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Significant improvement in the dehydriding properties of perovskite hydrides, NaMgH₃, by doping with K₂TiF₆

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ABSTRACT

In this study, perovskite hydrides (NaMgH₃) were synthesized in the presence and absence of a dopant, e.g., K₂TiF₆, by high-energy ball milling. Clear lattice distortion was observed in K₂TiF₆-doped NaMgH₃ as compared to pristine NaMgH₃. The doped sample exhibited better dehydriding properties, and the onset desorption temperature significantly decreased from 580 K to 328 K. The maximum amount of desorbed hydrogen was approximately 3.8 wt% at 638 K, and approximately 90% of hydrogen was desorbed within 20 min. Differential scanning calorimetry results indicated that the activation energy for the two steps in the decomposition of NaMgH₃ decreases by doping with K₂TiF₆. This result suggested that the lattice distortion and low decomposition energy of the NaMgH₃ phase, caused by the introduction of the K₂TiF₆ dopant, result in improved dehydriding properties for NaMgH₃.

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Introduction

NaMgH₃ has attracted considerable attention because of its high gravimetric and volumetric densities (6 wt% and 88 kg/m³, respectively), as well as reversible hydriding and dehydriding properties [1–6]. NaMgH₃ is characterized by an orthorhombic perovskite structure comprising [MgH₆] octahedra and [NaH₁₂] cubo-octahedra, which is analogous to GdFeO₃-type perovskite (space group Pnma). This space group is typical for low-tolerance-factor oxide perovskites, where the singly charged Na cation occupies eight-fold coordinated voids [7]. The desorption of NaMgH₃ is a two-step reaction: NaMgH₃ → NaH + Mg + H₂ → Na + Mg + 3/2H₂. Sheppard et al. [8] have measured the kinetic and thermodynamic data for

the decomposition of NaMgH₃ into NaH and Mg in the first desorption step. Desorption enthalpy and entropy are 86.6 ± 1.0 kJ/(mol H₂) and 132.2 ± 1.3 kJ/(mol H₂ K), respectively, indicating that NaMgH₃ is thermodynamically more stable than MgH₂. Some studies have reported that the kinetic properties of NaMgH₃ can be modified by doping with catalytic additives [9–11]. For example, Li et al. [10] have revealed that the *in situ* introduction of Mg₂NiH₄ and YH₃ nanoparticles into NaMgH₃ leads to significantly enhanced kinetics for hydrogen absorption and desorption cycling. Komiya et al. [12] have reported that MMgH₃ (M = Na, K, and Rb) hydrides, synthesized by ball milling, are decomposed at temperatures between 673 and 723 K by several pathways depending on M. Chaudhary et al. [11] have reported that the onset decomposition temperature decreases with the introduction of a Si

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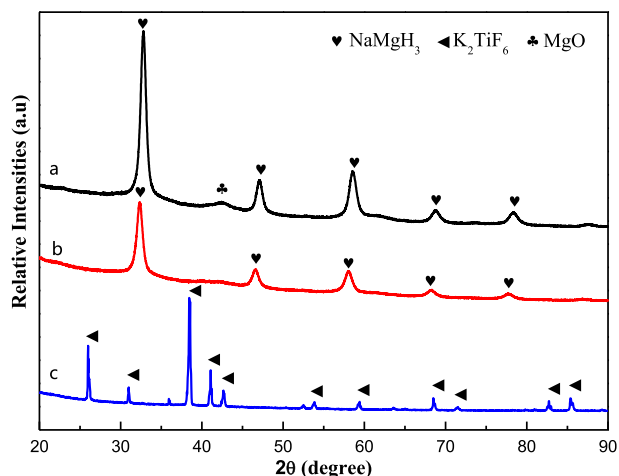


Fig. 1 – XRD patterns of as-synthesized NaMgH₃ samples. (a) NaMgH₃, (b) NaMgH₃-0.042K₂TiF₆, (c) Pristine K₂TiF₆.

dopant into NaMgH₃ by mechanical milling. Martínez-Coronado et al. [13] have reported that the hydrogen desorption temperature clearly decreases in Na_{1-x}Li_xMgH₃ ($x = 0, 0.25, 0.5$) because of the low structural stability of the Li-containing perovskite-type structure. Xiao et al. [14] have predicted that the substitution of Li in NaMgH₃ is favorable for onboard hydrogen storage applications based on density functional theory calculations. Pottmaier et al. [15] have also comprehensively investigated the structural and thermodynamic properties of NaMgH₃.

