x$, assuming a random distribution of Si and Ge atoms in the previous theoretical studies, and also provide an insight into the complete solubility of Mg_2Ge in Mg_2Si and vice versa at all temperature where the atomic diffusion is activated.

INTRODUCTION

As promising materials for fabrication of thermoelectric energy conversion devices operating at temperatures ranging from 500 K to 800 K, magnesium compounds exhibiting the antifluorite structure, *i.e.*, Mg_2Si , Mg_2Ge , and Mg₂Sn, have attracted considerable attention from the materials research community during the last few decades [1-7]. The reasons can be attributed not only to their prominent thermoelectric properties, but also to the fact that the compounds are non-toxic (this is, however, not true for all compounds containing Ge.) and their elemental components are abundant. Rather than bulk crystals, Mg₂Si, Mg₂Ge, and Mg₂Sn have lately been often considered in the form of thin solid films with aims to improve their thermoelectric performance via an effect of quantum confinement, for example, fabrication of a thin-film-based quantum well of $Mg_2Si/Mg_2Ge/Mg_2Si$ [8]. Such a quantum confinement system can in principle be achieved in a vacuum environment by using molecular beam epitaxy or physical vapor deposition [9–12]. In addition, the materials' thermoelectric properties may be further finetuned through formation of pseudo-binary $Mg_2Z_{1-x}^1Z_x^2$ alloys comprising of Mg_2Z^i , where $Z^i = Si$, Ge, Sn, and taking advantage of alloy phonon scattering arising from the difference in atomic mass between the group-14 elements [13-22]. Unlike the Mg₂Si-Mg₂Sn and Mg_2Ge-Mg_2Sn systems, exhibiting a tendency toward

local phase segregation of the alloy constituents due to the existence of immiscible regions below the critical temperature [16, 23–25], Mg₂Ge has been reported to be soluble in Mg₂Si and vice versa, forming complete series of Mg₂Si_{1-x}Ge_x random solid solutions [14–17, 19, 26– 28].

In general, successful syntheses of $\mathrm{Mg}_2\mathrm{Si}_{1-x}\mathrm{Ge}_x$ solid solutions are carried out at $T \gtrsim 600$ K through, for example, melt-grown [14], spark plasma sintering [15], and solid-state reaction [17, 27] techniques. As the as-grown solid solutions are quenched or cooled down to low temperature, $Mg_2Si_{1-x}Ge_x$ solid solutions might plausibly to display either chemical clustering of Si and Ge atoms within in a miscibility gap in analogy to $Mg_2Si_{1-x}Sn_x$ and $Mg_2Sn_{1-x}Ge_x$ [16, 23–25], or chemical ordering of Si and Ge atoms leading to formation of ordered solid solutions of $Mg_2Si_{1-x}Ge_x$. If the latter is really the case, it might not be possible to stabilize the heterostructure of Mg₂Si/Mg₂Ge/Mg₂Si, previously proposed in the literature [8], in thermodynamic equilibrium, when the substances are subjected to elevated temperature. Note that this, nevertheless, depends on the configurational thermodynamics and the temperature needed to activate noticeable diffusion of the group-14 elements in the Mg₂Si-Mg₂Ge system. At the same time, structural models for pseudo-binary $Mg_2Si_{1-x}Ge_x$ alloys regularly assume a random distribution of Si and Ge atoms [16, 19, 29], which may or may not suffice to describe their alloying behaviors, in

particular potential chemical ordering of the group-14 elements, if existing, in the low-temperature region. This thus gives rise to an ambiguity, concerning the alloying behaviour of $Mg_2Si_{1-x}Ge_x$, and further investigation on the configurational thermodynamics of Si and Ge atoms in the pseudo-binary $Mg_2Si_{1-x}Ge_x$ solid solutions must be done to clarify the issue.

