



Structure, thermal analysis and dehydriding kinetic properties of $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ hydrides



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ABSTRACT

NaMgH_3 hydride with perovskite structure has been synthesized by high-energy ball milling, the maximum hydrogen-desorbed amount of which is 3.42 wt.% at 638 K. Two decomposition steps have been detected for perovskite-type NaMgH_3 hydride, calculated values of activation energy for the two steps are 180.25 ± 8.25 kJ/mol and 156.23 ± 18.54 kJ/mol by Kissinger method. In comparison with NaMgH_3 hydride, $\text{Li}_{0.5}\text{Na}_{0.5}\text{MgH}_3$ hydride has better dehydriding kinetic properties and higher hydrogen-desorbed amount (4.11 wt.%) due to partial replacement of Na by Li. LiMgH_3 hydride with perovskite structure cannot be synthesized by milling of the mixture of LiH and MgH_2 hydrides. However, the maximum hydrogen-desorbed amount of this milled mixture is 5.54 wt.% at 638 K, this may suggest that LiH is a good catalyst for dehydrogenation of MgH_2 , but further research is needed.

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1. Introduction

Hydrogen has great potential as an efficient fuel and is a good energy carrier, especially in the terms of energy sustainability and environmental conservation. However, its large-scale use for mobile applications is still limited by storage issues. Hydrogen storage in the solid state is currently considered as the best option for a safe and long-term solution [1–10]. Recently, Mg-based perovskite-type hydrides, AMgH_3 (A = alkali-earth element), have received considerable attention [11–16].

NaMgH_3 was studied as a potential candidate for on-board applications because it has high gravimetric and volumetric densities (6 wt.% and 88 kg/m³) as well as reversible hydriding and dehydriding reactions [14]. Also, it was pointed out as a potential material for future generation of electronic devices due to the superior hydrogen mobility of the perovskite structure [11]. NaMgH_3 [17] 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. Sheppard et al. measured the kinetic and thermodynamic data for the decomposition of NaMgH_3 into NaH and Mg. The desorption enthalpy and entropy are

86.6 ± 1.0 kJ/(mol H_2) and 132.2 ± 1.3 kJ/(mol H_2 K) respectively, indicating that NaMgH_3 is thermodynamically more stable than MgH_2 [18].

It is shown that the thermodynamic properties of NaMgH_3 can be tuned by incorporating new elements or doping catalytic additives [19,20]. For example, the hydrogen storage properties of NaMgH_3 in situ embedded of Mg_2NiH_4 and YH_3 nanoparticles was studied by Li's group and they found that the composite material exhibited greatly enhanced kinetics for hydrogen absorption and desorption cycling after doping [10]. Moreover the onset temperature of decomposition was successfully decreased with the additions of Si element doped into NaMgH_3 by mechanical milling as reported by Anna-Lisa Chaudhary and co-workers [20]. Martínez-Coronado et al. [21] prepared $\text{Na}_{1-x}\text{Li}_x\text{MgH}_3$ (X = 0, 0.25, 0.5) ternary hydrides using a high-pressure technique, and found that as Li is introduced in the system, the unit-cell parameters decrease, the tilting angle increases and the MgH_6 octahedra become more distorted due to the smaller ionic size of Li^+ vs Na^+ . The hydrogen desorption temperature decreases due to the lower structural stability of the Li-containing perovskites. Xiao et al. [22] also predicted the same results based on density functional theory calculations.

The replacement of Na by Li would be advantageous for the hydrogen storage ability of NaMgH_3 hydrides [23,24] due to the following reasons: (i) Li is lighter than Na, so the amount of hydrogen per hydride mass should be improved and (ii) the stability of Li perovskite is found to be lower, therefore the hydrogen

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desorption proceeds at lower temperatures. In this work, high-energy ball-milling under H_2 , is employed to prepared $Na_{1-x}Li_xMgH_3$ ($x = 0, 0.5, 1.0$) hydrides, a comprehensive study of the phase structure before/after heat-treatment, thermal analysis and hydrogen-desorbed amount and dehydrogenating kinetic properties have been investigated.

