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Synthesis and crystal structure of a novel nitride hydride Sr_2LiNH_2

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ABSTRACT

The novel nitride hydride Sr_2LiNH_2 was synthesized by dehydrogenating a $LiNH_2 + 2SrH_2$ mixture at about 330 °C. It was found that Sr_2LiNH_2 crystallizes with a tetragonal structure in space group *I*4/*mmm* (no. 139), and with cell parameters: $a = b = 3.8104(4)$ Å and $c = 13.722(1)$ Å. The crystal structure of Sr_2LiNH_2 can be described as a stacking of [Sr_5Li] octahedra, which is different from those of nitride hydrides of lithium (Li_4NH) and strontium (Sr_2NH) as well as ternary imides (e.g. $Li_2Mg(NH)_2$ and $Li_2Ca(NH)_2$).

1. Introduction

Recently, metal–N–H systems have attracted great attention as potential candidates for hydrogen storage due to their high hydrogen capacity [1–21]. In 2002, Chen et al. [1] first reported that the $LiNH_2$–LiH (1:1) system could reversibly store 6.5 wt.% hydrogen according to the reaction:

$$LiNH_2 + LiH \leftrightarrow Li_2NH + H_2 \quad (1)$$

However, the operation temperature at 1.0 atm equilibrium hydrogen pressure is about 280 °C for reaction (1) [2], which is too high for the practical on-board hydrogen storage applications. In order to improve the thermodynamic properties of binary Li–N–H system, Li was compositionally substituted by other elements, and several types of ternary or multinary metal–N–H systems (e.g. Li–Mg–N–H [5–9], Li–Ca–N–H [10,11], Li–Al–N–H [12–14], Li–B–N–H [12,15], Li–Co–N–H [16] and Li–Mg–Al–N–H [17,18]) were developed.

The existing researches on metal–N–H systems mainly include two aspects. One is investigating the hydrogen absorption/desorption property [1–5,8–18]; the other is revealing the reaction mechanism involved in the hydrogen absorption/desorption processes [1,6,7,14–16,21]. It was reported that the new ternary imides with mixed alkali and alkaline earth cations, $Li_2Mg(NH)_2$ and $Li_2Ca(NH)_2$, were formed along with the dehydrogenation reaction in the Li–Mg–N–H and Li–Ca–N–H systems, respectively [5,8,11,19–21]. The synthetic route involving the reactions between metal amides and hydrides seems to be a new method for the synthesis of novel compound containing nitrogen and hydrogen [19].

For the purpose of enriching the knowledge and prompting the development of metal–N–H systems, our research was focused on the hydrogen storage property and reaction mechanism of $LiNH_2$–SrH_2 system. It was found that a novel nitride hydride Sr_2LiNH_2 was synthesized from the dehydrogenation reaction of the $LiNH_2 + 2SrH_2$ mixture. In the present paper, the synthesis process and crystal structure of Sr_2LiNH_2 are introduced.

2. Experimental details

2.1. Sample preparation

The starting material $LiNH_2$ (95%, J&K Chemical) was purchased and used as-received. SrH_2 powder was synthesized by reacting metallic Sr scraps (99%, Alfa Aesar) with hydrogen (99.999%). The powders of $LiNH_2$ and SrH_2 in a molar ratio of 1:2 were mixed manually, and then ball-milled for 2 h under hydrogen atmosphere (about 0.5 MPa). The ball milling was performed using a QM-1SP2 planetary mill at a rotation speed of 400 rpm, with stainless steel vials (250 ml in volume) and balls (10 mm in diameter). The ball to powder weight ratio was about 20:1. After ball milling, the $LiNH_2 + 2SrH_2$ mixture was vacuumed at room temperature, and then subjected to isothermal processing at the temperatures of 180, 220 and 330 °C, respectively. For keeping the sample from air-exposure, all the sample handling was carried out in an Ar-filled glove box equipped with a purification system, in which the typical O_2/H_2O levels are below 1 ppm.

2.2. Determination of hydrogen amount desorbed

The hydrogen amount desorbed from the as-milled $LiNH_2 + 2SrH_2$ mixture as a function of time was measured using a Sieverts-type apparatus at a constant temperature. Prior to dehydrogenation, the testing system of the apparatus was vacuumed.