COMPUTATIONAL METHODS

To examine the configurational thermodynamics of Si and Ge atoms in the pseudo-binary $Mg_2Si_{1-r}Ge_r$ alloys, we use a cluster-expansion formalism [30] in combination with first-principles calculations. Since the alloying process in $Mg_2Si_{1-x}Ge_x$ is involved particularly with sublattice sites of the group-14 elements, *i.e.*, Si and Ge, the Mg sublattice sites are assumed as fully occupied, by which Mg atoms residing in the Mg sublattice sites are considered as mere spectators and do not take part in the cluster expansion. In this work, the alloy-theoretical automated toolkit (ATAT) [31] is employed to perform the cluster expansion, whereas its implementation to investigate the mixing thermodynamics of pseudo-binary solid solutions is fully described in our previous work [32]. The first-principles total energies are, on the other side, calculated from the density functional theory within the generalized gradient approximation [33] and the project augmented wave method [34], as implemented in the Vienna ab initio simulation package (VASP) [35, 36]. The planewave energy cutoff is 900 eV, and the Brillouin integration is performed using the Monkhorst-Pack k-point meshes of $15 \times 15 \times 15$ [37]. For all first-principles calculations, volume, cell shape, and internal atomic coordinates of all $Mg_2Si_{1-x}Ge_x$ solid solutions are fully optimized and the total force, exerting on each atom, is smaller than 10^{-6} eV/Å. Besides, the calculated first-principles energies are ensured to be converged within an accuracy of 1 meV/f.u. with respect to the plane-wave energy cutoff and the number of Monkhorst-Pack k-point grids.

By following the procedure, mentioned in Ref. [32], the final cluster expansion utilizes a total of 33 effective cluster interactions (ECIs), including 19 pair and 12 triplet interactions, and it fits the energies of 145 ordered structures of Mg₂Si_{1-x}Ge_x with a leave-one-out cross validation score of 0.096 meV/f.u. With an aim to search for possible ground-state structures of Mg₂Si_{1-x}Ge_x, the final set of ECIs, as obtained from the cluster expansion, are used to predict the energies of Mg₂Si_{1-x}Ge_x solid solutions, exhibiting different ordered patterns of Si and Ge atoms, with up to 36 atoms in a primitive supercell. This is indeed equivalent to 12 primitive rhombohedral unitcells of Mg₂Si or Mg₂Ge, and thus results in a total of 10805 ordered structures of Mg₂Si_{1-x}Ge_x. To model solutions of Mg₂Si_{1-x}Ge_x, in which Si and Ge atoms

randomly occupy the group-14 sublattice sites, the special quasirandom structure technique [38] is employed. For this particular case, the models of Mg₂Si_{1-x}Ge_x random solid solutions are constructed within $2 \times 2 \times 2$ cubic supercells (96 atoms) with $0 \leq x \leq 1$ and $\Delta x = 0.25$.

In addition to the configurational thermodynamics, we derive elastic constants and phonon frequencies of $Mg_2Si_{1-x}Ge_x$ solid solutions to examine, respectively, their mechanical and dynamical stabilities. In the present work, the cube-averaged elastic constants and elastic moduli of $Mg_2Si_{1-x}Ge_x$ solid solutions are evaluated using the approaches, described in Ref. [39] and references therein. On the other hand, the vibrational frequencies due to the lattice dynamics of $Mg_2Si_{1-x}Ge_x$ solid solutions are obtained within the harmonic approximation by using the PHONOPY package for phonon calculations [40, 41], in which the small displacement method [42] is used to approximate the force constants within the $2 \times 2 \times 2$ cubic supercells (96 atoms). To assure the convergence of the derive phonon frequencies, the supercells are sampled with the Monkhorst-Pack kpoint meshes of $21 \times 21 \times 21$.

RESULTS AND DISCUSSION

FIG. 1(a) illustrating the mixing energies (ΔE_{mix}) at T = 0 of Mg₂Si_{1-x}Ge_x reveals that no Mg₂Si_{1-x}Ge_x solid solutions with ordered patterns of Si and Ge atoms are distinctly predicted to be stable with respect to Mg₂Si and Mg_2Ge . We note that, although a few ordered solid solutions of Mg₂Si_{1-x}Ge_x at $x \approx 0.857$ are predicted to exhibit negative ΔE_{mix} , the values being on the order of -0.063 meV/f.u. and -0.007 meV/f.u. are very tiny, and even falling below the limit of numerical accuracy of the current first-principles calculations of ΔE_{mix} and of the current predictive power of cluster expansion for ΔE_{mix} . With exception of a few structures predicted to possess tiny negative values of ΔE_{mix} , the remainder as majority exhibits positive values of ΔE_{mix} suggesting, at T = 0K, $Mg_2Si_{1-x}Ge_x$ might display a tendency toward phase segregation into Mg₂Si-rich and Mg₂Ge-rich regions under thermodynamic equilibrium condition.