2. Experimental procedure

Nominal composition $Na_{1-x}Li_xMgH_3$ ($x = 0, 0.5, 1.0$) samples, were prepared from stoichiometric mixtures of MgH_2 (>98% purity, Alfa-Aesar), NaH and LiH (>95% Purity, Sigma-Aldrich). The mixed powders were milled with stainless steel balls under H_2 atmosphere (0.8 MPa) for 45 h at 320 rpm using a YXQM-21 planetary mill at the ambient temperature. The weight ratio of ball to powder is 80:1. Partial as-milled samples were selected and heat-treated for 5 h under H_2 atmosphere (3 MPa) at 623 K, then cooled to room temperature for structure analysis and dehydrogenating test.

X-ray diffraction (XRD) analysis of samples were performed on Empyrean PIXcel 3D (Cu K α radiation) diffractometer. The powder samples were sealed in a special cell, coated with Kapton film to prevent exposure to air. The evaluation of hydrogen-desorbed amount and dehydrogenating kinetic properties of samples were measured on automatic Sievert-type apparatus (PCTpro2000, Setaram Co.). Thermostability properties of as-milled samples were investigated by DSC analysis (DSC, NETZSCH STA 449F3) at different heating rates (5, 10, 15 K/min) under a continuous argon flow (20 ml/min) from 298 K to 725 K, and testing samples were sealed with aluminum metal crucible. All sample handlings were undertaken in an argon atmosphere glovebox (Mbraun, Labstar, 1 ppm H_2O , 1 ppm O_2).

3. Results and discussion

3.1. Synthesis, dehydrogenating properties and thermal analysis of $NaMgH_3$ hydrides

Fig. 1 displayed the XRD patterns of as-milled $NaMgH_3$ samples before/after heat-treatment. The peaks of $NaMgH_3$ phase can be observed in as-milled sample, which is an orthorhombic perovskite structure, similar to the $GdFeO_3$ type (space group Pnma) [25,26]. More sharp peaks of $NaMgH_3$ phase can be seen in the sample after heat-treatment, accompanied with the peaks of MgH_2 and NaH

phases. This results indicate that the crystallinity of $NaMgH_3$ sample can be improved by heat-treatment at 623 K for 5 h (H_2 , 3 MPa). There are MgH_2 and NaH phases after heat treatment. This is why we think maybe heat treatment can make MgH_2 and NaH phases which are unreactive and have a broken crystal structure to form new crystals. The existence of MgO phase can be attributed to the slight oxidation of samples in the handling process [27].

Fig. 2 shows the isothermal dehydrogenating properties of as-milled $NaMgH_3$ samples at 638 K, and the hydrogen-desorption pressure is 10^{-2} bar. As illustrated in Fig. 2, dehydrogenating kinetics of as-milled $NaMgH_3$ hydride without heat-treatment is superior to that after heat-treatment, the maximum hydrogen-desorbed amount of the former is 3.42 wt.%, which will release above 3 wt.% of the amount within 40 min. However, the dehydrogenating process of the latter is quite slow with hydrogen-desorbed amount less than 3 wt.% after 170 min. Possible reasons may be: (1) Partial decomposition of $NaMgH_3$ perovskite hydride will occur in the heat-treated process, the products is MgH_2 and NaH hydrides, the dehydrogenating temperatures of the two products are higher than that of $NaMgH_3$ hydride [27–29], so results in the decrease of the total hydrogen-desorbed amount of as-milled $NaMgH_3$ hydride. (2) As-milled sample possesses some amorphous structure, more defects and large grain boundaries which will lead to the improvement of dehydrogenating kinetic properties, but such structure feature will greatly be disappeared after heat-treated process. In other word, the heat-treatment will increase the crystallinity of the sample, but reduce its dehydrogenating kinetic properties. The hydrogen-desorbed amounts of the sample before/after heat-treatment are also listed in Table 1.

