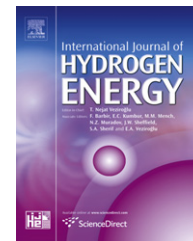


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High hydrogen content super-lightweight intermetallics from the Li–Mg–Si system

Volodymyr Pavlyuk^{a,b}, Grygoriy Dmytriv^a, Ihor Chumak^c, Oliver Gutfleisch^{d,e}, Inge Lindemann^d, Helmut Ehrenberg^{c,d,e,*}

^a Ivan Franko Lviv National University, Department of Inorganic Chemistry, Kyryla i Mefodia 6, 79005 Lviv, Ukraine

^b Częstochowa Jan Długosz University, Institute of Chemistry, Environmental Protection and Biotechnology, al. Armii Krajowej 13/15, 42200 Częstochowa, Poland

^c Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany

^d IFW Dresden, PO Box 270116, 01171 Dresden, Germany

^e Technische Universität Darmstadt, Institut für Materialwissenschaft, Petersenstr. 23, 64287 Darmstadt, Germany

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ABSTRACT

The existence of Li-rich super-lightweight intermetallics in the Li–Mg–Si ternary system has attracted attention for high capacity hydrogen storage materials. The hydrogenation properties of the alloys were studied by thermogravimetric analysis, differential scanning calorimetry in H₂ atmosphere and X-ray diffraction. The Li-rich alloy absorbs the highest amount of hydrogen (8.8% w/w for Li₇₀Mg₁₀Si₂₀), while the Mg-rich alloy (Li₃₀Mg₄₀Si₃₀) absorbs 6.0% w/w H₂ and shows the first experimental evidence for LiMgH₃ formation with LiNbO₃-type structure during hydrogenation.

The extension of homogeneity range of existing phases from Li–Mg–Si system was found and the crystal structures of four ternary phases, Li_{2+x}Mg_{1-x}Si ($x = 0.268$), Li_{65-x+y}Mg_{30+x-y}Si₃₃ ($x = 9.15$, $y = 1.23$), Li_{7-x+y}Mg_{5+x-y}Si₄ ($x = 1.14$, $y = 0.61$) and Li_{x+y}Mg_{2-x}Si ($x = 0.51$, $y = 0.39$), were solved and more precisely refined using X-ray single crystal diffraction data. Electronic structure calculations reveal an increased occupation of electronic states at the Fermi level for Li_{12+x}Mg_{3-x}Si₄ in comparison to Li_{2+x}Mg_{1-x}Si. The results of crystal orbital Hamilton population (COHP) and integrated crystal orbital Hamilton population (iCOHP) calculations for both structures indicate the strongest interactions between Mg–Si (–iCOHP = 1.999 eV) and the weakest between Li–Li (–iCOHP = 0.049 eV).

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1. Introduction

The main requirements for modern hydrogen storage materials in automotive applications are a high gravimetric density (above 6.5% w/w gravimetric capacity of hydrogen),

absorption/desorption of hydrogen at moderate temperatures and pressures, low-cost and environmental safety [1]. Conventional metal hydrides, such as LaNi₅ and its substitutional derivatives, titanium and zirconium alloys which are commonly used for hydrogen storage systems have storage

* Corresponding author. Karlsruhe Institute of Technology (KIT), Institute for Applied Materials (IAM), Hermann-von-Helmholtz-Platz 1, D-76344 Eggenstein-Leopoldshafen, Germany.

E-mail address: helmut.ehrenberg@kit.edu (H. Ehrenberg).

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capacities less than 2% w/w H₂ and cannot satisfy this need. New materials developed on the basis of light metals such as Li and Mg are promising candidates as potential light-weight hydrogen storage material. The binary system of lithium-magnesium does not form intermetallic phases, but ternary phases Li–Mg–Si and the isothermal section of the Li–Mg–Si phase diagram at 200 °C are known [2,3]. Later, the experimentally supported calculated phase equilibria in the entire composition and temperature range of the Li–Mg–Si system are presented, including the liquidus surface and invariant reactions [4]. Accordingly, five intermetallic compounds are known: Li₂MgSi, LiMg₂Si, Li₁₂Mg₃Si₄, Li₈MgSi₆ and Li₅MgSi₄. The crystal structure data of cubic Li₁₂Mg₃Si₄ and monoclinic Li₈MgSi₆ ternary phases are reported [5–7]. Later, the two compounds Li₈MgSi₆ (53.3 at.% Li, 6.7 at.% Mg, 40.0 at.% Si) and Li₅MgSi₄ (50.0 at.% Li, 10.0 at.% Mg, 40.0 at.% Si) were identified as the same phase with an extended homogeneity range [8]. Two possible structural models with $a \approx 6.4 \text{ \AA}$ (I) and $a \approx 12.8 \text{ \AA}$ (II), based on the space groups *F*-43*m*, *P*-43*m* and *Fm*-3*m* were proposed [2,9–11] for Li₂MgSi. These phases are described by the general formula Li_{2*x*}Mg_{2–*x*}Si, and model I is realized at $0 < x < 0.547$ in *Fm*-3*m*, at $0.55 < x < 0.65$ in *P*-43*m*, and the model II exists at $0.65 < x < 0.8$ [3]. The initial structure data for the Li_{2+*x*}Mg_{1–*x*}Si_{1–*x*/4} hexagonal phase with Na₃As-type structure ($a = 4.48 \text{ \AA}$, $c = 8.00 \text{ \AA}$) were described by Nesper and Curda [12]. Unfortunately, atomic parameters are not given.

