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Magnesium based Si-Ge alloys under pressure: DFT evolutionary search results

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Abstract. The search of minimal enthalpy structures of ternary magnesium alloys of different stoichiometry $Mg_xSi_yGe_z$ under pressure $P \leq 6$ GPa has been performed using the software suite USPEX implementing the evolution algorithm combined with the density functional theory (DFT) approach. The evolutionary search has yielded new possible ternary compounds of the stoichiometries $Mg_{12}Ge_3Si$, $Mg_6Ge_4Si_3$, $Mg_6Ge_3Si_4$, Mg_6GeSi_3, $Mg_4Ge_3Si_2$, $Mg_4Ge_3Si_2$, Mg_4SiGe, and Mg_2GeSi, which have negative enthalpy of formation at pressures in the range of 0 to 10 GPa and which are not substitution solutions of Ge on Mg_2Si matrix (or Si on Mg_2Ge matrix). These compounds have metallic properties and formation enthalpies comparable to those of binary silicides Mg_2Si. Phonon spectra investigations indicate that only first five of them are stable showing no imaginary frequencies.

Keywords: $Mg_xSi_yGe_z$, crystal structure, hydrostatic pressure, evolutionary search, density functional theory

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Кремниево-германиевые сплавы на основе магния: результаты эволюционного поиска из первых принципов

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Аннотация. С помощью пакета программ USPEX, реализующих эволюционные алгоритмы на базе теории функционала плотности, был проведен поиск оптимальных структур твердых растворов магния, олова и магния разной стехиометрии $Mg_xSi_yGe_z$ под давлением $P \leq 6$ ГПа. В результате эволюционного поиска обнаружены новые возможные трехкомпонентные структуры состава $Mg_{12}Ge_3Si$, $Mg_6Ge_4Si_3$, $Mg_6Ge_3Si_4$, Mg_6GeSi_3, $Mg_4Ge_3Si_2$, $Mg_4Ge_3Si_2$, Mg_4SiGe, и Mg_2GeSi, которые имеют отрицательную энтальпию формирования в диапазоне давлений $0 < P \leq 10$ ГПа и не являются твердыми растворами замещения атомов Si атомами Ge в Mg_2Si-матрице или атомов Ge атомами Si в Mg_2Ge-матрице. Эти соединения имеют металлические свойства и их энтальпия образования соизмерима с энтальпией образования бинарных силицидов Mg_2Si. Стабильность пяти из полученных структур подтверждается расчетами их фононных спектрах, в которых не наблюдается мнимых фононных мод.

Ключевые слова: $Mg_xSi_yGe_z$, кристаллическая структура, гидростатическое давление, эволюционный поиск, методы функционала плотности

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Introduction

Since the 1960s, Mg_2X (X = Si, Ge, Sn) compounds and their solid solutions have shown promise for thermoelectric energy conversion due to high efficiencies, high melting points, narrow band gaps, and environmental safety. These materials are used in thermal elements, infrared detectors, solar cells, and hydrogen energy storage. Despite waning interest in the early 2000s, compositional flexibility and similar crystal structures have revived interest. Mg_2Ge is soluble in Mg_2Si and *vice versa* [1–8], enhancing thermoelectric performance through improved conductivity [9]. Varying germanium concentration tailors properties for energy conversion. For example, $Mg_2Si_{1-x}Sn_x$ with low thermal conductivity is favorable for thermoelectric energy conversion [10]. However, challenges exist in forming solid solutions and optimizing microstructure. Successful synthesis requires uniform structures [11, 12], highlighting the need for thorough investigation. Further research is needed to improve properties by exploring dopants and optimizing synthesis techniques [13].

Computational methods are crucial in material discovery, being more efficient than experiments. These computational searches allow researchers to rapidly explore a wide range of systems, uncovering novel phenomena and facilitating the discovery of new promising materials. Recent successes with two-component magnesium-based compounds suggest potential for three-component $Mg_xSi_yGe_z$ alloys. Anti-fluorite structure is the only one considered in the analysis of magnesium stannides, as both magnesium silicide and magnesium germanide share this structural form. Evolutionary optimization has reproduced known phases and predicted new structures under high pressures. The aim of this study is to identify optimal structures in the three-component $Mg_xSi_yGe_z$ system using modern evolutionary optimization techniques [14], and to investigate the stability of these structures both at ambient pressure conditions as well as at pressures ranging from 0 to 10 GPa.