Fig. 3 shows the isothermal dehydrogenating properties of as-milled $NaMgH_3$ hydride at different temperature, and the hydrogen-desorbed amounts are also listed in Table 1. As can be seen, the hydrogen-desorption rate accelerated with increasing temperature. The maximum hydrogen-desorbed amount of $NaMgH_3$ sample is 3.42 wt.%, and about 90% of the amount is released within 47 min at 638 K, but the hydrogen-desorbed amount is 2.03 wt.% at 613 K, and only 1.13 wt.% (after 150 min) at 593 K.

The XRD patterns of $NaMgH_3$ samples after dehydrogenating at different temperature are shown in Fig. 4. As can be seen, peaks of $NaMgH_3$ phase are still in existence, and peaks of NaH phase and Mg phase can also be observed. With the increase of temperature from 593 K to 638 K, peaks of $NaMgH_3$ phase become weakened, and peaks of NaH phase and Mg phase become strengthened. The

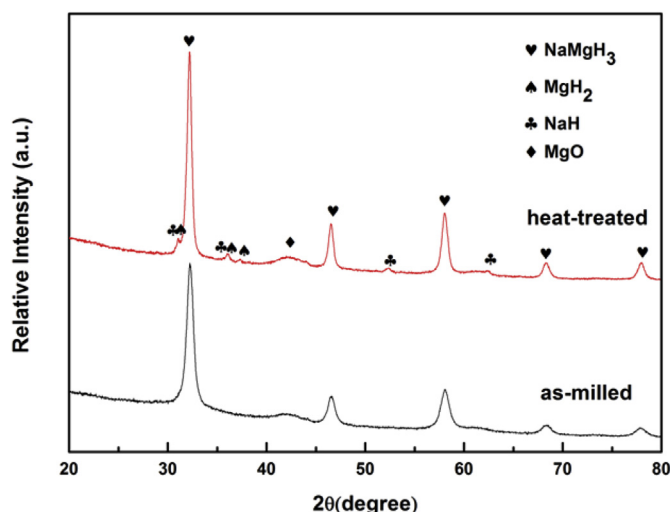


Fig. 1. XRD patterns of as-milled $NaMgH_3$ hydrides before/after heat-treatment.

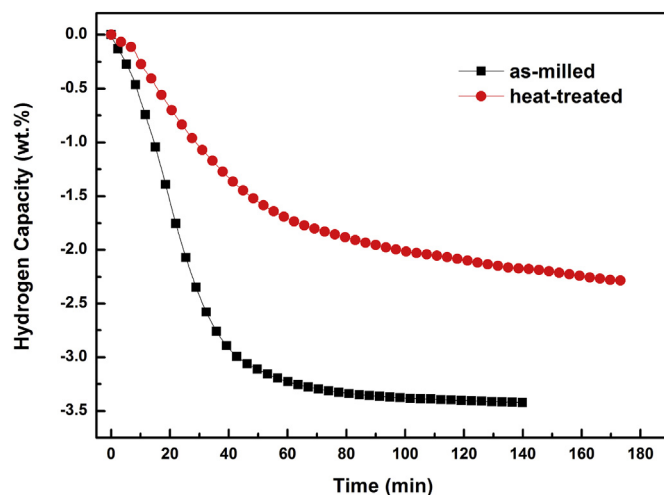


Fig. 2. Dehydrogenating kinetic curves of as-milled $NaMgH_3$ sample before/after heat-treatment at 638 K.

Table 1
The hydrogen-desorbed amounts of NaMgH₃ sample before/after heat-treatment.

Method	593 K	613 K	638 K
As-milled	1.13 wt.%	2.03 wt.%	3.42 wt.%
Heat-treated	/	/	2.28 wt.%

