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Bulk nanocrystalline gamma magnesium hydride with low dehydrogenation temperature stabilized by plastic straining via high-pressure torsion

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ABSTRACT

MgH_2 with the α tetragonal structure was plastically strained using the high-pressure torsion (HPT) method and fully transformed to a nanonocrystalline γ orthorhombic phase with increasing the strain. The formation of nanocrystalline high-pressure γ phase resulted in decreasing the dehydrogenation temperature by 80 K. First-principles phonon calculations showed that both α and γ phases are dynamically stable, but the γ phase with the ionic binding has weaker hydrogen binding energy and accordingly lower dehydrogenation temperature. This study confirms the significance of crystal structure on thermal stability of hydrides for hydrogen storage applications.

MgH_2 is a light hydride containing 7.6 wt% of hydrogen. Because of such a high hydrogen content, MgH_2 is considered as a candidate for solid-state hydrogen storage [1]. However, the main drawback of MgH_2 is its high dehydrogenation temperature due to strong Mg—H binding energy [1]. Addition of a third element to MgH_2 is currently the main strategy to weaken the hydrogen binding energy and reduce the dehydrogenation temperature [2]. However, this strategy reduces the hydrogen storage capacity (e.g., to 3.6 wt% in Mg_2NiH_4) [2]. As will be shown in this work, changing the crystal structure is another strategy for weakening the hydrogen binding energy.

MgH_2 has a rutile-type α-tetragonal crystal structure at ambient pressure and transforms to the γ-orthorhombic and β-cubic phases under 0.39–5.5 and 3.9–9.7 GPa, respectively (see Fig. 1(a)) [3]. Theoretical studies suggested that two other orthorhombic structures (δ and ε phases) can form under higher pressures [4]. Despite some reports on the partial formation of γ phase after ball milling [5], electrochemical synthesis [6], plasma sputtering [7] and high-pressure torsion (HPT) processing [8], there have been no attempt to examine the dehydrogenation behavior of MgH_2 with fully metastable phases.

The HPT method [9], in which high pressure and shear strain ($\gamma = 2\pi rN/h$; γ: shear strain; r: distance from disc center, N: number of turns, h: disc thickness [10]) are simultaneously applied to a disc sample, has high potential to stabilize high-pressure phases in various materials such as the ω phase in Ti [11], Zr [12] and their alloys [13], the cubic phase in $BaTiO_3$ [14] and ZnO [15], the orthorhombic phase in TiO_2 [16], and the monoclinic phase in Y_2O_3 [17]. In this study, bulk nanocrystalline γ-MgH_2 is stabilized by HPT processing and its dehydrogenation is examined experimentally as well as theoretically by first-principles calculations.

For experiments, α-MgH_2 micropowders were processed at room temperature by HPT under pressures of 0.6, 1.2, 3 and 5 GPa for 0 (mere compression), 0.5, 1, 4 and 15 turns with a rotation speed of 1 rpm to form discs with 10 mm diameter and 0.8 mm thickness. The samples were evaluated by X-ray diffraction (XRD) using the Cu Kα radiation, Raman spectroscopy using a 532 nm laser, transmission