Calculation procedure

For evolutionary modeling of the three-component Mg-Si-Ge system, Universal Structure Predictor: Evolutionary Xtallography (USPEX) algorithms were applied in the variable composition mode [15–17]. During the evolutionary search, from 40 to 60 generations of structures were produced depending on the convergence, which was considered to be achieved when the most energetically favorable structure remained unchanged for 20 consecutive generations. Each generation contained 20 structures and the first generation contained more than 120 structures, with 4 to 32 atoms per every structure. The structures of the first generation were randomly selected from the list of 230 space groups. In the following generations, 50% of the lowest-energy structures were inherited from the previous generation, 10% of the structures were produced by lattice mutation, 10% of the structures were obtained by atom transmutation, and the remaining 30% of the structures were generated randomly. All USPEX generated structures were then relaxed using the conjugate gradient method implemented in the VASP software [18], the one-electron wave functions were expanded in a plane-wave basis with a kinetic energy cutoff of E_{cut} = 500 eV. The exchange-correlation potential chosen based on the Purdue-Burke-Ernzerhof parameterization in the generalized gradient approximation [19]. Brillouin zone sampling was performed using a Monkhorst-Pack mesh with a *k*-point resolution of π×0.1 Å^{-1}. The enthalpy at a zero temperature was determined using relationship $F = E + PV$, where E is the total energy, P is the external pressure, and V is the primitive cell volume.

Results and Discussion

For calculations of three-component structures at ambient pressure conditions it is useful to carry out their studies at several pressures [20–22]. Then there are quite a lot of them compared to the calculations at ambient pressure conditions, which allows to study their $E(P)$ dependences in more detail and to select the most stable compounds. Three pressure values of 1 GPa, 4 GPa and 6 GPa were used to calculate germanium-silicon alloys and more than five and a half thousand structures were obtained by evolutionary search. Thus, if at 6 GPa we more than a hundred structures with negative enthalpy of formation, at 4 GPa there are only two, and at 1 GPa there are only three with energy close to zero. Since too few three-component systems are stable at low pressures, the structures obtained at non-zero pressures were used for their calculation, as will be shown below.

Table shows the lattice parameters and enthalpies of formation of the most stable convex hull compounds of magnesium, silicon and germanium obtained by evolutionary methods at external hydrostatic pressures of 1, 4 and 6 GPa. At a pressure of $P = 1$ GPa, the convex hull is formed by five vertices, one of which corresponds to the ternary compound Mg_6GeSi_3 of space group 146 and two of which correspond to the binary silicides Mg_2Si and Mg_3Si_2 of space groups 129 and 167, respectively.

Table

Structures, corresponding to the vertices of the convex shell at pressures of 1, 4 and 6 GPa

Pressure/ Composition	Lattice parameters	Symmetry
1 GPA/ Mg_6Si_3Ge	$a = b = c = 7.46$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	$R3$ (146)
1 GPA/ Mg_3Si_2	$a = b = 7.44$ Å, $c = 12.22$ Å, $\alpha = \beta = \gamma = 90°$	R-$3C$ (167)
1 GPA/ Mg_2Si	$a = b = 4.14$ Å, $c = 6.90$ Å, $\alpha = \beta = \gamma = 90°$	$P4/nmm$ (129)
4 GPA/ $Mg_6Si_4Ge_3$	$a = 8.4$ Å, $b = 5.31$ Å, $c = 5.25$ Å, $\alpha = 93.9°$, $\beta = 90.2°$, $\gamma = 95.3°$	$P1$(1)
4 GPA/ $Mg_6Si_3Ge_4$	$a = 8.46$ Å, $b = 5.34$ Å, $c = 5.26$ Å, $\alpha = 93.8°$, $\beta = 90.4°$, $\gamma = 95.6°$	$P1(1)$
4 GPA/ Mg_2Si	$a = b = c = 6.23$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	$Fm\overline{3}m$ (225)
6 GPA/ Mg_2SiGe	$a = 4.17$ Å, $b = 3.66$ Å, $c = 5.00$ Å, $\alpha = 90°$, $\beta = 70.6°$, $\gamma = 90°$	Pm (6)
6 GPA/ $Mg_4Si_2Ge_3$	$a = 5.06$ Å, $b = 8.46$ Å, $c = 8.04$ Å, $\alpha = 78.0°$, $\beta = 90.5°$, $\gamma = 73.3°$	$P1$(1)
6 GPA/ Mg_6Si_3Ge	$a = 4.95$ Å, $b = 5.68$ Å, $c = 6.59$ Å, $\alpha = 76.3°$, $\beta = 103.9°$, $\gamma = 98.1°$	$P1$(1)
6 GPA/ Mg_2Si	$a = b = 4.52$ Å, $c = 5.82$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	$P6_3/mmc$ (194)
6 GPA/ MgSi	$a = 5.38$ Å, $b = 5.25$ Å, $c = 5.19$ Å, $\alpha = 89.4°$, $\beta = 79.7°$, $\gamma = 111.4°$	P-1(2)
6 GPA/ $MgSi_3$	$a = b = 7.62$ Å, $c = 15.05$ Å, $\alpha = \beta = 90°$, $\gamma = 120°$	R-3m (166)