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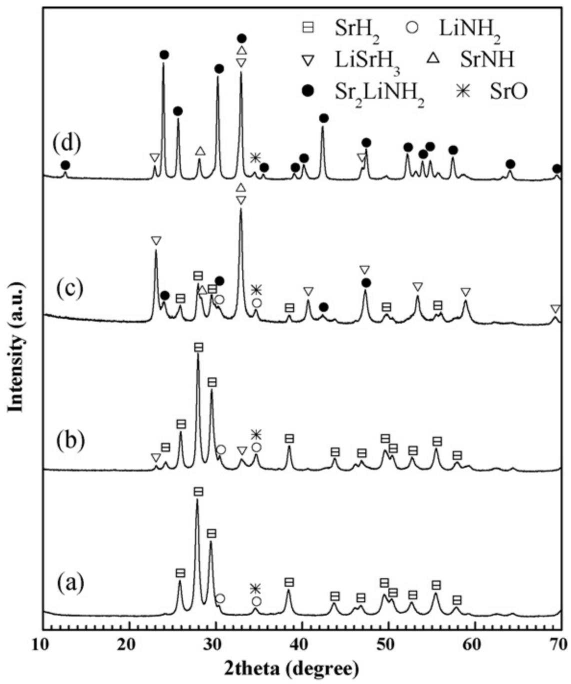

Fig. 1. XRD patterns of the $LiNH_2 + 2SrH_2$ mixture after ball milling (a), as well as after isothermal processing at 180 °C (b), 220 °C (c) and 330 °C (d), respectively.

2.3. Composition and crystal structure characterization

The contents of nonmetallic elements (N and H) in the isothermally processed product of $LiNH_2 + 2SrH_2$ mixture were measured by an element analyzer (Elementar Vario EL III). The temperatures used for the burning and reducing tubes were 950 and 500 °C, respectively. To evaluate the phase structures of the samples, X-ray diffraction (XRD) measurements were carried out using a Rigaku D/Max 2500VL/PC diffractometer with Cu Kα radiation at 50 kV and 150 mA. The XRD samples were loaded and sealed in a special holder that can keep the sample under argon atmosphere in the course of measurement. The software program, TREOR90 [22], was firstly used to index the XRD pattern for Sr_2LiNH_2; the crystal structure of Sr_2LiNH_2 was then determined with the EXPO program [23,24]. Based on the structural model, the XRD profile was finally refined by the Rietveld program RIETAN-2000 [25].

3. Results and discussion

3.1. Synthesis of Sr_2LiNH_2

Fig. 1 presents the XRD patterns of the $LiNH_2 + 2SrH_2$ mixture after ball milling, as well as after isothermal processing at different temperatures. As shown in Fig. 1a, the as-milled $LiNH_2 + 2SrH_2$ mixture is composed of the starting materials, implying that no obvious reaction was occurred during ball milling for 2 h. When the as-milled $LiNH_2 + 2SrH_2$ mixture was isothermally processed at 180 °C, a little amount of $LiSrH_3$ formed (see Fig. 1b). Increasing the heat treatment temperature up to 220 °C, as indicated in Fig. 1c, the phase content of $LiSrH_3$ increased drastically. Moreover, the characteristic diffraction peaks assigned to SrNH appear obviously in Fig. 1c. The results above suggest the occurrence of reaction (2) during the heat treatment process (~220 °C).

$$LiNH_2 + 2SrH_2 \rightarrow LiSrH_3 + SrNH + H_2 \quad (2)$$

Note that, some additional and weak peaks (indicated by solid circle) emerge in Fig. 1c, which indicates the formation of a new phase. In order to increase the yield of the new phase, the as-milled $LiNH_2 + 2SrH_2$ mixture was isothermally processed at 330 °C. As shown in Fig. 1d, the diffraction peaks from the new phase are dominant, while those of $LiSrH_3$ and SrNH are very weak in the XRD pattern. The structure determination (see Section 3.2) shows that the newly formed phase could be expressed as Sr_2LiNH_x. Meanwhile, the element analysis for the product isothermally processed at 330 °C indicates a composition of $Sr_2LiN_{0.95}H_{2.12}$. The nitrogen content calculated by the element analysis agrees well with that obtained by the structure determination.