With that being said, it should, nevertheless, be noted that the absolute values of ΔE_{mix} of 10850 ordered structures of Mg₂Si_{1-x}Ge_x do not exceed 1.50 meV/f.u. Such small absolute values of ΔE_{mix} can be directly attributed to weak ECIs between Si and Ge atoms, resulting in a driving force for Mg₂Si and Mg₂Ge to readily mix with each other and to form Mg₂Si_{1-x}Ge_x random solid solutions stable in the limit $V/T \rightarrow 0$, where V stands for the strongest interaction in the Mg₂Si-Mg₂Ge system. According to our calculations, the magnitude of the ECIs, derived from the final cluster expansion of Mg₂Si_{1-x}Ge_x, is smaller than 0.1 meV/f.u. (see Supplementary FIG.



FIG. 1: (a) Mixing energies (ΔE_{mix}) at T = 0 K of Mg₂Si_{1-x}Ge_x solid solutions, calculated with respect to Mg₂Si and Mg₂Ge. Red crosses and Open black circles are, respectively, the cluster-expansion (CE) predicted and density-functional-theory (DFT) calculated ΔE_{mix} of Mg₂Si_{1-x}Ge_x solid solutions exhibiting different ordered patterns of Si and Ge atoms. Filled blue squares stand for the DFT-calculated ΔE_{mix} of ideal random solid solutions of Mg₂Si_{1-x}Ge_x, modeled by using the special quasirandom structure (SQS) method. (b) Mixing Gibbs free energies (ΔG_{mix}) of Mg₂Si_{1-x}Ge_x ideal random solid solutions at T = 0, 50,100, 150, and 200 K, as obtained from the mean-field approximation for the mixing entropy ΔS_{mix} (see the main text for description).

S1) That is, the qualitative criterion of $V/T \rightarrow 0$, giving rise to a random solid solutions can be said to be practically fulfilled also well below room temperature.

For comparison to the results derived from the cluster expansion, optimized first-principles ΔE_{mix} at T = 0 K for Mg₂Si_{1-x}Ge_x random solid solutions are also included in FIG. 1(a) . By taking into consideration the contribution arsing from the random distribution of Si and Ge atoms, the thermodynamic stability of Mg₂Si_{1-x}Ge_x random solid solutions can then be derived from the mixing Gibbs free energy per formula unit (ΔG_{mix});

$$\Delta G_{mix}(x,T) = \Delta E_{mix}(x,T) - T\Delta S_{mix}(x,T), \quad (1)$$

where ΔS_{mix} denotes the mixing entropy per formula unit of ideally random solid solutions, stable in the limit of $V/T \rightarrow 0$, and it can thus be reasonably approximated through the mean-field approach to be

$$\Delta S_{mix}(x) = -k_B [x \ln(x) + (1-x) \ln(1-x)]. \quad (2)$$

As first-principles ΔE_{mix} of Mg₂Si_{1-x}Ge_x random solid solutions are obtained at discrete grids with $\Delta x =$ 0.25, the cubic spline interpolation is implemented to interpolate ΔE_{mix} with $\Delta x = 0.01$ and interpolated ΔE_{mix} are then combined with $-T\Delta S_{mix}$ for a given composition x to obtain ΔG_{mix} of the random solid solutions.

FIG. 1(b) displays ΔG_{mix} curves of Mg₂Si_{1-x}Ge_x random solid solutions, derived from the mean-field approximation for ΔS_{mix} , at 0 K $\leq T \leq 200$ K with $\Delta T = 50$ K. We find that, at $T \gtrsim 50$ K, ΔG_{mix} of

