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## Variable Temperature Neutron Diffraction Studies of Single Crystals of LiND<sub>2</sub>

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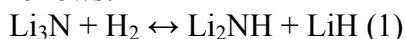
### ABSTRACT

We have synthesized a single crystal of lithium amide (LiNH<sub>2</sub>, LiND<sub>2</sub>) by melting method, and performed neutron diffraction of the single crystal at variable temperature. LiND<sub>2</sub> is tetragonal structure and I-4 space group. Lattice parameters and unit cell volume of LiND<sub>2</sub> 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 LiND<sub>2</sub> to be  $222 \cdot 10^{-6}/K$ . 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:





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 LiND<sub>2</sub> was prepared by heat-treatment of LiND<sub>2</sub> powder. Firstly, we prepared the powder of LiND<sub>2</sub> by ball-milling of LiD under 0.5 MPa ND<sub>3</sub> gas in same method as synthesizing LiNH<sub>2</sub> [17]. LiD (98 atom% D) and ND<sub>3</sub> (99 atom% D) gas were purchased from Aldrich and ISOTEC, respectively. The powder LiND<sub>2</sub> was put into high-pressure cell made of SUS, and 0.5 MPa ND<sub>3</sub> gas was introduced at room temperature. Here, ND<sub>3</sub> gas can avoid LiND<sub>2</sub> decomposing to Li<sub>2</sub>ND during the heat-treatment. The heat-treatment of the LiND<sub>2</sub> 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 LiND<sub>2</sub> is 380 °C, therefore solid LiND<sub>2</sub> should be completely melted at Step 2, and then we slowly cool liquid LiND<sub>2</sub> for crystal growth. After the heat-treatment, we obtained several granules of LiND<sub>2</sub>, which are approximately 2\*2\*2 mm<sup>3</sup> 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 LiNH<sub>2</sub> 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 LiNH<sub>2</sub>, which was prepared by same method as single crystal LiND<sub>2</sub>, are shown in Figure 2. Sharp peaks, corresponding to NH<sub>3</sub> desorption and endothermic reaction, appear at 374 °C in both profiles of TDMS and DTA, respectively. These peaks should originate with a decomposition from LiNH<sub>2</sub> to Li<sub>2</sub>NH (2LiNH<sub>2</sub> → Li<sub>2</sub>NH + NH<sub>3</sub>) and melting of LiNH<sub>2</sub> itself [7]. Certainly, the weight loss (–40 wt.% at 450 °C) of NH<sub>3</sub> desorption by TG agrees with the expected amount from the decomposition. In the case that

we performed DTA and TDMS for powder of LiNH<sub>2</sub> as purchased, which was not single crystal, much broader peaks are shown in those profiles [7].

LiND<sub>2</sub> 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  $\alpha_V$  of LiND<sub>2</sub>.  $\alpha_V$  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  $\pm 1.4 * 10^{-6}/K$ .) Schematic structures with thermal ellipsoids of LiND<sub>2</sub> 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 LiND<sub>2</sub> by the melting method. The melting point of single crystal of LiND<sub>2</sub> is 374 °C with decomposition from LiND<sub>2</sub> to Li<sub>2</sub>ND and ND<sub>3</sub>. By the results of neutron diffraction on the single crystal at variable temperature, coefficient of volumetric thermal expansion  $\alpha_V$  of LiND<sub>2</sub> is estimated to be  $222 * 10^{-6}/K$ . Schematic structures with thermal ellipsoids of LiND<sub>2</sub> 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.

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## Figure captions

### Figure 1

Picture and SEM image of single crystal  $\text{LiNH}_2$ , which was synthesized from  $\text{LiH}$  and  $\text{NH}_3$  by same method as  $\text{LiND}_2$

### Figure 2

Thermal properties (TG, DTA and TDMS with 2 °C/min heating rate) of single crystal  $\text{LiNH}_2$ , which was synthesized from  $\text{LiH}$  and  $\text{NH}_3$  by same method as  $\text{LiND}_2$

### 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<sub>2</sub> 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<sub>2</sub> at room temperature, 50 °C, 100 °C, 150 °C and 200 °C

Parameter	Room Temp.	50 °C	100 °C	150 °C	200 °C
Structure	tetragonal				
Space group	I-4				
a	5.0369 (17)	5.0459 (8)	5.0533 (8)	5.0972 (10)	5.1102 (10)
b	5.0369	5.0459	5.0533	5.0972	5.1102
c	10.284 (4)	10.2818 (18)	10.2953 (18)	10.3573 (22)	10.3510 (24)
Unit cell volume	260.91 (16)	261.79 (7)	262.90 (7)	269.10 (9)	270.31 (10)