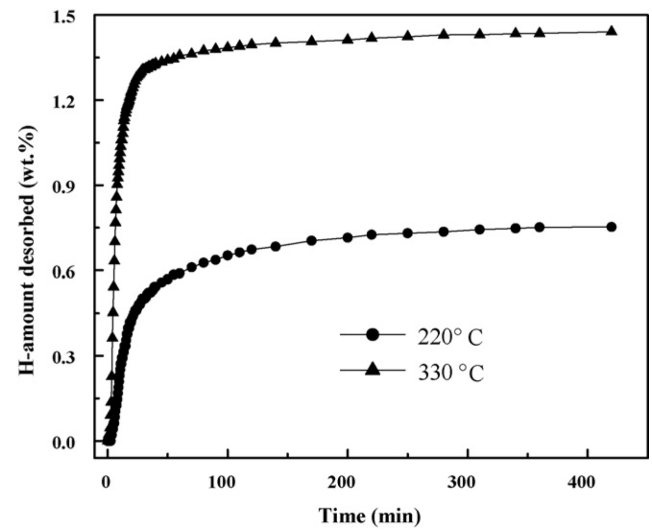

Fig. 2. Time dependences of the hydrogen amount desorbed from the as-milled $LiNH_2 + 2SrH_2$ mixture at 220 and 330 °C, respectively.

To further determine the hydrogen content in the new compound, the hydrogen amount desorbed as a function of time for the as-milled $LiNH_2 + 2SrH_2$ mixture was measured at the temperatures of 220 and 330 °C, respectively. It can be seen from Fig. 2 that the hydrogen amount desorbed at 220 °C is about 0.75 wt.%. In view of that one equivalent (0.99 wt.%) of H_2 per $LiNH_2 + 2SrH_2$ was desorbed during the transformation process from $LiNH_2 + 2SrH_2$ to $LiSrH_3 + SrNH$, reaction (2) was not completed entirely during the isothermal process at 220 °C, which is also confirmed by the XRD pattern in Fig. 1c. Similarly, the hydrogen amount (1.44 wt.%) desorbed at 330 °C should also be lower than its theoretical value. Considering the fact that the hydrogen amount desorbed at 330 °C is about twice as high as that desorbed at 220 °C, the hydrogen gas desorbed must be two equivalents per $LiNH_2 + 2SrH_2$ during the transformation process from $LiNH_2 + 2SrH_2$ to Sr_2LiNH_x. Thus, the x value in Sr_2LiNH_x can be believed to be 2, which is consistent with the value measured by element analysis. Hence, the reaction describing the formation of Sr_2LiNH_2 from the $LiNH_2 + 2SrH_2$ mixture can be written as

$$LiNH_2 + 2SrH_2 \rightarrow Sr_2LiNH_2 + 2H_2 \quad (3)$$

3.2. Crystal structure of Sr_2LiNH_2

The XRD pattern for Sr_2LiNH_2 was indexed to be a tetragonal unit cell in space group $I4/mmm$ (no. 139), which is different from those of nitride hydrides of lithium (Li_4NH, space group $I4_1/a$ [26]) and strontium (Sr_2NH, space group $R\bar{3}m$ [27]) as well as ternary imides co-containing alkali and alkaline earth cations ($Li_2Mg(NH)_2$, space group $Iba2$ [20]; $Li_2Ca(NH)_2$, space group $P\bar{3}m1$ [19]). The cell parameters were determined to be $a = b = 3.8104(4)$ Å and $c = 13.722(1)$ Å. The refined coordinates of non-hydrogen atoms are listed in Table 1. Fig. 3 shows the observed and calculated XRD patterns of the Sr_2LiNH_2 sample prepared by isothermally processing the $LiNH_2 + 2SrH_2$ mixture at 330 °C, indicating that the refined pattern fits the observed data points very well. By the Rietveld analysis, the relative amounts of the Sr_2LiNH_2, $LiSrH_3$, SrNH and SrO phases were determined to be 82, 5, 9 and 4 wt.%, respectively.

The crystal structure of Sr_2LiNH_2 is illustrated in Fig. 4, which is built up from $[Sr_5Li]$ octahedra. Similar to the Sr_2ZnN_2 structure

Table 1
Atomic coordinates, isotropic thermal parameters and occupation numbers for Sr_2LiNH_2 refined from X-ray powder diffraction data.

Atom	Site	*g*	*x*	*y*	*z*	*B* (Å^2)
Sr	4*e*	1	0	0	0.363(1)	1.2(3)
Li	2*a*	1	0	0	0	0.7(3)
N	4*e*	0.5	0	0	0.167(2)	0.8(2)

Note: Space group *I*4/*mmm* (no. 139); cell parameters: $a = b = 3.8104(4)$ Å, $c = 13.722(1)$ Å; $Z = 2$. $R_{wp} = 9.51\%$, $R_p = 7.09\%$, $S = 2.93$. The coordinates of hydrogen atoms were not determined. Bond lengths: Sr–N: 2.73(1) Å × 4, 2.69(1) Å × 1; Li–N: 2.29(1) Å × 2.