 $Mg_2Si_{1-x}Ge_x$ random solid solutions exhibits a positive This curvature across the entire composition range. indicates formation of a complete series of single-phase random solid solutions. Note that the order-disorder transition temperatures, derived in the present work, can be overestimated by up to ~ 30 % due to the absence of the short-range effects in ordering and clustering allov systems in the mean-field approximation [32, 43]. These findings are not only in line with the experimental syntheses of $Mg_2Si_{1-x}Ge_x$ random solid solutions, generally performed at high temperature $(T \gtrsim 600)$ K) [14, 15, 17, 27], but also justify the uses of structural models of $Mg_2Si_{1-x}Ge_x$ assuming a random distribution of Si and Ge atoms residing in the sublattice sites in the previous theoretical studies of pseudo-binary $Mg_2Si_{1-x}Ge_x$ alloys [16, 19]. The calculated cubic lattice parameters of Mg₂Si and Mg₂Ge are 6.365 Å and 6.422 Å, respectively, whereas those of $Mg_2Si_{1-x}Ge_x$ random solid solutions are deviating from the Vegard's law by less than 0.05 % and in good agreement with the experimental observation [26, 27].

The elastic constants and moduli of Mg₂Si, Mg₂Ge, and Mg₂Si_{1-x}Ge_x random solid solutions with x = 0.25, 0.50, and 0.75, calculated in the present work, are listed in Table I. We find that the Born's stability criteria (C_{11} $-C_{12} > 0$; $C_{11} + 2C_{12} > 0$; $C_{44} > 0$) [48], stating the generic requirement for elastic stability of any cubic crystal system, are satisfied for all considered compositions of Mg₂Si_{1-x}Ge_x. This thus indicates that Mg₂Si_{1-x}Ge_x random solid solutions and their constituent compounds

TABLE I: Cube-averaged elastic constants C_{11} , C_{12} , C_{44} (GPa), bulk modulus B_H (GPa), shear modulus G_H (GPa), Young's modulus E_H (GPa, and B_H/G_H ratio in the Voigt-Reuss-Hill (VRH) approach for Mg₂Si, Mg₂Ge, and Mg₂Si_{1-x}Ge_x random solid solutions, where x = 0.25, 0.50, and 0.75. Comparison is made with experimental and theoretical values, previously reported in the literature.

	C_{11}	C_{12}	C_{44}	B_H	G_H	E_H	B_H/G_H	Ref.
Mg ₂ Si	116.01	23.19	45.11	54.13	45.62	106.85	1.18	Calc. (This work)
	116.00	22.90	46.80	54.00	46.70	108.00	1.16	Calc. [44]
	121.20	23.70	49.50	56.20	49.20	113.5	1.14	Calc. [45]
	116.70	23.10	45.30					Calc. [46]
	126.00	26.00	48.50					Expt. [47]
$\mathrm{Mg_2Si_{0.75}Ge_{0.25}}$	111.96	24.13	41.24	53.41	42.29	100.38	1.26	Calc. (This work)
$\mathrm{Mg_2Si_{0.50}Ge_{0.50}}$	106.70	25.14	38.26	52.33	39.25	94.19	1.33	Calc. (This work)
$\mathrm{Mg_2Si_{0.25}Ge_{0.75}}$	100.93	26.32	33.56	51.19	35.01	85.53	1.46	Calc. (This work)
Mg ₂ Ge	96.81	27.23	31.10	50.42	32.52	80.31	1.55	Calc. (This work)
	106.00	19.80	42.80	48.60	42.90	99.40	1.13	Calc. [44]
	118.10	23.60	48.00	55.10	47.70	111.10	1.15	Calc. [45]
	107.3	21.1	41.80					Calc. [46]
	117.9	23.00	46.50					Expt. [47]



FIG. 2: Phonon density of states of (a) Mg_2Si , (b) $Mg_2Si_{0.5}Ge_{0.5}$ random solid solution, and (c) Mg_2Ge , all derived from the harmonic approximation.

are mechanically stable. We also find that our calculated elastic constants and moduli of Mg₂Si and Mg₂Ge are comparable to the existing experimental and theoretical values, previously report in the literature (see Table I). According to our results, the elastic moduli of Mg₂Si are higher than those of Mg_2Ge , demonstrating that Mg₂Si possesses lower compressibility under hydrostatic pressure, higher resistance to shear deformation, and higher stiffness than Mg_2Ge . Moreover, according to Pugh's criteria, determining intrinsic ductility and brittleness of non-metallic materials via the values of B_H/G_H ratio [49], our results reveal that the ratio of B_H/G_H of both Mg₂Si and Mg₂Ge are smaller than the critical value of 1.75, indicating that the compounds are brittle, and the degree of brittleness in Mg₂Ge is relatively lower than that of Mg₂Si. These findings are indeed in line with the previously theoretical studies [44].

confirming the reliability of our calculations. The elastic constants and moduli, similar to the lattice parameters, of $Mg_2Si_{1-x}Ge_x$ random solid solutions are found to well follow the Vegard's law with deviation smaller than 3%.