The remaining two structures, corresponding to the bulk structures of germanium and silicon, are not shown in Table and described below. At a pressure $P = 4$ GPa, the convex hull includes bulk Ge and Si structures, two asymmetric ternary compounds $Mg_6Ge_4Si_3$ and $Mg_6Ge_3Si_4$, and a binary silicide Mg_2Si of correctly defined space symmetry group 225. At a pressure $P = 6$ GPa, the convex hull is formed by three ternary alloys $Mg_4Si_2Ge_3$, Mg_6Si_3Ge, Mg_2SiGe and three binary silicides of different stoichiometries from 2/3 of Mg and 1/3 of Si (Mg_2Si) to 1/4 of Mg and 3/4 of Si ($MgSi_3$), in addition to the bulk Ge and Si structures. The ternary alloys at this pressure have symmetries down to 1 (P1) for $Mg_4Si_2Ge_3$ and Mg_6Si_3Ge and 6 (Pm) for Mg_2GeSi. The binary silicides have symmetries as low as 2 for MgSi and as high as 166 for $MgSi_3$ and 194 for Mg_2Si.

For a detailed study of the stability of energetically favorable structures under various pressures, Table results were recalculated for pressures from 0 to 10 GPa with geometry re-optimization. Fig. shows the most stable structures with negative formation enthalpy obtained by optimizing evolutionary search results. It also includes calculations for ternary compounds formed by Sn→Ge substitution or rearrangement in Mg-Si-Sn structures [23], as well as optimized convex hull structures from Si↔Ge atom exchange. Surprisingly, these structures are more stable than those obtained from evolutionary search. For example, Mg_6SiGe_3, derived from Mg_6Si_3Ge by Si↔Ge atoms exchange and relaxation, is the most stable structure in the 1.15–10 GPa range. At ambient pressure, only the cubic anti-fluorite Mg_2Si structure (Fm$\overline{3}$m symmetry) is more stable than them. Linear extrapolation from Fig. suggests Mg_6Si_3Ge will become less stable at around 11.5 GPa, with Mg_4SiGe being the most stable above 15 GPa. $Mg_{12}SiGe3$ structure (I4/mmm symmetry) was created from $Mg_{12}SiSn_3$ by replacing Sn atoms with Ge ones. Another structure, Mg_4SiGe (P-1 symmetry), was derived similarly from Mg_4SiSn, At pressures $P > 44$ GPa, Mg_4SiGe becomes more stable than both Mg_6SiGe_3 structures. Mg_6Si_3Ge structures from evolutionary search, shown on Fig., are lower in enthalpy than Mg_2Si one at pressures $P > 8$ GPa, but higher than $Mg_6Si_3Ge_4$ and Mg_2SiGe ones at $P = 4$ GPa and $P = 6$ GPa, respectively. The latter structures may become more stable at higher pressures based on linear extrapolation of $E(P)$ dependencies. Therefore, their electronic structures should also be examined.

