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Structural, electronic, and hydriding properties of Li₂MgSi

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1. Introduction

Materials containing light elements such as Li and Mg are of great interest as potential hydrogen storage media, particularly in mobile applications for which high gravimetric hydrogen density is extremely desirable. Recently studied systems, among a large variety of examples, include Li₄BN₃H₁₀ [1,2], Mg(BH₄)₂ [3–5], and the LiNH₂ + LiH [6] and LiBH₄ + MgH₂ [7] reactions. Ternary Li₂MgX compounds are known to form for many elements X, and in our opinion their hydriding properties also merit exploration in view of their high Li and Mg contents. Here we investigate Li₂MgSi. Interestingly, formation of Li₂MgSi has been observed in work on Mg₂Si as a potential negative electrode material for Li-ion batteries [8,9]. We determine a new crystal structure for Li₂MgSi, demonstrate that its hydriding behavior is governed by the reversible reaction:

$$Li_2MgSi + H_2 \leftrightarrow \tfrac{1}{2}Mg_2Si + 2LiH + \tfrac{1}{2}Si$$

and derive relevant electronic energies via density functional theory (DFT).

2. Experimental and computational methods

 $\rm Li_2MgSi$ was prepared by mechanically alloying the elemental constituents in a SPEX 8000 mill for 5 h. Hydrogen sorption measurements were conducted in a Cahn TG-2151 high-pressure thermogravimetric analyzer (hTGA) pressurized to 82 bar of hydrogen and heated to 450 °C. A SRS CIS 100 mass spectrometer was used to analyze exhaust gases during desorption.

ABSTRACT

An investigation of Li₂MgSi, with particular emphasis on its potential as a hydrogen storage material, is reported. A cubic $P\overline{4}3m$ crystal structure, differing from previous determinations, is established. We find that the material reversibly sorbs ~2.8 mass% hydrogen at $T \sim 300$ °C according to the reaction Li₂MgSi + H₂ $\leftrightarrow \frac{1}{2}$ Mg₂Si + 2LiH + $\frac{1}{2}$ Si. Electronic structure calculations indicate that Li₂MgSi is a semiconductor with a small, indirect gap of ~0.2 eV.

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Total electronic energies were calculated with the Vienna *ab initio* Simulation Package (VASP), which implements density functional theory [10] with a plane wave basis set [11,12]. Potentials obtained via the projector-augmented wave approach [13,14] were employed for the elements in conjunction with the generalized gradient approximation of Perdew and Wang [15,16] for the exchange-correlation energy functional. The Si, Li, Mg, and H potentials contained 4, 3, 8, and 1 valence electrons and were constructed with augmentation wave energy cutoffs of 245 eV, 272 eV, 266 eV, and 700 eV, respectively. In all calculations a plane wave cutoff energy of at least 900 eV was imposed, and the k-point spacings of the reciprocal space meshes were no larger than 0.1 Å^{-1} . At least two full-cell optimizations of the lattice constants and nuclear coordinates were performed for each material of interest; the total energies were converged to 10^{-6} eV/cell and the forces relaxed to 10^{-4} eV Å⁻¹.

3. Li₂MgSi crystal structure and electronic properties

For the structural determination we used a mechanically alloyed sample that was subsequently heated to 600 °C to promote grain growth and sharpen the diffraction signature. Preliminary X-ray diffraction (Cu K α) work revealed three minor contaminants: MgO. Li₂Si, and Li₈MgSi₆. Indexing of the lines belonging to Li₂MgSi suggested the Pm3m (No. 221), P43m (No. 215), Pm3 (No. 200), and P23 (No. 195) cubic space groups as candidates. We conducted fourcomponent Rietveld analyses employing the known structures of the impurity phases and various site assignments for Li₂MgSi in the candidate groups. Our diffraction data are best described by the $P\bar{4}3m$ structure specified in Table 1, which also lists the parameters obtained from optimization of the structure with VASP. The agreement between the experimental and calculated values is quite favorable; the largest disparity occurs for the x-coordinate of the Li 4e sites and the associated Li nearest-neighbor distances, a not unexpected result since Li is by far the weakest scatterer of X-rays in the sample and hence its position information most uncertain.