Next, we consider the phonon density of states of Mg₂Si, Mg₂Ge, and Mg₂Si_{0.5}Ge_{0.5} random solid solution. As can be seen from Fig. 2, no imaginary phonon frequencies are observed for $Mg_2Si_{1-x}Ge_x$ with x =0, 0.5 and 1, indicating their dynamical stabilities. It is worth emphasizing here that the phonon density of states of Mg₂Si and Mg₂Ge, derived in the present work, is found to agree well with the experimentally measured theoretically calculated phonon densities of states of Mg_2Si and Mg_2Ge , previously reported by Bessas *et* al. [50] in terms of both phonon frequencies and features of corresponding density of states. This not only further confirms the reliability of our theoretical prediction, but also strengthens the accuracy of our derived phonon density of states of Mg₂Si_{0.5}Ge_{0.5} random solid solution. Although Mg₂Si and Mg₂Ge are isostructural and, as estimated from our calculations, the lattice parameter of Mg_2Ge is different from that of Mg_2Si by less than ~ 1 %, the two compounds exhibit somewhat different features of phonon density of states. This can be attributed to a difference in the elemental bonding and atomic mass between Mg_2Si and Mg_2Ge [45, 50]. Through a comparison of the phonon density of states of Mg₂Si_{0.5}Ge_{0.5} random solid solution with that of Mg₂Si and Mg_2Ge , we find that in spite of tiny frequency shifts due to the differences in local atomic environment between Mg₂Si, Mg₂Ge, and Mg₂Si_{0.5}Ge_{0.5}, the features of the partial density of states of Mg, Si, and Ge in the binary compounds are mostly retained in those of $Mg_2Si_{0.5}Ge_{0.5}$ random solid solution. Based on these results, one can expect that the phonon density of $Mg_2Si_{1-x}Ge_x$ random solid solutions with x < 0.5 and x

> 0.5 are likely to behave similarly to Mg₂Si_{0.5}Ge_{0.5} and are also dynamically stable. We note that, since the SQS method used for modeling any random solid solutions in a finite-size supercell, in principle, break the point-group symmetry of the crystal lattice, analysis of vibrational modes for Mg₂Si_{1-x}Ge_x random solid solutions through the phonon band dispersion is a challenge and not discussed in the present work. A detailed discussion of vibrational mode analysis for Mg₂Si and Mg₂Ge is, however, can be found elsewhere [45, 50, 51].