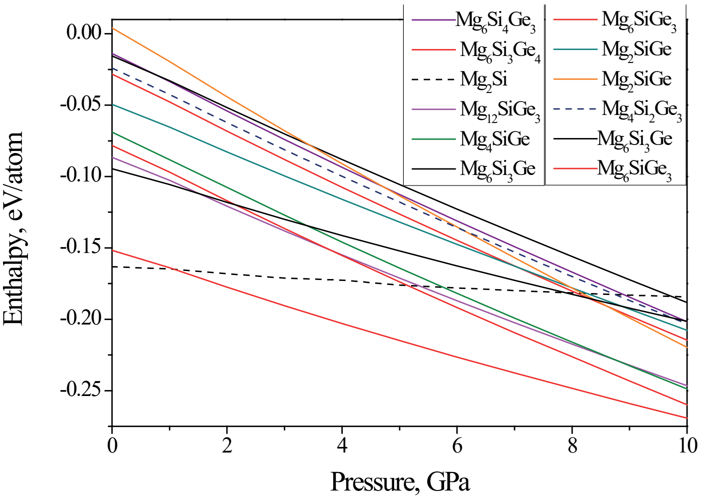

Fig. Enthalpy-pressure $E(P)$ dependence for the most energetically favorable crystal structures obtained by optimizing the results of the evolutionary search and their corresponding derivatives from the Mg-Si-Sn structures (see text for details)

In order to investigate the conductive properties of three-component systems at ambient pressure conditions, the band structures and total density of states of the most energetically favorable compounds $Mg_xSi_yGe_z$ have been calculated. All of the alloys considered have states at the Fermi level, indicating that they all exhibit metallic properties to some extent, unlike the binary compounds Mg_2Si and Mg_2Ge, which are semiconductors under normal conditions.

To verify the dynamical stability of three-component alloys, phonon dispersion curves at ambient pressure conditions have been calculated for most of the lowest energy structures – see additive materials in [24]). This analysis was conducted by deriving force constants from atomic forces and displacements, as implemented in the PHONOPY code [25, 26]. The results indicate that the phonon dispersion curves do not exhibit any imaginary frequencies for $Mg_{12}Ge_3Si$, $Mg_6Ge_4Si_3$, $Mg_6Ge_3Si_4$, triclinic Mg_6SiGe_3, $Mg_4Ge_3Si_2$, thereby confirming the stability of the respective compounds. In contrast, the spectra of hexagonal Mg_6SiGe_3, orthorhombic Mg_2SiGe and monoclinic Mg_4SiGe structures displays a pronounced negative dip near special *k*-points (see additive materials in [24]), providing evidence for their instability relative to the other ones. Nevertheless, structures energetically favorable at high pressures non-symmetric Mg_6SiGe_3 and cubic $Mg_{12}SiGe_3$ are still stable, which makes it possible for them to exist along with the known Mg_2Si and Mg_2Ge structures.

Conclusion

The results of the evolutionary search of three-component systems allowed to obtain new possible structures of the stoichiometries Mg_6SiGe_3, Mg_6GeSi_3, $Mg_{12}Ge_3Si$, Mg_4SiGe, $Mg_4Ge_3Si_2$, Mg_2SiGe, $Mg_6Si_4Ge_3$ and $Mg_6Si_3Ge_4$ with the ternary compound $Mg_{12}Ge_3Si$ being the most stable one. All of them have a negative enthalpy of formation, comparable to the enthalpy of formation of binary structures Mg_2Si and Mg_2Ge in the studied pressure range $0 < P \leq 10$ GPa. Phonon dispersion and density of states calculations confirmed the dynamical stability and metallic properties of the newly identified ternary alloys besides the Mg_2SiGe, Mg_4SiGe and Mg_6SiGe_3 ones. Density of states calculations indicate the ternary alloys exhibit metallic properties, unlike the binary silicides and germanides.