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Table 1

Experimental and VASP-optimized parameters for the $P\bar{4}3m$ (No. 215) Li₂MgSi crystal structure, and minimum interatomic distances, determined in this study. The lattice constant is a, and the site positions are Li 1b ($\frac{1}{2}\frac{1}{2}\frac{1}{2}$), 3c ($0\frac{1}{2}\frac{1}{2}$), 4e (xxx); Mg 1a (000), 3d ($\frac{1}{2}$ 00); and Si 4e (xxx). The calculated density is 1.707 g/cm³.

Structure parameter	Experiment	Calculation
a (Å)	6.387	6.365
Li 4e x	0.680	0.727
Si 4e x	0.252	0.253
Minimum interatomic distances		
d(Li–Li) (Å)	1.986	2.503
d(Li–Mg) (Å)	3.114	2.851
d(Li–Si) (Å)	2.743	2.721
d(Mg-Mg)(Å)	3.194	3.183
d(Mg-Si) (Å)	2.774	2.768
d(Si–Si) (Å)	4.479	4.444



Fig. 1. Observed Cu K α X-ray diffraction profile (blue) and Rietveld refinement including the primary component Li₂MgSi (red) as well as MgO, Li₂Si, and Li₈MgSi₆ impurity phases (green).

Fig. 1 displays the observed and refined diffraction patterns; the weighted pattern error for the refinement is R_{wp} = 9.9%. A diagram of the structure is shown in Fig. 2.

To our knowledge three other distinct Li_2MgSi structural models, all cubic, are available in the published literature. Pavlyuk et al. [17] reported a $F\bar{4}3m$ structure observed in an experimental study of the Li–(Si,Mg)–Al phase diagram, and Wengert et al. [18]



Fig. 2. Diagram of the $P\bar{4}3m$ Li₂MgSi crystal structure determined in this work (Table 1).



Fig. 3. Electronic band structure of Li₂MgSi in the $P\bar{4}3m$ structure of this work (Table 1). The energy zero is the Fermi level $\varepsilon_{\rm F}$.

obtained $P\bar{4}3m$ and $Fm\bar{3}m$ structures from molecular dynamics simulations. The models are summarized in Table 2. None of them leads to a diffraction profile that reproduces our data as well as the structure of Table 1. The $F\bar{4}3m$ [17] and $P\bar{4}3m$ [18] models do not generate the $2\theta = 13.8^{\circ}$ (d = 6.39 Å) and $2\theta = 31.3^{\circ}$ (d = 2.86 Å) lines we observe (Fig. 1), while the $Fm\bar{3}m$ structure [18], with Z = 32Li₂MgSi formula units per unit cell as opposed to Z = 4 for all the other structures in Table 2, produces many lines that do not appear in our data. To further elucidate this issue we optimized all the structures in Table 2 with VASP, and the relaxed total electronic energies $E_{\rm el}$ are listed in the final column of Table 2. The Li₂MgSi model reported in Table 1 features the lowest energy, providing further support that it is the most accurate structure.

The E_{el} for the $F\bar{4}3m$ [17] and $P\bar{4}3m$ [18] models in Table 2 are equal since the structures are identical. Although the 4e (*xxx*) position is variable in the $P\bar{4}3m$ space group, the Li 4e *x* = 1/4 and Mg 4e *x* = 3/4 site parameters specified in [18] make that structure precisely equivalent to the $F\bar{4}3m$ [17] model having all positions fixed by the space group; on relaxation with VASP the Li 4e and Mg 4e *x* site parameters for the $P\bar{4}3m$ model [18] remain essentially unchanged, so that the equivalency to $F\bar{4}3m$ persists. We note that the calculations show that the $Fm\bar{3}m$ entry in Table 2 is metallic, while all others are semiconducting.

Fig. 3 displays the calculated band structure, and Fig. 4 the corresponding density of states, for the $P\bar{4}3m$ Li₂MgSi structure reported here. The compound is a semiconductor with a computed gap of 0.21 eV. Fig. 3 shows that the gap is indirect: the valence band maximum occurs between the Γ and M high symmetry points in the Brillouin zone, while the conduction band minimum is located



Fig. 4. Electronic density of states for Li₂MgSi in the $P\bar{4}3m$ structure of Table 1. The zero energy is the Fermi level $\varepsilon_{\rm F}$.