As briefly mentioned in section 1, thin films of Mg₂Si, Mg₂Ge, and Mg₂Sn have increasingly been of interest to materials researchers and engineers due to their potential in, for example, thermoelectric energy harvesting devices [9–12]. It is, however, worth evaluating an influence of residual gas contamination, in particular hydrogen and oxygen, into Mg₂Si, Mg₂Ge, or $Mg_2Si_{1-x}Ge_x$ samples, which may take place during the synthesis of the materials under varying vacuum conditions. Such contamination could either impure the as-grown materials in the form of structural defects or results in precipitation of possible competing phases in thermodynamic equilibrium, subsequently affecting the materials' properties. Herein, we preliminarily study effects of substitutional/interstitial defects of oxygen or hydrogen in the dilute limit, modeled in a 2×2 \times 2 cubic supercell of Mg₂Z (96 atoms), denoted by $Mg_{64}Z_{32}$, where Z = Si or Ge. For the substitutional defects, an oxygen atom or a hydrogen atom substitutes for one of the magnesium atoms $(Mg_{63}X)Z_{32}$ or for one of the group-14-element atoms $Mg_{64}(Z_{31}X)$, while, for the interstitial ones, an oxygen atom or a hydrogen atom occupies one of the interstitial 4b Wyckoff positions $Mg_{64}Z_{32}X$, where X = O or H. In order to access information on the thermodynamic stability of the defective structures of Mg₂Si and Mg₂Ge with ~ 1 at.% O or H, we estimate their energies of formation with respect to 15 possible competing phases. Those are, Mg, Si, Ge, H₂, O₂, Mg₂Si, Mg₂Ge, MgH₂, SiH₄, SiO_2 , MgO, Mg₂SiO₄, GeH₂, GeO₄, and Mg₂GeO₄. We note that the first-principles total energies of all considered defective structures and completing phases are optimized with respect to volume, cell shape, and internal atomic coordinates. Our calculations reveal that the energies of formation for all considered defective structures are ranging between +18.78meV/atom and +76.26 meV/atom, in turn suggesting that under thermodynamic equilibrium condition the defective structures of Mg₂Si (Mg₂Ge) are likely to decompose into Mg_2Si (Mg_2Ge) and relevant competing phases. For example, $(Mg_{63}O)Si_{32}$ tends to undergo phase separation into Mg₂Si, MgO, and Si. Details about the competing phases and decomposition of the defective structures can be found in the Supplemental Material. Since $Mg_2Si_{1-x}Ge_x$ random solid solutions are predicted to be thermodynamically stable with respect to Mg₂Si and Mg₂Ge at low temperature, it can also be implied from these results that, for a given composition x, Mg₂Si_{1-x}Ge_x cooperating with substitutional/interstitial defects of oxygen or hydrogen in the dilute limit would as well phase separate into Mg₂Si_{1-x}Ge_x and relevant competing phases.

The formation of complete series of random solid solutions in the pseudo-binary Mg₂Si-Mg₂Ge system at relatively low temperature may, according to Hume-Rothery rules [52], be explained by a small lattice misfit between Mg₂Si and Mg₂Ge. To verify this, we investigate the mixing thermodynamics of Mg₂Sn_{1-x}Ge_x and Mg₂Si_{1-x}Sn_x alloys by following the exactly same procedure, previously applied to Mg₂Si_{1-x}Ge_x alloys. We note that the cubic lattice parameter of Mg₂Sn, estimated in this work, is 6.808 Å, which is in good agreement with the experimental and theoretical values, previously reported in the literature [16, 18, 46]. This thus results in a lattice mismatch between Mg₂Sn and Mg₂Ge with ~ 6 % difference in lattice spacing, whereas it is ~ 7 % between Mg₂Si and Mg₂Sn.

FIG. 3(a) and 3(b) illustrate ΔE_{mix} at T = 0 K of $Mg_2Sn_{1-x}Ge_x$ and $Mg_2Si_{1-x}Sn_x$ alloys, respectively. We find that ΔE_{mix} of Mg₂Sn_{1-x}Ge_x (Mg₂Si_{1-x}Sn_x) alloy is positive for all considered structures, suggesting that no ordered pattern of Sn and Ge atoms (Si and Sn atoms) is thermodynamically stable at T = 0 K, and thus solid solutions of $Mg_2Sn_{1-x}Ge_x$ ($Mg_2Si_{1-x}Sn_x$) are likely to decompose into their constituent compounds as $T \rightarrow 0$ K in thermodynamic equilibrium. Note that the values of ΔE_{mix} can be as high as +50 (+65) meV/f.u. for $Mg_2Sn_{1-x}Ge_x$ ($Mg_2Si_{1-x}Sn_x$) solid solutions. This is a result of relatively stronger ECIs in the Mg₂Sn-Mg₂Ge and Mg₂Si-Mg₂Sn systems, as compared to those of the Mg₂Si-Mg₂Ge system (see also FIG. S2 and S3). Again, we estimate through the mean-field approach ΔG_{mix} of Mg₂Sn_{1-x}Ge_x and Mg₂Si_{1-x}Sn_x random solid solutions, modeled by the SQS technique, as a function of composition and temperature. For the pseudo-binary Mg_2Sn-Mg_2Ge (Mg_2Si-Mg_2Sn) system, ΔG_{mix} of $Mg_2Sn_{1-x}Ge_x$ ($Mg_2Si_{1-x}Sn_x$) random solid solutions exhibits a positive curvature across the entire composition range, which indicates formation of a complete series of single-phase random solid solutions of $Mg_2Sn_{1-x}Ge_x$ $(Mg_2Si_{1-x}Sn_x)$ at $T \gtrsim 900$ (1100) K, see FIG. S4 and S5 in the Supplemental Material. By comparing with the Mg₂Sn-Mg₂Ge (Mg₂Si-Mg₂Sn) system, exhibiting the lattice misfit of ~ 6 % (~ 7 %), the approximately twenty times lower critical temperature of $Mg_2Si_{1-x}Ge_x$ random solid solutions can thus be directly attributed to the small degree of lattice misfit between Mg₂Si and Mg_2Ge . We note that, although the use of the mean-field approach in general results in an overestimation of the critical temperature at which a complete series of single-phase random solid solutions of any alloy system is formed, our prediction on the thermodynamic



