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Revealing New Compositions in the MgH_2-TiH_2-H Phase Diagram Under Pressure

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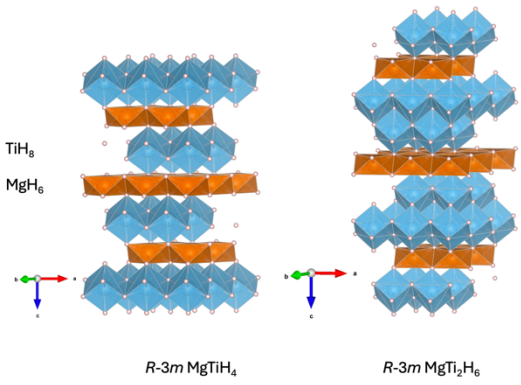
In order to achieve a sustainable hydrogen economy, one needs to develop materials capable of storing hydrogen. While studies of binary hydrides have blossomed in recent years, only a few studies of ternary hydrides were carried out under high pressure, both from a theoretical and experimental point of view. The discovery of new ternary hydrides may be guided by numerical simulations through crystal structure prediction (CSP). Over the past decade, evolutionary (genetic) algorithms and other have demonstrated considerable success in identifying (meta)stable structures for a given chemical composition, at any pressure.
In this study,[1] we chose to investigate ternary hydride phase diagrams that contain electropositive metals, an s-block element associated with a group 2-3 transition metal, such as Mg-Ti, Ca-Sc, and Li-V couples in which strong metal-hydrogen bonding can stabilize the hydride phases.[2,3] The potential of using thermodynamic variable pressure to obtain new viable compounds in the range of 0-50 GPa was investigated. The objective is to identify high-pressure H-rich compounds that can be recovered at ambient conditions, therefore we focus on the MgH_2-TiH_2-H_2 phase diagram. In this work, we employed an evolutionary (genetic) algorithm[4] implemented in the USPEX code with first-principles calculations (DFT PBE and r^{2}SCAN levels of theory, VASP code) that enables to scan the configurational, structural, and composition spaces of Mg-Ti-H compounds at 50 GPa, with the objective of identifying local minima on the potential energy surface (PES).



Our research identified seven thermodynamically stable $Mg_xTi_yH_z$, as well as all the experimentally known unary and binary phases of this ternary phase diagram at 50 GPa. Subsequently, the quenchability to atmospheric pressure of each high-pressure ternary phase was studied. Five metastable compounds $Mg_xTi_yH_z$ were found to be dynamically stable at 1 atm. The viability of each phase is currently under investigation, with a range of criteria being examined, including thermodynamic, mechanical, and thermal (AIMD at 300-600 K) properties.

Figure 1. Crystal structures of *R*-3*m* $MgTiH_4$ and $MgTi_2H_6$ at 1 atm

References

[1] HYDROPTERE, ANR PRC Project, 2023–2027; Laversenne, L. (exp.); Frapper, G. (theo.).
[2] Zurek, E. Hydrides of the Alkali Metals and Alkaline Earth Metals under Pressure. *Comments Inorg. Chem.* **2017**, *37* (2), 78–98.
[3] Otomo, T. et al. Structural Studies of Hydrogen Storage Materials with Neutron Diffraction: A Review. *J. Phys. Soc. Jpn.* **2020**, *89* (5), 051001.
[4] Oganov, A. R. et al. Crystal Structure Prediction Using *Ab Initio* Evolutionary Techniques: Principles and Applications. *J. Chem. Phys.* **2006**, *124*, 244704.