Table 2

 Li_2MgSi structures and corresponding electronic total energies E_{el} obtained by relaxation of each structure with VASP.

Li ₂ MgSi structure						$E_{\rm el}~({\rm eV}/{\rm Li}_2{\rm MgSi})$
Reference	Space group	a (Å)	Lattice sites	Lattice sites		
			Li	Mg	Si	
[17] [18] [18] This work	F43m (No. 216) P43m (No. 215) Fm3m (No. 225) P43m (No. 215)	6.37 6.4 12.8 6.387	4b, 4c 1b, 3d, 4e 8c, 24e, 32f 1b, 3c, 4e	4d 4e 32f 1a. 3d	4a 1a, 3c 4a, 4b, 24d 4e	-11.72 -11.72 -11.67 -11.76

between the X and Γ points. Orbital decomposition reveals that the Si s-type states are mostly confined to the lower set of valence bands ($-8.8 \text{ eV} < E - \varepsilon_F < -7.0 \text{ eV}$) and the Si p-like states occur almost exclusively in the upper valence bands ($-4.4 \text{ eV} < E - \varepsilon_F < 0$). Since the Si–Si nearest-neighbor distance given in Table 1 is large, 4.48 Å (the corresponding distance in elemental Si is 2.35 Å), there is very little mixing of Si 3s and 3p states; the lower (upper) valence band structures arise from hybridization of Si 3s (3p) states with Mg and Li levels. A substantial gap of 2.6 eV separates them. Charge transfer from Li and Mg to Si evidently leads to weakly ionic bond character and the concomitant opening of the small gap at ε_F .

Computation of the total electronic energies E_{el} for Li, Mg, and Si as well as for Li₂MgSi (Table 1 structure) enables derivation of:

$$\begin{array}{ll} \Delta H_{el}(\text{Li}_2\text{MgSi}) &\equiv E_{el}(\text{Li}_2\text{MgSi}) - 2E_{el}(\text{Li}) - E_{el}(\text{Mg}) - E_{el}(\text{Si}) \\ &= -101 \text{ kJ/mole } \text{Li}_2\text{MgSi}. \end{array}$$

 $\Delta H_{\rm el}$ is the calculated standard enthalpy of formation at zero temperature in the absence of zero point energy contributions. We are unaware of any experimental determinations of the formation enthalpy.



Fig. 5. (a) Hydriding and (b) dehydriding (into 1.3 bar He) of $\rm Li_2MgSi$ measured by thermogravimetry.

4. Hydriding behavior

Fig. 5 displays the first hydriding/dehydriding cycle for mechanically alloyed Li₂MgSi. On exposure to H₂ at a pressure ramped to P=82 bar hydrogen uptake commences near T=100 °C and completes near T=300 °C after absorption of 2.74 mass% H₂ [Fig. 5 (a)]. Desorption measurements were performed in helium at a pressure of 1.3 bar; Fig. 5(b) shows that dehydriding begins near T=300 °C with the total release of ~2.78 mass% by T=450 °C. Residual gas analysis confirmed that the desorbed gas is H₂. Two additional cycles exhibited essentially the same behavior, demonstrating that the reaction is reversible.

X-ray diffraction profiles of as-prepared, hydrided, and dehydrided samples of Li₂MgSi are displayed in Fig. 6. Aside from minor impurity lines, it is clear that the dehydrided sample [Fig. 6(c)] exhibits all the Li₂MgSi peaks of the as-prepared material [Fig. 6(a)]. The principal peaks in the pattern of the hydrided sample [Fig. 6(b)], on the other hand, are those of Mg₂Si (solid dots). Although the Li₂MgSi and Mg₂Si profiles are similar, the 2θ = 27.9° peak of Mg₂Si



Fig. 6. Cu K α X-ray diffraction profiles of (a) as-prepared, (b) hydrided, and (c) dehydrided Li₂MgSi. Major peak positions expected for LiH (cubic, *a* = 4.085 Å) are indicated by inverted triangles in (b).

in Fig. 6(b) is not present in either the as-prepared [Fig. 6(a)] or the dehydrided pattern [Fig. 6(c)] and, conversely, the $2\theta = 13.8^{\circ}$ and $2\theta = 31.3^{\circ}$ lines of Li₂MgSi in Fig. 6(a) and (c) do not appear in Fig. 6(b).