Recently, Liu et al. [16] have reported that the combination of K, Ti, and F exerts a synergistic catalytic effect on the improvement of the reversible hydrogen storage properties of NaAlH₄ via the introduction of K₂TiF₆ as a catalyst precursor: Approximately 4.4 wt% of hydrogen is released from NaAlH₄-0.025 K₂TiF₆ within 40 min at 413 K. Li et al. [17] have investigated the effect of K₂TiF₆ on the dehydrogenation properties of LiAlH₄ and suggested that TiH₂, Al₃Ti, KH, and LiF, formed *in situ*, play a crucial role in the improvement of the dehydrogenation properties of LiAlH₄. Mustafa et al. [18] have reported that the addition of 10 wt% K₂TiF₆ to MgH₂ leads to a lower onset desorption temperature of 518 K, corresponding to a decrease of approximately 105 K and 205 K as compared with those observed for as-milled and as-received MgH₂, respectively. With this background, K₂TiF₆ exhibited

superior catalytic effects. Hence, some interesting results can be obtained using K₂TiF₆ as the catalyst while it is introduced into AMgH₃ perovskite-type hydrides (where A = alkaline earth metal).

To improve dehydrogenating properties of NaMgH₃, NaMgH₃ samples with and without the K₂TiF₆ dopant were synthesized by high-energy ball milling. The structure and dehydrogenating properties of NaMgH₃ hydride with and without the K₂TiF₆ dopant were investigated and compared by X-ray diffraction (XRD), temperature-programmed desorption (TPD), and differential scanning calorimetry (DSC) analysis. Experimental results indicated that the addition of K₂TiF₆ leads to clear improvement in the dehydrogenating kinetic properties of NaMgH₃.

Materials and methods

NaMgH₃ samples with and without the K₂TiF₆ dopant were prepared from stoichiometric mixtures of MgH₂ (>98% purity, Alfa Aesar), NaH (>95% purity, Sigma Aldrich), and K₂TiF₆ (97% purity, Sigma Aldrich). The mixing molar ratio of NaH:MgH₂:K₂TiF₆ was 0.75:1:0.042. All chemicals were directly used without further purification. The mixed powders were milled with stainless steel balls under H₂ (0.8 MPa) for 45 h at 350 rpm using a QM-3SP2 planetary mill at ambient temperatures. The weight ratio of ball to powder was 80:1. All material operations were conducted in an argon-filled glove box to eliminate the effect of oxygen and water moisture.

X-ray diffraction (XRD) measurements were conducted on an Empyrean PIXcel 3D (Cu K_α radiation) diffractometer. Powder samples were sealed in a special cell, which was coated with a Kapton film to prevent exposure to air. To determine the phase structure, samples were annealed at 473 K for 4 h under H₂ (1.0 MPa) to eliminate the internal strain resulting from ball milling. The collected XRD data were evaluated by the Rietveld profile refinement method with Jade 6.5 (XRD analysis software). The amount of desorbed hydrogen and dehydrogenating kinetic properties of samples were measured on an automatic Sievert-type apparatus (PCTpro2000, Setaram Co.). For TPD experiments, the sample was heated from 298 K to 673 K in a vacuum chamber (10⁻³ Pa) at a heating rate of 5 K/min. Dehydrogenating kinetics measurements were conducted at 638 K and 593 K in vacuum (10⁻³ Pa),

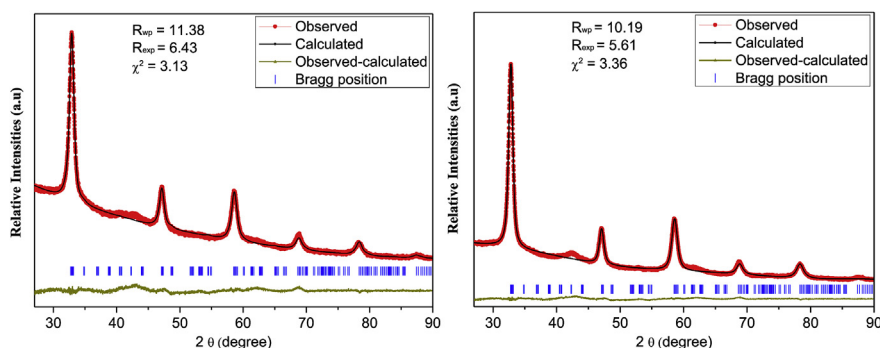


Fig. 2 – Refined XRD patterns for pristine NaMgH₃ (Left) and NaMgH₃-0.042K₂TiF₆ (Right).

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