



High-pressure synthesis of $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ perovskite hydrides

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ABSTRACT

Magnesium base alloys are very attractive for hydrogen storage due to their large hydrogen capacity, small weight and low-cost. We have designed a new synthesis method for the ternary metal hydride perovskite system $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$, based on the direct reaction of simple hydrides under high-pressure and moderate-temperature conditions. Well-crystallized samples were obtained in a piston-cylinder hydrostatic press at moderate pressures of 2 GPa and temperatures around 750 °C from mixtures of MgH_2 , NaH and LiH enclosed in gold capsules. X-ray and neutron powder diffraction analysis were used to identify the purity of the samples and provide an accurate description of the crystal structure features (GdFeO₃ type). $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides series ($0 \leq x \leq 0.18$) show an orthorhombic symmetry with space group *Pnma* (No. 62). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been carried out to determine the hydrogen desorption temperatures.

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1. Introduction

Ternary compounds with perovskite structure ABX_3 have been exhaustively investigated over the last fifty years, due to their astonishingly varied panoply of properties, including dielectric, electronic, magnetic and optical phenomena. Most of the better known materials are oxides ($\text{X}=\text{O}$), for which the crystal chemistry has been deeply studied in connection with the properties of interest. Much less scarce are the perovskites containing hydrogen ions at the X sublattice. Some of them have been recently described, and immediately attracted the attention of the sustainable technologies community [1], since they can be used as hydrogen storage materials. In particular, ternary hydrides between magnesium and alkali elements are particularly good candidates for advanced hydrogen storage systems, due to their light weight and low cost [2]. The perovskite-type hydrides composed of light elements are expected to present as much as twice energy density as the conventional ones, based upon LaNi_5 alloys. The perovskite hydrides are formulated as ABH_3 , where A and B are monovalent and divalent cations, respectively [3–5]. Thus, most of the perovskite-type hydrides are mainly composed by 1A group elements and 2A group elements of the periodic table. In the Mg-based perovskite-type hydrides, AMgH_3 ($\text{A}=\text{Na}, \text{K}, \text{Rb}$), the main types of structural distortion described in

perovskite-oxide have been identified [6]. For instance, NaMgH_3 [7] has an orthorhombic perovskite structure analogous to the GdFeO_3 type (space group *Pnma*) which is common in low tolerance factor oxide perovskites, where the singly charged Na cation occupies eight-fold coordinated voids. Along the series of hydrides NaMgH_3 , KMgH_3 , and RbMgH_3 [8–10] a progressive structural distortion is observed; NaMgH_3 is orthorhombic as mentioned, KMgH_3 is reported to occur in the ideal cubic perovskite structure, while RbMgH_3 has a non-ferroelectric hexagonal $\text{P6}_3/\text{mmc}$ structure, of the type seen in some high tolerance factor oxides and fluorides [11].

The usual procedure to prepare metal hydrides is by hydrogenation of metal alloys, for instance, $\text{TiFe}_{1-x}\text{M}_x$ ($\text{M}=\text{Co}, \text{Ni}$, or Al , $x \leq 0.5$) intermetallic samples were prepared in an arc furnace under an argon atmosphere and then hydrogenated by exposing them to 5.0 MPa H_2 at room temperature for several cycles [12]. An alternative, traditional method is the mechanochemical synthesis, by high-energy ball-milling under H_2 , which presents several disadvantages since (i) the sample can be easily polluted by the steel balls, (ii) the sample can be easily oxidized in air, (iii) the reaction times are, in general, very long and (iv) the obtained samples exhibit a poor crystallization, which make them not suitable for a complete structural characterization. Concerning NaMgH_3 and related hydrides, they have been synthesized by heating mixtures composed of NaH and Mg (or MgH_2) in a molar ratio $\text{Na}:\text{Mg}=1:1$ [1,7,13]. Ternary hydrides were obtained by sintering or melting methods at temperatures lower than 500 °C and under a hydrogen pressure between 10 and 200 bar, at temperatures spanning from 400 °C to 480 °C [4,7,14,15].