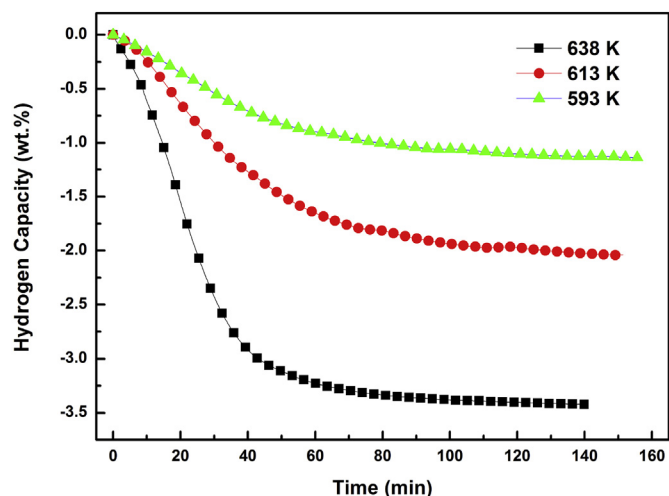


Fig. 3. Dehydrogenating kinetic curves of as-milled NaMgH₃ hydride at different temperature.

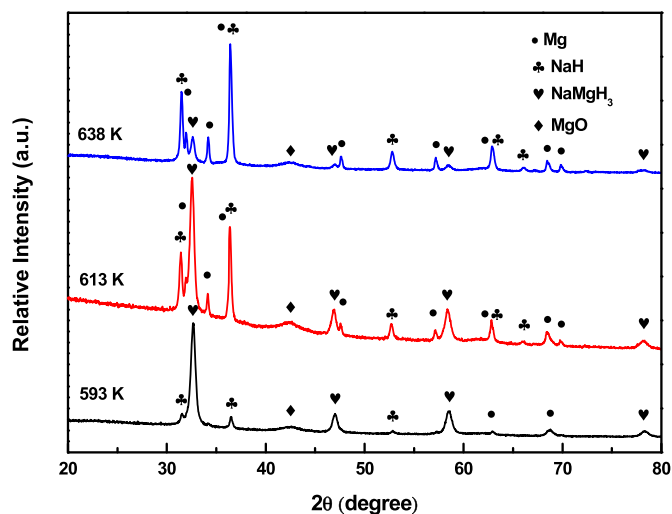


Fig. 4. XRD patterns of as-milled NaMgH₃ hydride after dehydrogenating at different temperature.

result indicates that the decomposition of NaMgH₃ hydride will occurred in the dehydrogenating process and the decomposition products are MgH₂, NaH and H₂. The decomposed H₂ will contribute to the hydrogen-desorbed amount of the sample, but this decomposition is not fully finished at this condition.

Fig. 5 shows the DSC curves of as-milled NaMgH₃ hydride at different heating rates (5, 10, 20 K/min) under a continuous argon flow from 298 to 750 K. Herein T_x and T_p stand for the start and peak temperature of dehydrogenation, respectively. We observed that there are two dehydrogenating processes, T_x and T_p rise clearly with increased heating rate and these data are listed in **Table 2**. According to results of **Figs. 4 and 5**, the following dehydrogenation steps can be deduced:

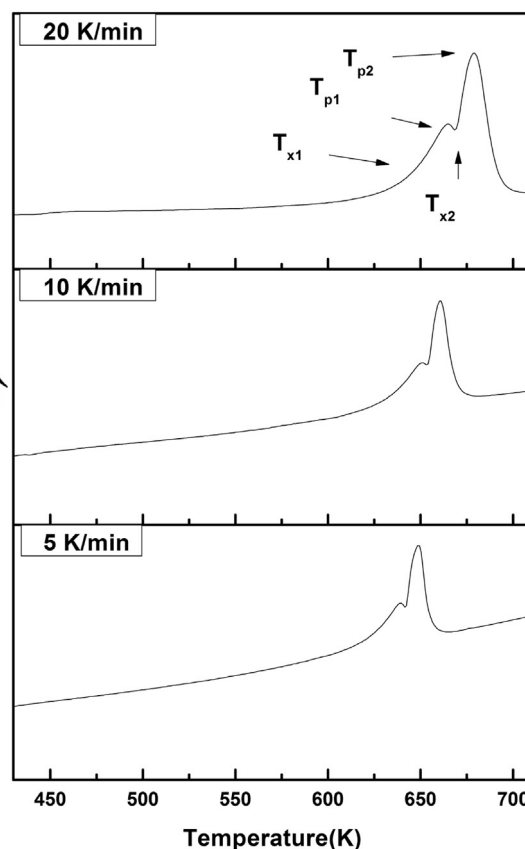


Fig. 5. DSC curves of as-milled NaMgH₃ hydride at different heating rate.