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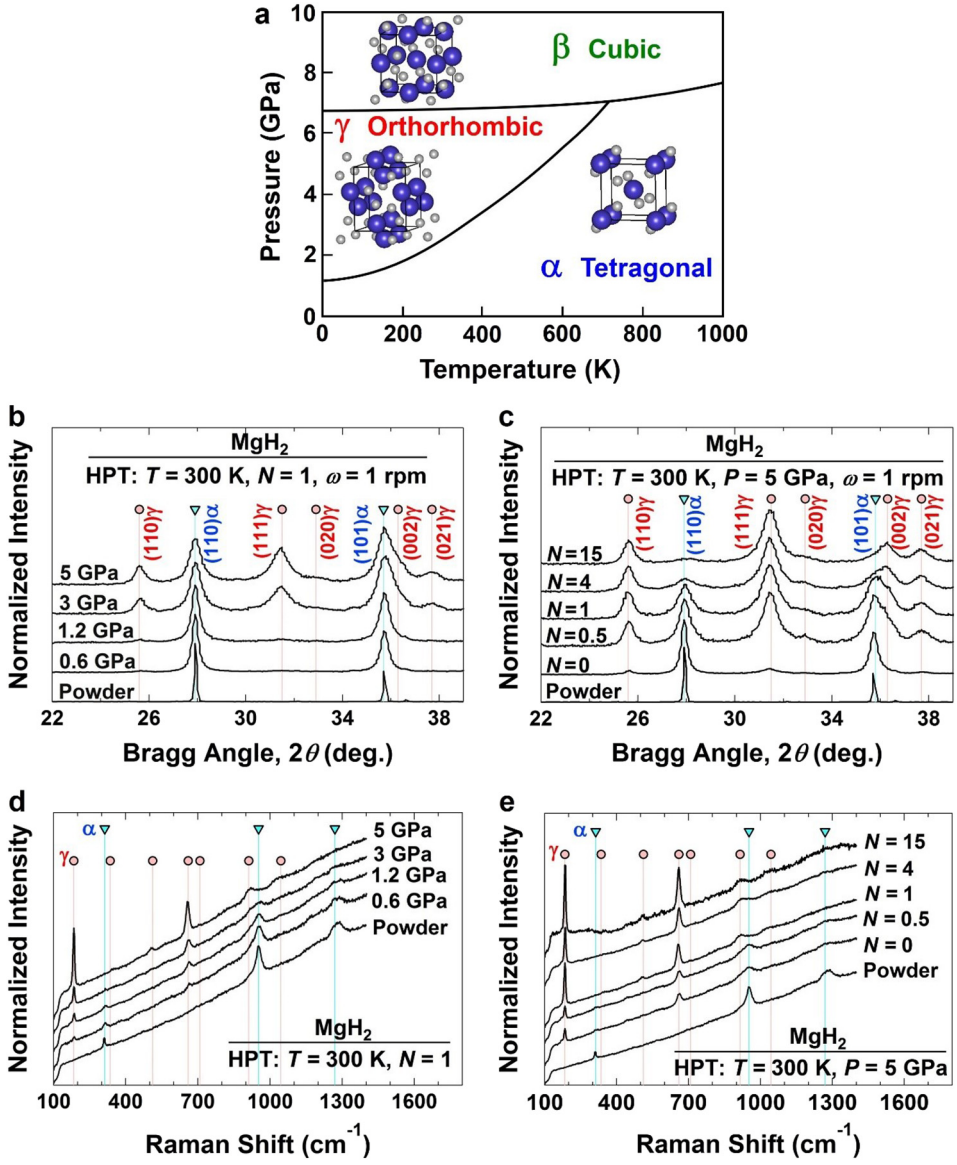

Fig. 1. (a) Theoretical pressure-temperature phase diagram of MgH_2 reproduced from data in Ref. [3]. (b, c) XRD profiles and (d, e) Raman spectra for MgH_2 processed by HPT under (b, d) various pressures for 1 turn and (c, e) 5 GPa for various turns.

electron microscopy (TEM) using an acceleration voltage of 200 kV, differential scanning calorimetry (DCS) and thermogravimetry (TG) with the heating rates of 5 K/min (all evaluations were conducted at 3.5–5 mm from the disc center). TEM foils were prepared by a crushing technique and examined by bright-field and high-resolution modes as well as by selected-area electron diffraction (SAED) from areas with ~0.8 μm diameter.

First-principles calculations were conducted with the plane-wave basis projector augmented wave (PAW) method [18] in the framework of density functional theory (DFT) within the generalized gradient approximation (GGA) in the form of Perdew and Wang (PW91) [19] as implemented in the Vienna Ab initio Simulation Package (VASP) [20]. A plane-wave energy cutoff of 400 eV was used. The Brillouin zones were sampled with the Γ-centered meshes given in Supplementary Table S1 using the Methfessel-Paxton scheme [21] with the smearing width of 0.2 eV. Mg 3d and H 1 s orbitals were treated as the valence states. The energies and residual forces were converged within 10^{-8} eV and 10^{-2} eV/nm, respectively. Both the lattice shape and the internal atomic positions were optimized for Mg and MgH_2, while interatomic distance of the H_2 molecule was optimized in the fixed simulation cell of $2 \times 2 \times 2$ nm^3. The enthalpy of formation for the α, γ and β phases (ΔH) was calculated by comparing the energies of hydrides, Mg and H_2.

$$\Delta H = E(MgH_2) - [E(Mg) + E(H_2)] \quad (1)$$

Average Born effective charge tensors (BECTs) were computed based on the linear response theory [22] and phonon frequencies were calculated using the PHONOPY code [23]. Force constants were computed using the direct method with the atomic displacement of 10^{-3} nm from the supercells in Supplementary Table S1 and the zero-point vibration energies and the phonon densities of states (DOSs) were computed from the phonon frequencies on the Γ-centered meshes in the Brillouin zone in Supplementary Table S1 using the tetrahedron method [24]. The correction by dipole-dipole interaction [25] was incorporated for the phonons of MgH_2.

The effect of pressure and strain on phase transformations of MgH_2 are shown in Fig. 1 using (b, c) XRD analysis and (d, e) Raman