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<td>Author(s)</td>
<td>Isobe, Shigehito; Ohnuki, Somei; David, William I. F.; Gutmann, Matthias; Jones, Martin O.; Edwards, Peter P.; Ichikawa, Takayuki; Kojima, Yoshitsugu</td>
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Variable Temperature Neutron Diffraction Studies of Single Crystals of LiND₂

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ABSTRACT
We have synthesized a single crystal of lithium amide (LiNH₂, LiND₂) by melting method, and performed neutron diffraction of the single crystal at variable temperature. LiND₂ is tetragonal structure and I–4 space group. Lattice parameters and unit cell volume of LiND₂ at room temperature, 50 °C, 100 °C, 150 °C and 200 °C were determined. Both of the lattice parameters and the unit cell volume increase with increase of temperature. From these results, we have estimated coefficient of volumetric thermal expansion $\alpha_V$ of LiND₂ to be $222 \times 10^{-6}$/K. With increase of temperature, all thermal ellipsoids gradually expand because of thermal vibration.

Key words: hydrogen storage, lithium amide, single crystal, neutron diffraction

1. INTRODUCTION
It is necessary to establish high–performance hydrogen storage (H–storage) technologies, for utilizing hydrogen as one of the secondary energies. Three H–storage containers of liquid hydrogen, high–pressure gas hydrogen and absorbed hydrogen in H–storage materials are considered for future practical use as H–storage tanks. Among them, H–storage materials can more densely store hydrogen than high–pressure gas or liquid hydrogen [1, 2]. Therefore, the tank system using the H–storage materials has been considered as the most suitable one for H–storage. As one of the most promising H–storage materials, variable amide–imide of light metal such as Li, Na, Mg and Ca has been studied [3–16]. Among them, Li–N–H system was firstly reported by Chen et al. [3]. Lithium nitrides can absorb and desorb a large amount of hydrogen in the two consecutive reactions as follows:

$$\text{Li}_3\text{N} + \text{H}_2 \leftrightarrow \text{Li}_2\text{NH} + \text{LiH} \ (1)$$
Lii2NH + H2 ↔ LiNH2 + LiH (2)

So far a lot of research on this system has been reported, such reaction mechanism [5–9], catalytic effect of titanium compound on the dehydrogenating property [10, 11], and thermodynamic property of Li–N–H [12]. In this work, we have synthesized single crystal of lithium amide, and then we have performed thermal analyses and neutron diffraction of the single crystal at variable temperature.

2. EXPERIMENTAL

Single crystal of LiND2 was prepared by heat–treatment of LiND2 powder. Firstly, we prepared the powder of LiND2 by ball–milling of LiD under 0.5 MPa ND3 gas in same method as synthesizing LiNH2 [17]. LiD (98 atom% D) and ND3 (99 atom% D) gas were purchased from Aldrich and ISOTEC, respectively. The powder LiND2 was put into high–pressure cell made of SUS, and 0.5 MPa ND3 gas was introduced at room temperature. Here, ND3 gas can avoid LiND2 decomposing to Li2ND during the heat–treatment. The heat–treatment of the LiND2 powder was programmed as follows,

Step 1: Heating from 20 °C to 400 °C for 2 hrs,
Step 2: Plateau at 400 °C for 40 hrs,
Step 3: Cooling down from 400 °C to 380 °C for 60 hrs,
Step 4: Plateau at 380 °C for 60 hrs,
Step 5: Cooling down from 380 °C to 360 °C for 60 hrs,
Step 6: Cooling down from 360 °C to 260 °C for 20 hrs,
Step 7: Cooling down from 260 °C to 20 °C for 10 hrs.

The melting point of LiND2 is 380 °C, therefore solid LiND2 should be completely melted at Step 2, and then we slowly cool liquid LiND2 for crystal growth. After the heat–treatment, we obtained several granules of LiND2, which are approximately 2*2*2 mm3 of size and transparent, as shown in Figure 1.

Scanning Electron Microscope (SEM) measurement was performed on JEOL JSM–6380. Thermal properties of the single crystal LiNH2 were simultaneously examined by thermogravimetry (TG), differential thermal analysis (DTA), and thermal desorption mass spectroscopy (TDMS) from room temperature to 450 °C with 2 °C/min heating rate. The TG–DTA equipment (Rigaku, TG8120) connected to the TDMS apparatus (Anelva, M–QA200TS) is installed into the glove–box (Miwa MFG Co. Ltd., MP–P60W) filled with purified argon. All treatments are operated without exposing the samples to air for avoiding unexpected reactions with oxygen or moisture.

We performed neutron diffraction measurement at variable temperature of the single crystals on SXD (the Single Crystal Diffractometer) in ISIS [18]. Structural refinements were completed using the GSAS/EXPGUI software package [19].