Table 2
Dehydrogenating temperatures of NaMgH₃ hydride at different heating rate.

Rate	T _{x1}	T _{p1}	T _{x2}	T _{p2}
5 K/min	623.3 K	639.4 K	642.6 K	649.0 K
10 K/min	632.8 K	651.0 K	654.6 K	660.8 K
20 K/min	639.3 K	665.0 K	669.9 K	679.0 K
ΔE	180.25 ± 8.25 kJ/mol		156.23 ± 18.54 kJ/mol	



This explanation agrees well with the previous works [19,20]. Based on the two decomposition steps of NaMgH₃ hydride, the theoretical hydrogen-desorbed amount of the first step is 4 wt.%, and 2 wt.% for the second step. In this work, the experimental data is 3.42 wt.% at 638 K, which is about 85.5% of the theoretical hydrogen-desorbed amount of the first step. The second step was not carried out due to the limitation of working temperature of PCI apparatus.

In order to estimate the activation energy (ΔE) for dehydrogenation of the as-milled NaMgH₃ hydride, the Kissinger relation is frequently used for non-isothermal DSC analysis, and can be expressed in the form as [30].

$$\ln(T_p^2/\nu) = \Delta E/RT + \ln(\Delta E/Ru_0). \quad (3)$$

where R is the gas constant, and ν and u₀ are heating rate and frequency factor respectively. Fitting curves by Kissinger method are shown in **Fig. 6**, which represent a good linear relation between

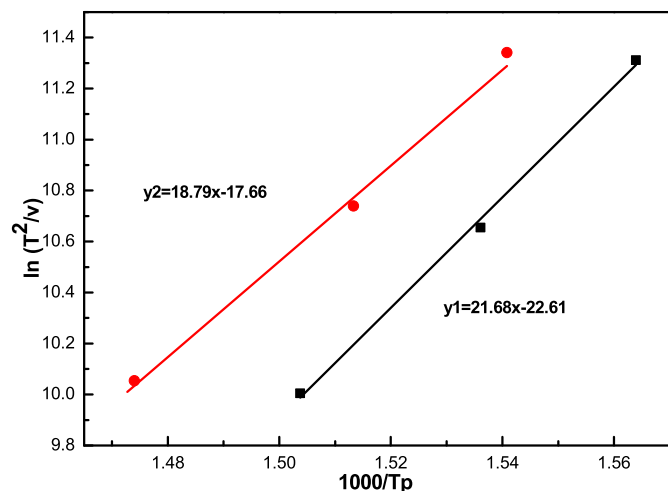


Fig. 6. The relationships between $\ln(Tp^2/v)$ and $(1000/Tp)$ for NaMgH₃ hydride fitted by Kissinger method.

$\ln(Tp^2/v)$ and $(1000/Tp)$ with a slope of $\Delta E/R$. It can be found that ΔE_1 for the first decomposition step of as-milled NaMgH₃ hydride is 180.25 kJ/mol, and 156.23 kJ/mol (ΔE_2) for the second step. Where measured NaMgH₃ sample was synthesized by a two-step method (consisting of ball milling and hydriding combustion synthesis). This work suggests that as-milled NaMgH₃ hydride has better dehydriding property.