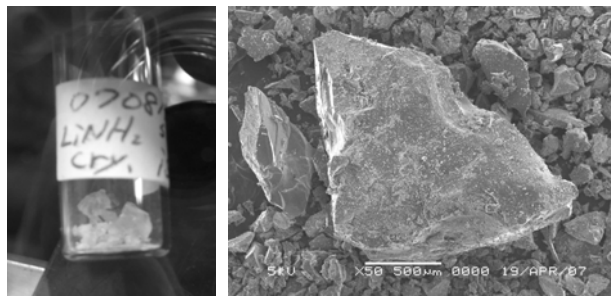


Figure 1

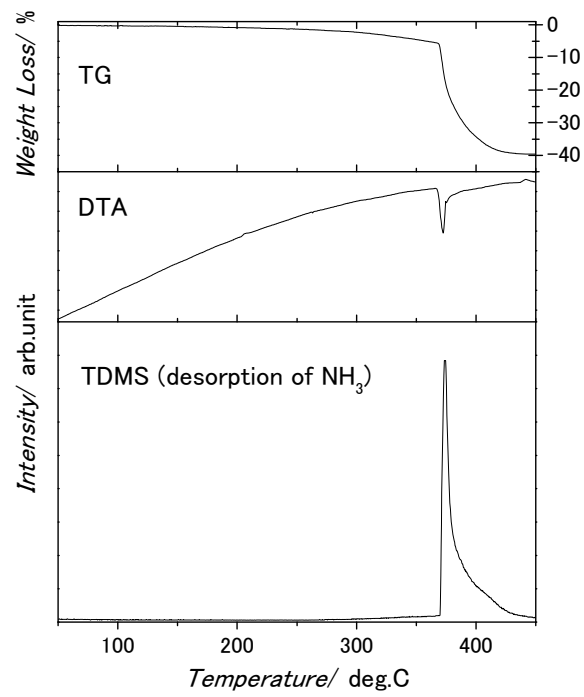


Figure 2



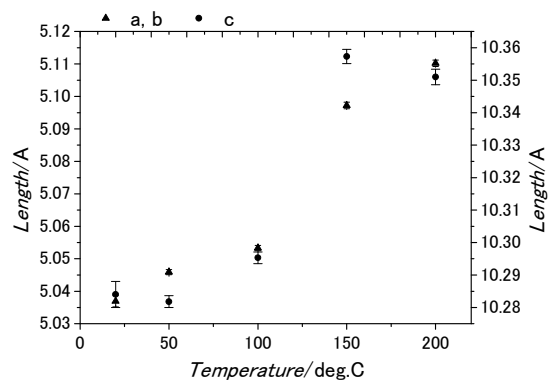


Figure 3

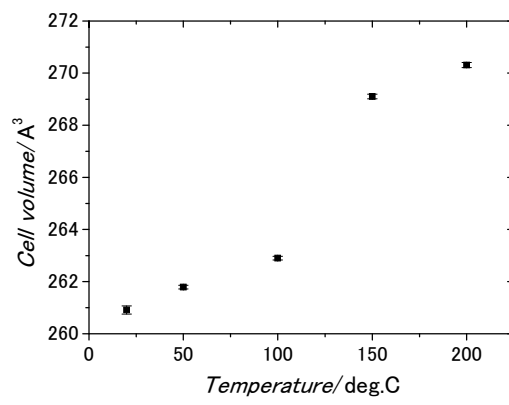


Figure 4

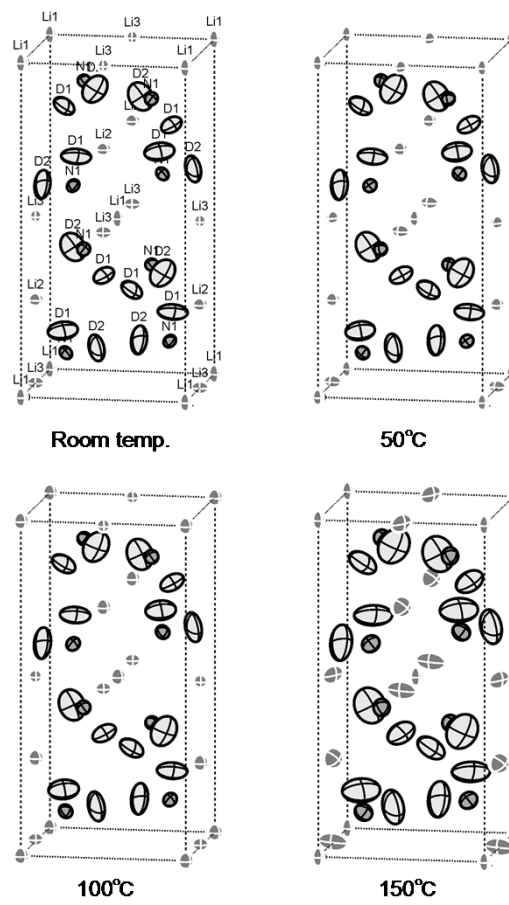


Figure 5