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

Shigehito Isobe, Somei Ohnuki
Graduate School of Engineering, Hokkaido University

N-13, W-8
Sapporo 0608628, Japan

William I. F. David, Matthias Gutmann
ISIS Facility, Rutherford Appleton Laboratory

Chilton, Didcot
Oxon OX11 0QX, U.K.

Martin O. Jones, Peter P. Edwards
Inorganic Chemistry Laboratory, University of Oxford

South Parks Road
Oxford OX1 3QR, U.K.

Takayuki Ichikawa, Yoshitsugu Kojima
Institute for Advanced Materials Research, Hiroshima University

1-3-1 Kagamiyama
Higashi Hiroshima 739-8530, Japan

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 α_V of LiND₂ to be $222 \times 10^{-6}/\text{K}$. 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 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 ($2\text{LiNH}_2 \rightarrow \text{Li}_2\text{NH} + \text{NH}_3$) 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 α_V of LiND₂. α_V is defined as,

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

The estimated value is $222 \times 10^{-6}/\text{K}$. (The standard deviation is $\pm 1.4 \times 10^{-6}/\text{K}$.) 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 α_V of LiND₂ is estimated to be $222 \times 10^{-6}/\text{K}$. 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.

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Figure captions

Figure 1

Picture and SEM image of single crystal LiNH_2 , which was synthesized from LiH and NH_3 by same method as LiND_2

Figure 2

Thermal properties (TG, DTA and TDMS with 2 °C/min heating rate) of single crystal LiNH_2 , which was synthesized from LiH and NH_3 by same method as 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 LiND₂ 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 LiND₂ 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