3.2. Structure and dehydriding properties of $Li_xNa_{1-x}MgH_3$ hydrides

The XRD patterns of nominal composition $Li_xNa_{1-x}MgH_3$ ($x = 0, 0.5, 1.0$) samples are shown in Fig. 7. The following points can be deduced from Fig. 7, (1) In the case of $x = 1.0$, peaks of unreacted LiH and MgH₂ are detected, no new phase can be formed indicating that LiMgH₃ hydride cannot be synthesized by mechanical ball-milling of the mixture of LiH and MgH₂ hydrides. (2) In the case of $x = 0.5$, Peaks of NaMgH₃ and MgH₂ phases have been observed, LiH is not observed, probably because the latter is eventually present as an amorphous phase after ball-milling [21]. (3) In $Li_{0.5}Na_{0.5}MgH_3$ sample, peaks of NaMgH₃ phase shift to higher

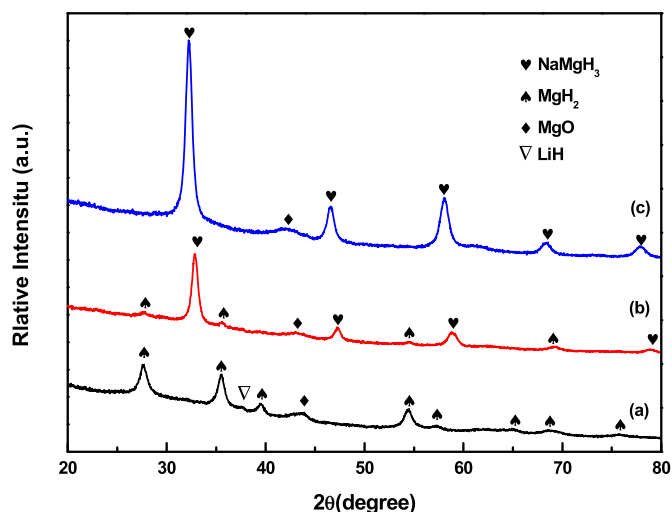


Fig. 7. The XRD patterns of nominal composition $Li_xNa_{1-x}MgH_3$ samples (a) $x = 1$ (b) $x = 0.5$ (c) $x = 0$.

diffraction angles as Na atoms are replaced by Li. This is due to the smaller size of the Li cations.

In addition, tolerance factor (t) can be used to predict structure stability of ABX₃ perovskite-type compound. When H is X, the equation is expressed as follow:

$$t = (R_A + R_H) / \sqrt{2}(R_B + R_H) \quad (4)$$

Here R_A and R_B stand for cationic ionic radius of A and B respectively, R_H is hydrogen anion radius. Electronic distribution of H is not spherical-scattering type in hydride pattern, R_H is not fixed, and the covalent bond length varied with different cationic ions. The calculation of tolerance factor (t) is based on the fixed ion radius, so R_H is set as 0.140 nm [26,31]. No accurate tolerance factor range for perovskite-type hydrides is given at present. However, by analogy with perovskite-type oxides and halides, Ikeda et al. reported that a reasonable range of tolerance factor is $0.77 < t < 1.00$, and perovskite-type hydride with stable structure are suggested to be existent within this range [32]. The calculated tolerance factor (t) are listed in Table 3. The results illustrate that perovskite-type NaMgH₃ hydride can be stably existing at $t = 0.807$, whereas t value of $Li_xNa_{1-x}MgH_3$ ($x = 0.5$) perovskite structures is 0.767 (near 0.77), indicating that partial replacement of Na with Li will reduce the tolerance factor, and form distorted perovskite structure. LiMgH₃ perovskite hydride cannot be formed for $t = 0.727$. In fact, LiMgH₃ ternary hydride has not been successfully synthesized so far. Vajeeston et al. reported that LiMgH₃ is a stable trigonal structure of LiTaO₃ via first-principles prediction [33].

The replacement of Na by Li would be advantageous for the hydrogen storage ability of the parent material [23,24] 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. Fig. 8 shows dehydriding kinetic curves of $Li_xNa_{1-x}MgH_3$ hydrides at 638 K. The maximum hydrogen-desorbed amount increases with the increase of x , In comparison with NaMgH₃ hydride, $Li_{0.5}Na_{0.5}MgH_3$ hydride has better dehydriding kinetic properties, and released about 90% of the maximum hydrogen-desorbed amount within 28 min, which is possibly due to the formation of distorted perovskite structure caused by partial replacement of Na by Li. However, $Li_xNa_{1-x}MgH_3$ ($x = 1.0$) can be regarded as a ball-milled mixture of LiH and MgH₂ hydrides, which has 5.54 wt. % of the maximum hydrogen-desorbed amount, and releases about 90% of the maximum hydrogen-desorbed amount within 23 min at 638 K further indicating that LiH has good catalytic effect for dehydriding properties of MgH₂ in this milling condition.