FIG. 3: ΔE_{mix} at T = 0 K of (a) Mg₂Sn_{1-x}Ge_x and (b) Mg₂Si_{1-x}Sn_x solid solutions, calculated with respect to their constituent binary compounds. Red crosses and Open black circles are, respectively, the cluster-expansion (CE) predicted and density-functional-theory (DFT) calculated ΔE_{mix} of the solid solutions exhibiting different ordered patterns of atoms of the group-14 elements. Filled blue squares stand for the DFT-calculated ΔE_{mix} of ideal random solid solutions, modeled by using the SQS method. For the pseudo-binary Mg₂Si-Mg₂Ge (Mg₂Si-Mg₂Sn) system, the cluster expansion fits the energies of 145 ordered structures of the solid solutions with the cross-validation score of 0.916 (0.550) meV/f.u. by using a total of 33 ECIs. See also Supplementary FIG. S2 and S3 showing the ECIs, obtained from the final cluster expansion of Mg₂Sn_{1-x}Ge_x and Mg₂Si_{1-x}Sn_x alloys, respectively.

stability of $Mg_2Sn_{1-x}Ge_x$ and $Mg_2Si_{1-x}Sn_x$ random solid solutions, is qualitatively in line with pseudo-binary phase diagrams of Mg_2Sn-Mg_2Ge and Mg_2Si-Mg_2Sn systems previously proposed in the literature [16, 23–25].

CONCLUSIONS

In summary, we investigate in the present work the configurational thermodynamics of Si and Ge atoms in isostructural $Mg_2Si_{1-x}Ge_x$ alloys using the firstprinciples cluster expansion and the mean-field approach for the mixing entropy. Our findings reveal that although $Mg_2Si_{1-x}Ge_x$ is likely to display a tendency toward local phase segregation into Mg₂Si-rich and Mg₂Ge-rich regions at T = 0 K without forming any ordered pattern of Si and Ge atoms, Mg₂Ge is readily soluble in Mg₂Si and vice versa, resulting in formation of complete series of single-phase random solid solutions in the Mg₂Si-Mg₂Ge system at $T \gtrsim 50$ K. The reason can be attributed to unusually weak effective cluster interactions between Si and Ge atoms, which is a consequence of a small lattice misfit between Mg₂Si and Mg₂Ge. Through alloying Mg₂Ge with Mg_2Si , some intrinsic properties, for example, lattice parameters and elastic moduli, of $Mg_2Si_{1-x}Ge_x$ random solid solutions suitably follow the Vegard's law, and according to our prediction, the random solid solutions of $Mg_2Si_{1-x}Ge_x$ are dynamically and mechanically stable. On the other hand, because of the alloy phonon scattering, arising from the mass different between Si and Ge atoms, the thermal conductivity of $Mg_2Si_{1-x}Ge_x$ solid solution is expected to be reduced relative to that of its constituent compounds, thus likely improving the materials' thermoelectric figures of merit.

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Supplemental Material

A comparison of the mixing thermodynamics of the antifluorite-structured Mg₂Si_{1-x}Ge_x, Mg₂Sn_{1-x}Ge_x and Mg₂Si_{1-x}Sn_x alloys from first principles

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FIG. S1: Strength of effective cluster interactions (ECIs), obtained from the final cluster expansion including the 145 ordered structures of $Mg_2Si_{1-x}Ge_x$.