The properties of Li₂MgSi as a hydrogen storage material were investigated and a reversible hydrogen uptake and release of about ~2.8% w/w at $T \sim 300 \text{ °C}$ was measured [10].

This work reports on syntheses, phase diagram, crystal structures, electron density distributions and hydrogenation properties of some alloys from the ternary Li–Mg–Si system.

2. Material and methods

2.1. Synthesis and phase analysis

The investigated samples were prepared from the following reactants: lithium rod (99.9%, Alfa Aesar, Karlsruhe, Germany), magnesium and silicon (99.999 at.%). Appropriate amounts were mixed according to the aimed stoichiometry of the product and filled into tantalum crucibles in the glove box under argon atmosphere. These crucibles have been sealed by arc-welding in dry argon atmosphere. The reaction between the metals was carried out in an induction furnace at 1100 °C. After 15 min, the samples were rapidly cooled down to room temperature by removing the crucibles from the furnace into ambient conditions. The reaction product was powdered in an agate mortar, filled into a capillary of 0.3 mm diameter and sealed for X-ray powder diffraction (XRD) on a STOE STADI P diffractometer (Co-K α_1 radiation) in Debye-Scherrer mode with a linear position sensitive detector with 6° aperture.

2.2. Structure analysis and refinement

The crystal structures of Li_{2+*x*}Mg_{1–*x*}Si ($x = 0.268$; τ_3), Li_{*x*+*y*}Mg_{2–*x*}Si ($x = 0.51$, $y = 0.39$; τ_7), Li_{65–*x*+*y*}Mg_{30+*x*–*y*}Si₃₃ ($x = 9.15$, $y = 1.23$; τ_5) and Li_{7–*x*+*y*}Mg_{5+*x*–*y*}Si₄ ($x = 1.14$, $y = 0.61$)

were determined by single crystal X-ray diffraction and confirmed by powder diffraction. The single crystals were selected under dried paraffin, fixed and sealed in a glass capillary. Intensity data for Li_{2+*x*}Mg_{1–*x*}Si and Li_{*x*+*y*}Mg_{2–*x*}Si were collected using a BRUKER Kappa Apex II diffractometer, while for Li_{65–*x*+*y*}Mg_{30+*x*–*y*}Si₃₃ and Li_{7–*x*+*y*}Mg_{5+*x*–*y*}Si₄ intensity data were collected using a SuperNova (Agilent Technologies) diffractometer, equipped with a CCD detector. The structures have been solved by direct methods and were refined using the SHELX-97 program package [13]. An initial parameter set was obtained from automatic interpretations of direct methods using SHELXS-97, and this structure model was further refined until convergence was reached using SHELXL-97.

The crystal structure refinement from X-ray powder diffraction was performed by the Rietveld method using the FullProf software package [14].

Further details of the crystal structure investigations can be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany, (Fax: +(49)7247-808-666; e-mail: crysdata@fiz-karlsruhe.de, http://www.fizkarlsruhe.de/request_for_deposited_data.html) on quoting the appropriate CSD numbers 425657, 425658, 425659, 425660 and 425661.

2.3. Hydrogenation measurements

Thermogravimetric analysis (TGA) was performed with the IGA (Hiden Isochema) in 5 bar static H₂ pressure heating with 5 K/min up to 500 °C. The reaction products were sealed in 0.7 mm capillaries and analysed by XRD on a STOE STADI P diffractometer (Mo-K α_1 radiation). Differential scanning calorimetry (DSC) was carried out using a Netzsch DSC 204 HP heating in different H₂ pressures with 5 K/min up to 590 °C.

3. Calculation

3.1. Electronic structure calculations

The linear muffin-tinorbital (LMTO) method [15–17] in its tight-binding (TB) representation [18] is a fast linearized form of the Korringa–Kohn–Rostoker (KKR) method [19,20] for electronic structure calculations and was applied on the Li–Mg–Si system. Basis sets composed of short-ranged atom-centered TB-LMTOs without empty spheres were used for the calculations using the TB-LMTO-ASA4.7 program with a scalar-relativistic Hamiltonian and atomic-spheres approximations [21]. Electronic energies were calculated via density-functional theory (DFT) based on the local-density approximation (LDA) for the exchange-correlation functional as parametrized by von Barth and Hedin [22]. Diagonalization and integration in reciprocal space were performed with the help of an improved tetrahedron method [23]. In order to evaluate various orbital interactions, density of states (DOS), the crystal orbital Hamilton population (COHP) curves [24], and the integrated COHP values (iCOHPs) were also calculated. The mapping of the electrons in the real space was obtained using the

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