Measured and theoretical hydrogen-desorbed amounts of nominal composition $Li_xNa_{1-x}MgH_3$ hydrides are listed in Table 3. The theoretical value is related to the first decomposition step of NaMgH₃ hydride. The hydrogen-desorbed amount increases according to $x = 1.0 > x = 0.5 > x = 0$, which suggest Li doping is beneficial for dehydriding properties of Li–Na–Mg–H system hydrides. In fact, based on density functional theory calculation, Xiao's group [22] found that the dehydrogenation enthalpy of perovskite-

Table 3
Calculated tolerance factor (t) of $Li_xNa_{1-x}MgH_3$ samples.

Sample	$x = 0$	$x = 0.5$	$x = 1.0$
t	0.807	0.767	0.727
Desorp. H ₂ (wt. %)	3.42	4.11	5.54
Theoretical H ₂ (wt. %)	4.01	4.77	5.88
Percentage (%)	85.5	86.2	94.2

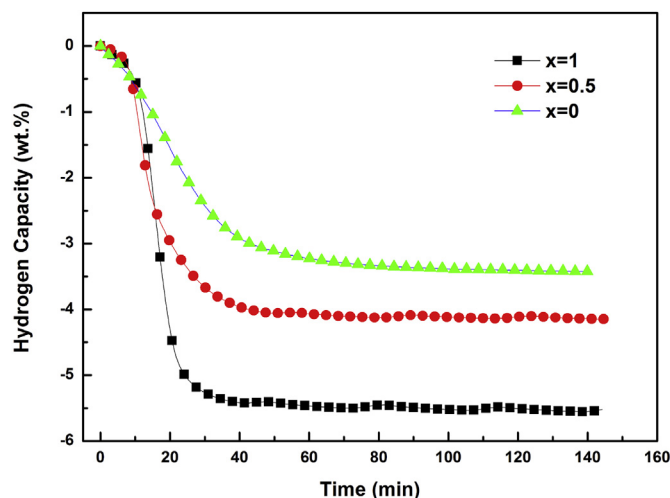


Fig. 8. Dehydrogenating kinetic curves of nominal composition $\text{Li}_x\text{Na}_{1-x}\text{MgH}_3$ ($x = 0, 0.5, 1.0$) samples at 638 K.

type NaMgH_3 hydride can be reduced by the replacement of Na by Li, thereby enhance its dehydrogenating properties. Our results are consistent with this theoretical prediction.

4. Conclusions

- 1) NaMgH_3 hydride with perovskite structure has been synthesized by high-energy ball milling and the maximum hydrogen-desorbed amount is 3.42 wt. % at 638 K. The crystallinity of as-milled NaMgH_3 will be improved by above-adopted heat-treatment, but its dehydrogenating properties will be reduced obviously.
- 2) Two decomposition steps have been detected for perovskite-type NaMgH_3 hydride. Based on Kissinger method, calculated values of activation energy for the two steps are 180.25 ± 8.25 kJ/mol (ΔE_1) and 156.23 ± 18.54 kJ/mol (ΔE_2) respectively.
- 3) In comparison with NaMgH_3 hydride, $\text{Li}_{0.5}\text{Na}_{0.5}\text{MgH}_3$ hydride has better dehydrogenating kinetic properties and higher hydrogen-desorbed amount (4.11 wt.%) due to partial replacement of Na by Li, which can release about 90% of the maximum hydrogen-desorbed amount within 28 min.
- 4) LiMgH_3 hydride with perovskite structure cannot be synthesized with the mixture of LiH and MgH_2 hydrides. However, the maximum hydrogen-desorbed amount of this ball-milled mixture is 5.54 wt.% at 638 K, indicating LiH is a good catalyst for dehydrogenation of MgH_2 .

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