3. RESULTS AND DISCUSSIONS

The results of TG, DTA and TDMS of the single crystal LiNH2, which was prepared by same method as single crystal LiND2, are shown in Figure 2. Sharp peaks, corresponding to NH3 desorption and endothermic reaction, appear at 374 °C in both profiles of TDMS and DTA, respectively. These peaks should originate with a decomposition from LiNH2 to Li2NH (2LiNH2 → Li3NH + NH3) and melting of LiNH2 itself [7]. Certainly, the weight loss (~40 wt.% at 450 °C) of NH3 desorption by TG agrees with the expected amount from the decomposition. In the case that
we performed DTA and TDMS for powder of LiNH₂ as purchased, which was not single crystal, much broader peaks are shown in those profiles [7].

LiND₂ has a tetragonal structure at room temperature, 50 °C, 100 °C, 150 °C and 200 °C are reported in Table 1. The lattice parameters at room temperature are in agreement with those reported in the literature [20]. Both of the lattice parameters and the unit cell volume increase with increase of temperature, as shown in Figure 2 and 3. From these results, we estimate coefficient of volumetric thermal expansion αᵥ of LiND₂. αᵥ is defined as,

$$\alpha_v = \frac{1}{V} \frac{\Delta V}{\Delta T} \quad (3).$$

The estimated value is 222 * 10⁻⁶/K. (The standard deviation is ± 1.4* 10⁻⁶/K.) Schematic structures with thermal ellipsoids of LiND₂ determined by neutron diffraction at room temperature, 50 °C, 100 °C and 150 °C are shown in Figure 4. The refinements were carried out using GSAS program. With increase of temperature, all thermal ellipsoids gradually expand because of thermal vibration.

4. CONCLUSIONS
We have succeeded to synthesize the single crystal of LiND₂ by the melting method. The melting point of single crystal of LiND₂ is 374 °C with decomposition from LiND₂ to Li₂ND and ND₃. By the results of neutron diffraction on the single crystal at variable temperature, coefficient of volumetric thermal expansion αᵥ of LiND₂ is estimated to be 222 * 10⁻⁶/K. Schematic structures with thermal ellipsoids of LiND₂ determined by neutron diffraction show that all thermal ellipsoids gradually expand because of thermal vibration with increase of temperature. For designing the tank of hydrogen storage materials in Fuel Cell Vehicle, it is important for to consider the volumetric thermal coefficient of hydrogen storage materials.

ACKNOWLEDGMENTS
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REFERENCES


[18]. http://www.isis.rl.ac.uk/Crystallography/SXD/


Figure captions

Figure 1
Picture and SEM image of single crystal LiNH₂, which was synthesized from LiH and NH₃ by same method as LiND₂

Figure 2
Thermal properties (TG, DTA and TDMS with 2 °C/min heating rate) of single crystal LiNH₂, which was synthesized from LiH and NH₃ by same method as LiND₂

Figure 3
Plot of lattice parameters “a, b” and “c” at room temperature, 50 °C, 100 °C, 150 °C and 200 °C
Figure 4
Plot of unit cell volume at room temperature, 50 °C, 100 °C, 150 °C and 200 °C

Figure 5
Schematic structures with thermal ellipsoids of LiND$_2$ determined by neutron diffraction at room temperature, 50 °C, 100 °C and 150 °C, refined using GSAS/EXPGUI software

Table 1
Structural parameters of single crystal LiND$_2$ at room temperature, 50 °C, 100 °C, 150 °C and 200 °C

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<th>Parameter</th>
<th>Room Temp.</th>
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<td>Space group</td>
<td>tetragonal</td>
<td></td>
<td></td>
<td></td>
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<td>Structure</td>
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<td></td>
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<tr>
<td>a</td>
<td>5.0369 (17)</td>
<td>5.0459 (8)</td>
<td>5.0533 (8)</td>
<td>5.0972 (10)</td>
<td>5.1102 (10)</td>
</tr>
<tr>
<td>b</td>
<td>5.0369</td>
<td>5.0459</td>
<td>5.0533</td>
<td>5.0972</td>
<td>5.1102</td>
</tr>
<tr>
<td>c</td>
<td>10.284 (4)</td>
<td>10.2818 (18)</td>
<td>10.2953 (18)</td>
<td>10.3573 (22)</td>
<td>10.3510 (24)</td>
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<tr>
<td>Unit cell volume</td>
<td>260.91 (16)</td>
<td>261.79 (7)</td>
<td>262.90 (7)</td>
<td>269.10 (9)</td>
<td>270.31 (10)</td>
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Figure 2
Figure 3
Figure 4