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Solid-state high-pressure synthesis is a powerful and effective technique to explore new compounds in a variety of research areas. In the field of the hydrogen storage materials, this method is being used recently to obtain new hydrides as a different approach from traditional methods [16]. The aim of the present study was to investigate the formation of NaMgH_3 under hydrostatic pressure conditions at moderate temperatures, as well as the formation of new Li-substituted derivatives with nominal composition $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ ($x=0, 0.25$ and 0.5). The replacement of Na by Li would be advantageous for the hydrogen storage ability of the parent material [17,18] since (i) Li is lighter than Na, so the amount of hydrogen per hydride mass should be improved and (ii) the stability of the Li perovskite is found to be lower, therefore the hydrogen desorption proceeds at lower temperatures. In this work we describe a comprehensive study of the crystal structure and thermal analysis of the $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ series, prepared by the mentioned high-pressure method.

2. Experimental procedure

Polycrystalline samples of nominal composition $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$, $x=0, 0.25$ and 0.5 were prepared from stoichiometric mixtures of MgH_2 , NaH and LiH. The reactants were intimately mixed and ground in a glove box under N_2 atmosphere. This mixture was placed into a gold capsule (8 mm diameter, 10 mm length), sealed inside the glove box and then set into a cylindrical graphite heater (10 mm internal diameter). The reaction took place in a piston-cylinder press (Rockland Research Co.), at a moderate reaction pressure (2 GPa) and temperature (750 °C), for short reaction times of less than 1 h. Then, the products were quenched under pressure. The ramp-up for the material synthesis is rather fast, near $150^\circ\text{C min}^{-1}$; we reach 750 °C in approximately 5 min. The ramp-down is a quenching process; in a matter of seconds the sample is quenched from 750 °C down to RT. We found these optimal synthesis conditions after performing several experiments upon different conditions (temperature, starting materials, synthesis time, etc.).

The initial characterization was carried out by X-ray diffraction (XRD) with a Bruker-axs D8 Advanced diffractometer (40 kV, 30 mA), controlled by a DIFFRACT^{PLUS} software, in Bragg–Brentano reflection geometry with $\text{Cu K}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) and a PSD (Position Sensitive Detector). A filter of nickel allows the complete removal of $\text{Cu K}\beta$ radiation. For the study of the crystal structure, neutron powder diffraction (NPD) experiments were carried out in the high-resolution powder diffractometer D2B at the Institut Laue-Langevin at Grenoble, with a wavelength of 1.594 Å. The patterns were collected at room temperature. About 0.8 g of sample was contained in a vanadium can, and a time of 3 h was required to collect a full diffraction pattern. The NPD data were analyzed by the Rietveld method [19] with the FULLPROF program [20]. A pseudo-Voigt function was chosen to generate the line shape of the diffraction peaks. The following parameters were refined in the final run: scale factor, background coefficients, zero-point error, pseudo-Voigt corrected for asymmetry parameters, positional coordinates and isotropic thermal factors for all the atoms. The coherent scattering lengths for Na, Li, Mg and H were 3.63, -1.90 , 5.375 and -3.739 fm , respectively.

Thermal analysis was carried out in a Mettler TA3000 system equipped with a TC10 processor unit. Thermogravimetric (TGA) curves were obtained in a TG50 unit, working at a heating rate of $10^\circ\text{C min}^{-1}$, in a reducing $\text{H}_2(5\%)/\text{N}_2(95\%)$ flow of 0.3 L min^{-1} . About 50 mg of sample were used for each experiment. Differential Scanning Calorimetry (DSC) experiments were performed in a DSC30 unit, in the temperature range of 35–500 °C. The heating rate was $10^\circ\text{C min}^{-1}$, using about 70 mg of sample in each run.

3. Results and discussion

3.1. Crystal structure

The samples were prepared under an external hydrostatic pressure of 2 GPa. The x-ray diffraction patterns of the $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides show sharp and well-defined reflections, as shown in Fig. 1. The samples present a high crystallinity, in contrast with the compounds obtained by the traditional ball-milling method. This feature is important in order to determine the nature and proportion of the different phases present in the patterns, refined by the Rietveld method, and to define some structural peculiarities. The diffraction peaks of unreacted MgH_2 and MgO were detected in the samples with nominal compositions $x=0.25$ and 0.5 (♦ and ○ symbols in Fig. 1, respectively). Excess Li is not observed by XRD, probably because it is eventually present as an amorphous phase.