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REFERENCES

1. **Akasaka M., Iida T., Nishino K., Takanashi Y.,** Composition dependent thermoelectric properties of sintered $Mg_2Si_{1-x}Ge_x$ (x = 0 to 1) initiated from a melt-grown polycrystalline source, Thin Solid Films. 515(22) (2007) 8237–8241.
2. **Hayakawa Y., et al.,** Growth of homogeneous polycrystalline $Si_{1-x}Ge_x$ and $Mg_2Si_{1-x}Ge_x$ for thermoelectric application, Thin Solid Films. 519(24) (2011) 8532–8537.
3. **Viennois R., Colinet C., Jund P., Tedenac J.C.,** Phase stability of ternary antifluorite type compounds in the quasi-binary systems Mg_2X–Mg_2Y (X, Y= Si, Ge, Sn) via ab-initio calculations, Intermetallics. 31 (2012) 145–151.
4. **You S.W., Kim I.H.,** Thermoelectric properties of $Mg_2Si_{1-x}Ge_x$ prepared by using a solid-state reaction, Journal of the Korean Physical Society. 64 (5) (2014) 690–694.
5. **Bhattacharya S., Madsen G.K.H.,** High-throughput exploration of alloying as design strategy for thermoelectrics, Physical Review. B. 92 (8) (2015) 085205.
6. **Zhang L.M., Leng Y.G., Jiang H.Y., Chen L.D., Hirai T.,** Synthesis of $Mg_2Si_{1-x}Ge_x$ thermoelectric compound by solid phase reaction, Materials Science and Engineering B. 86 (3) (2001) 195–199.
7. **Aizawa T., Song R., Yamamoto A.,** Solid-state synthesis of thermoelectric materials in Mg-Si-Ge system, Materials transactions. 46 (7) (2005) 1490–1496.
8. **Mizuyoshi Y., Yamada R., Ohishi T., Saito Y., Koyama T., Hayakawa Y., Matsuyama T., Tatsuoka H.,** Growth of $Mg_2Si_{1-x}Ge_x$ layers on silicon–germanium substrates, Thin Solid Films. 508(1-2) (2006) 70–73.
9. The International Energy Agency (IEA), URL: https://www.iea.org.
10. **Beretta D., Neophytou N., Hodges J.M., Kanatzidis M.G., Narducci D., Martin-Gonzalez M., Beekman M., Balke B., Cerretti G., Tremel W., Zevalkink A.,** Thermoelectrics: From history, a window to the future, Materials Science and Engineering: R: Reports. 138 (2019) 100501.
11. **Clark C.R., Wright C., Suryanarayana C., Baburaj E.G. and Froes F.H.,** Synthesis of Mg_2X (X = Si, Ge, or Sn) intermetallics by mechanical alloying, Materials Letters. 33 (1997) 71–75.
12. **Busch G., Winkler U.,** Elektrische Leitfahigkeit Und Hall-Effekt Intermetallischer Verbindungen, Helvetica Physica Acta. 26 (3-4) (1953) 395–398.

13. **Laboz R.J., Mason D.R., Okane D.F.,** The thermoelectric properties of mixed crystals of $Mg_2Ge_xSi_{1-x}$, Journal of the Electrochemical Society. 110 (1963) 127–134.

14. **Oganov A.R., Pickard C.J., Zhu Q., Needs R.J.,** Structure prediction drives materials discovery, Nature Reviews Materials. 4 (5) (2019) 331–348.

15. **Lyakhov A.O., Oganov A.R., Stokes H.T., Zhu Q.,** New developments in evolutionary structure prediction algorithm USPEX, Computer Physics Communications. 184 (4) (2013) 1172–1182.

16. **Oganov A.R., Lyakhov A.O., Valle M.,** How Evolutionary Crystal Structure Prediction Works – and Why, Accounts of chemical research. 44 (3) (2011) 227–237.

17. **Oganov A.R., Glass C.W.,** Crystal structure prediction using ab initio evolutionary techniques: Principles and applications, The Journal of chemical physics. 124 (24) (2006) 244704.

18. **Kresse G., Furthmuller J.E.,** Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, Physical Review B. 54 (16) (1996) 11169–11186.

19. **Perdew J.P., Burke K., Ernzerhof M.,** Generalized Gradient Approximation Made Simple, Physical Review Letters. 77 (18) (1996) 3865–3868.

20. **Lunyakov Yu.V.,** Mg_2Si silicide under pressure: first-principles evolution search results, Physics of the Solid State. 62 (5) (2020) 880–884.

21. **Lunyakov Yu.V.,** Mg_2Sn stannide under pressure: first-principles evolutionary search results. Physics of the Solid State. 63 (4) (2021) 590–594.

22. **Lunyakov Yu.V.,** Mg_2Ge germanide under pressure: first principle evolutionary search results, Physics of the Solid State. 64 (10) (2022) 1414–1419.

23. **Lunyakov Yu.V.,** Magnesium based tin-silicon alloys under pressure: first-principles evolution search results, Nanosystems: physics, chemistry, mathematics. 15 (2024) 621–631.

24. **Lunyakov Yu.V.,** Phonon dispersion curves of Mg-Si-Ge compounds, see files in https://doi.org/10.17605/OSF.IO/KE2J8.

25. **Togo A., Chaput L., Tadano T., Tanaka I.,** Implementation strategies in phonopy and phono3py, Journal of Physics: Condensed Matter. 35 (35) (2023) 353001.

26. **Togo A.,** First-principles phonon calculations with Phonopy and Phono3py. Journal of the Physical Society of Japan. 92 (1) (2023) 012001.

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