Given the observations that (i) \sim 2.8 mass% hydrogen cycles in our experiments, (ii) Mg₂Si is present in the hydrided state, and (iii) compositional analysis of the hydrided material confirms the 2:1:1 Li:Mg:Si ratio, we infer that the reversible reaction of Li₂MgSi and H₂ is

$$Li_2MgSi + H_2 \leftrightarrow \frac{1}{2}Mg_2Si + 2LiH + \frac{1}{2}Si,$$
 (2)

for which the hydrogen content is 2.95 mass%. Since Fig. 6(b) for the hydrided sample shows no unambiguous signature of either LiH or Si, either of which could be nanocrystalline or amorphous, this inference is admittedly indirect, but nevertheless sound. Additional support is provided by the fact that a compound having a stoichiometry near Li₄SiH₄ would be needed to replace LiH and Si on the right side of Eq. (2), but no Li–Si hydrides of any kind are known.

We estimate the reaction enthalpy via calculation of the total electronic energy for each component of Eq. (2):

$$\Delta H_{\rm R} \sim \frac{1}{2} \Delta H_{\rm el}({\rm Mg}_{2}{\rm Si}) + 2\Delta H_{\rm el}({\rm LiH}) - \Delta H_{\rm el}({\rm Li}_{2}{\rm Mg}{\rm Si})$$

= $\frac{1}{2}E_{\rm el}({\rm Mg}_{2}{\rm Si}) + 2E_{\rm el}({\rm LiH}) + \frac{1}{2}E_{\rm el}({\rm Si}) - E_{\rm el}({\rm Li}_{2}{\rm Mg}{\rm Si}) - E_{\rm el}({\rm H}_{2})$ (3)
= -93 kJ/mole H₂.

Approximating the accompanying entropy change by that of H₂ gas alone, $-\Delta S_{\rm R}$ = 130 J/mole H₂-K (300 K), the van't Hoff relation:

$$\ln P(\text{bar}) = \frac{\Delta H_{\text{R}}}{\text{RT}} - \frac{\Delta S_{\text{R}}}{R}$$
(4)

yields $T_{eq} \sim 700 \,^{\circ}\text{C}$ for the equilibrium temperature at 82 bar H₂ pressure. This value is consistent with our observation of hydriding at $T \sim 300 \,^{\circ}\text{C}$ and a hydrogen pressure of 82 bar.

Although we have not calculated phonon spectra for all the materials in Eqs. (1) and (3) to obtain zero point energy (ZPE) and finite temperature vibrational corrections, we estimate that $\Delta H_{el}(\text{Li}_2\text{MgSi})$ and ΔH_{R} approximate the corresponding room temperature enthalpies ΔH_{298} to about the 10% level. The values $E_{ZPE}(\text{Li}) \sim 4 \text{ kJ/mole Li}$, $E_{ZPE}(\text{LiH}) \sim 22 \text{ kJ/mole Li}$, and $E_{ZPE}(\text{H}_2) \sim 26 \text{ kJ/mole H}_2$, are available in the literature [19,20]. The ZPE corrections ΔH_{ZPE} to Eqs. (1) and (3) (given by the same expressions with E_{ZPE} replacing E_{el}) will involve significant cancel-

lation of the individual terms. For Eq. (3) in particular, $E_{ZPE}(LiH)$ and $E_{ZPE}(H_2)$, undoubtedly the two largest ZPEs of all, are nearly equal but occur with opposite signs. Furthermore, the finite temperature phonon corrections $\delta \Delta H_{298}$ to ΔH_{298} will also work against the total ZPE contribution ΔH_{ZPE} and bring ΔH_{el} into closer agreement with $\Delta H_{298} = \Delta H_{el} + \Delta H_{ZPE} + \delta \Delta H_{298}$. In Ref. [20] (Table 3) it was found that ΔH_{el} (electronic energies only) departs from ΔH_{298} (ZPE and finite temperature phonon terms included) by 13%, 1%, and 5% (in the GGA) for the very light compounds LiNH₂, LiH, and Li₂NH, respectively.

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