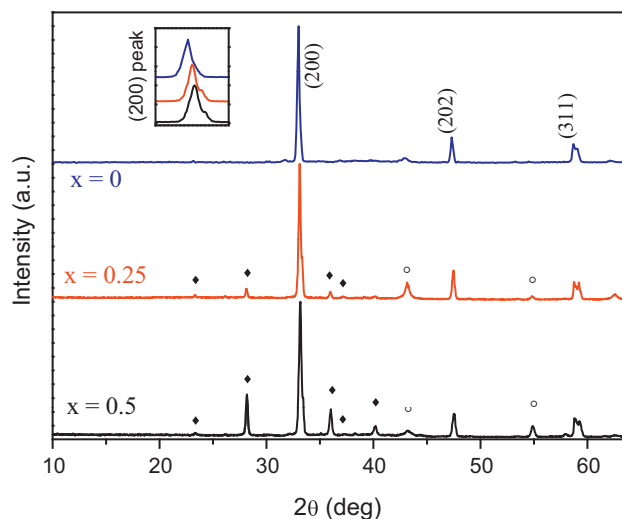


Fig. 1. XRD patterns of $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides prepared by high-pressure techniques. The indexed peaks correspond to ♦ MgH_2 and ○ MgO .

In the NaMgH_3 pattern, the Bragg reflections were identified to be those belonging to a distorted perovskite structure. These peaks, corresponding to the main phase structure, shift to higher diffraction angles as Na atoms are replaced by Li (inset of Fig. 1). This is due to the smaller size of the Li cations, which initially confirmed that Li ions are incorporated into the perovskite crystal structure.

In order to carry out a more accurate structural study and also to identify, locate and quantify light atoms as H and Li, we performed a neutron powder diffraction investigation at room temperature for all the samples. NPD on hydrides (instead of deuterides) is possible nowadays owing to the availability of better neutron diffraction facilities. Henry and Weller have demonstrated the possibilities and limits of NPD on ^1H (protium) in much detail [21–23]. Despite the incoherent scattering of H, good NPD patterns were collected in the present case, showing an excellent crystallinity for the samples. The analysis of the obtained data confirms the perovskite structure for the $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides with $Pnma$ space group (No. 62), corresponding to the orthorhombically distorted GdFeO_3 type. In this setting, the Na/Li cations are placed at $4c(x, 1/4, z)$ sites, the Mg cations at $4b(0, 0, 1/2)$ sites, and the two kinds of nonequivalent hydrogen atoms (H1 and H2) at $4c(x, 1/4, z)$ and at $8d(x, y, z)$ sites, respectively.

Fig. 2 illustrates the good agreement between the observed and calculated NPD patterns at room temperature for $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides and Table 1 summarizes the unit-cell, atomic, thermal parameters and discrepancy factors after the Rietveld refinements of the crystal structures. The lattice parameters of the $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides decrease as the amount of Li increases, as shown in Fig. 3a, being the shrinkage more pronounced along the c axis. It is due to the smaller ionic size of Li^+ respect to the replaced Na^+ ions. This effect can clearly be seen in the reduction of the unit-cell volume along the series (Fig. 3b). The occupancy factors for Na/Li as well as for H atoms were refined in order to obtain the stoichiometric formula for each compound; the results are included in Table 1. After the final refinement, the crystallographic formulae for the three ternary hydrides are $\text{NaMgH}_{3.0}$, $\text{Na}_{0.95}\text{Li}_{0.05}\text{MgH}_{2.73}$ and $\text{Na}_{0.82}\text{Li}_{0.18}\text{MgH}_{2.58}$. The hydrogen deficiency found in the Li-containing samples can be due to H desorption from the sample after their synthesis. The maximum Li content in the samples was 0.18 (for nominal $x=0.5$), indicating the difficulty of Li atoms to be introduced in this system.

Table 2 contains the main interatomic distances and angles. The MgH_6 octahedra maintain a nearly ideal configuration with

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