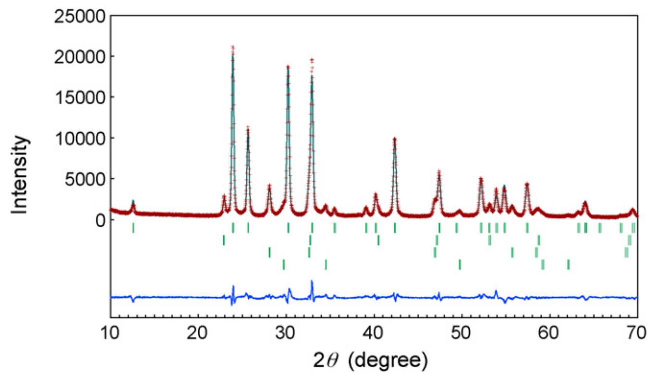

Fig. 3. Rietveld refinement of the XRD pattern for Sr_2LiNH_2 prepared by isothermally processing the $LiNH_2 + 2SrH_2$ mixture at 330 °C. The vertical bars (from above) indicate the positions of Bragg diffraction for Sr_2LiNH_2, $LiSrH_3$, SrNH and SrO, respectively.

[28], the Sr–Sr edge-sharing double octahedral layers are linked by sharing of the apical Li atoms. Somewhat differently, only half of [Sr_5Li] octahedra in the Sr_2LiNH_2 structure are centered by N^{3-}. In the N-centered [Sr_5Li] octahedron, the Sr–N bond lengths ranging from 2.69 to 2.73 Å are in good agreement with those in Sr_2ZnN_2 (2.536–2.733 Å [28]) and the Li–N bond length (2.29 Å) compares well with those in $Li_2Ca(NH)_2$ (2.167–2.291 Å [21]). Unfortunately, the atomic coordinates for hydrogen in Sr_2LiNH_2 structure were not determined since X-ray is not sensitive to hydrogen. Thus it is unknown whether the other half [Sr_5Li] octahedra are occupied by hydrogen atoms. For obtaining the information of H atoms coordinates and metal–H bonds in Sr_2LiNH_2 lattice, further studies on the

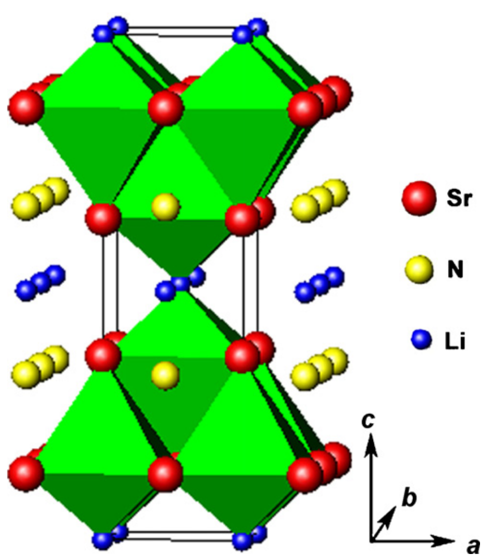

Fig. 4. Crystal structure of Sr_2LiNH_2 compound in which half of the [Sr_5Li] octahedra are centered by N^{3-}. The positions of H atoms were not determined.

structure of the deuteried Sr_2LiNH_2 by using neutron diffraction are in progress.

To be a neutral molecule, N and H in the Sr_2LiNH_2 compound should be negatively charged and not bond with each other, which is similar to the nitride hydrides of single alkali metal or alkaline earth metal (e.g. Li_4NH [26], Ca_2NH [29], Sr_2NH [27] and Ba_2NH [30]). In ternary imides (e.g. $Li_2Mg(NH)_2$ and $Li_2Ca(NH)_2$), however, N and H are covalently bonded to form the imide group $[NH]^{2-}$, in which H is somewhat positively charged [21].

4. Conclusions

In this paper, a new nitride hydride Sr_2LiNH_2 co-containing formal N^{3-} and H^-anions was synthesized by the dehydrogenation reaction between $LiNH_2$ and SrH_2 at about 330 °C. Moreover, the crystal structure of Sr_2LiNH_2 was investigated by XRD. The results showed that Sr_2LiNH_2 crystallizes in space group *I*4/*mmm* (no. 139) with cell parameters of $a = b = 3.8104(4)$ Å and $c = 13.722(1)$ Å. The Sr–Sr edge-sharing double octahedral [Sr_5Li] layers are linked by sharing of the apical Li atoms in the Sr_2LiNH_2 lattice.

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