Figure S2



FIG. S2: Strength of effective cluster interactions (ECIs), obtained from the final cluster expansion including the 145 ordered structures of $Mg_2Sn_{1-x}Ge_x$.



FIG. S3: Strength of effective cluster interactions (ECIs), obtained from the final cluster expansion including the 145 ordered structures of $Mg_2Si_{1-x}Sn_x$.



FIG. S4: Mixing Gibbs free energy (ΔG_{mix}) of Mg₂Sn_{1-x}Ge_x random solid solutions at T = 0, 300, 600, 900, and 1200 K, derived from the mean-field approach for configurational entropy (ΔS_{mix}).



FIG. S5: Mixing Gibbs free energy (ΔG_{mix}) of Mg₂Si_{1-x}Sn_x random solid solutions at T = 0, 300, 600, 900, and 1200 K, derived from the mean-field approach for configurational entropy (ΔS_{mix}).

Competing phases

In the present work, except H₂ and O₂ molecules, crystal structures of the remaining competing phases are taken from the Materials Project database (*https://materialsproject.org*). Those are, Mg (mp-153), Si (mp-149), Ge (mp-32), Mg₂Si (mp-1367), Mg₂Ge (mp-408), MgH₂ (mp-23710), SiH₄ (mp-23739), SiO₂ (mp-546794), MgO (mp-1265), Mg₂SiO₄ (mp-2895), GeH₄ (mp-1205379), GeO₂ (mp-733), and Mg₂GeO₄ (mp-3904).

Thermodynamic stability of defective structures of Mg₂Si and Mg₂Ge

List of phase separation in Mg₂Si and Mg₂Ge, cooperating with substitutional/ interstitial defects of oxygen or hydrogen in the dilute limit with respect to the competing phases is given as follows;

$$(Mg_{63}O)Si_{32} \rightarrow 31Mg_2Si + MgO + Si (\Delta E_{form} = +76.26 \text{ meV/atom}),$$

 $Mg_{64}(Si_{31}O) \rightarrow 31Mg_2Si + MgO + Mg (\Delta E_{form} = +35.99 \text{ meV/atom}),$

 $Mg_{64}Si_{32}O \rightarrow 31.5Mg_2Si + MgO + 0.5Si (\Delta E_{form} = +43.17 \text{ meV/atom}),$

$$(Mg_{63}H)Si_{32} \rightarrow 31.375Mg_2Si + 0.25SiH_4 + 0.625Si (\Delta E_{form} = +41.84 \text{ meV/atom}),$$

 $Mg_{64}(Si_{31}H) \rightarrow 31Mg_2Si + 0.25SiH_4 + 1.75Mg (\Delta E_{form} = +37.99 \text{ meV/atom}),$

 $Mg_{64}Si_{32}H \rightarrow 31.875Mg_2Si + 0.25SiH_4 + 0.125Si (\Delta E_{form} = +20.62 \text{ meV/atom}),$

 $(Mg_{63}O)Ge_{32} \rightarrow 31Mg_2Ge + MgO + Ge (\Delta E_{form} = +54.75 \text{ meV/atom}),$

 $Mg_{64}(Ge_{31}O) \rightarrow 31Mg_2Ge + MgO + Mg (\Delta E_{form} = +37.32 \text{ meV/atom}),$

 $Mg_{64}Ge_{32}O \rightarrow 31.5Mg_2Ge + MgO + 0.5Ge (\Delta E_{form} = +38.48 \text{ meV/atom}),$

 $(Mg_{63}H)Ge_{32} \rightarrow 31.375Mg_2Ge + 0.25SiH_4 + 0.625Ge (\Delta E_{form} = +36.91 \text{ meV/atom}),$

 $Mg_{64}(Ge_{31}H) \rightarrow 31Mg_2Ge + 0.25SiH_4 + 1.75Mg (\Delta E_{form} = +37.58 \text{ meV/atom})$, and

 $Mg_{64}Ge_{32}H \rightarrow 31.875Mg_2Ge + 0.25SiH_4 + 0.125Ge (\Delta E_{form} = +18.78 \text{ meV/atom}).$

Note that ΔE_{form} denotes the energy of formation, evaluated with respect to the relevant competing phases.