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Variable temperature neutron diffraction studies of single crystals of $LiND_2$

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ABSTRACT

We have synthesized a single crystal of lithium amide ($LiNH_2$, $LiND_2$) by melting method, and performed neutron diffraction of the single crystal at variable temperature. $LiND_2$ is tetragonal structure and I–4 space group. Lattice parameters and unit cell volume of $LiND_2$ 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 $LiND_2$ to be 222×10^{-6}/K. With increase of temperature, all thermal ellipsoids gradually expand because of thermal vibration.

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:

$$Li_3N + H_2 \leftrightarrow Li_2NH + LiH \quad (1)$$

$$Li_2NH + H_2 \leftrightarrow LiNH_2 + LiH \quad (2)$$

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.

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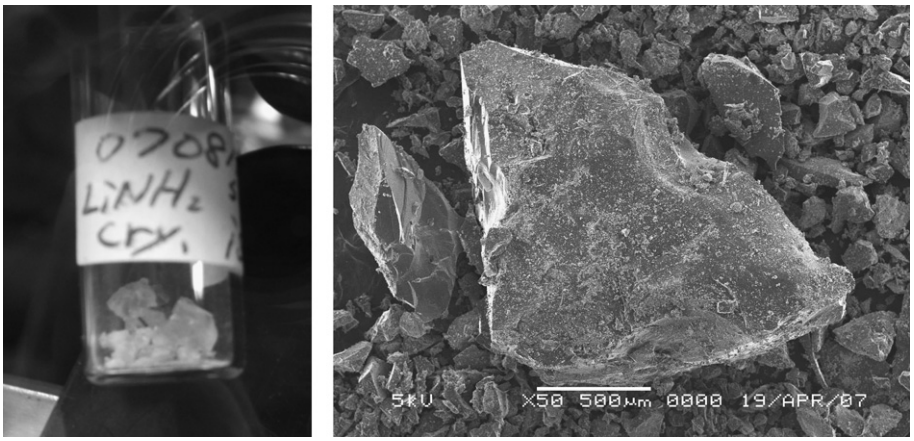

Fig. 1 – Picture and SEM image of single crystal $LiNH_2$, which was synthesized from LiH and NH_3 by same method as $LiND_2$.

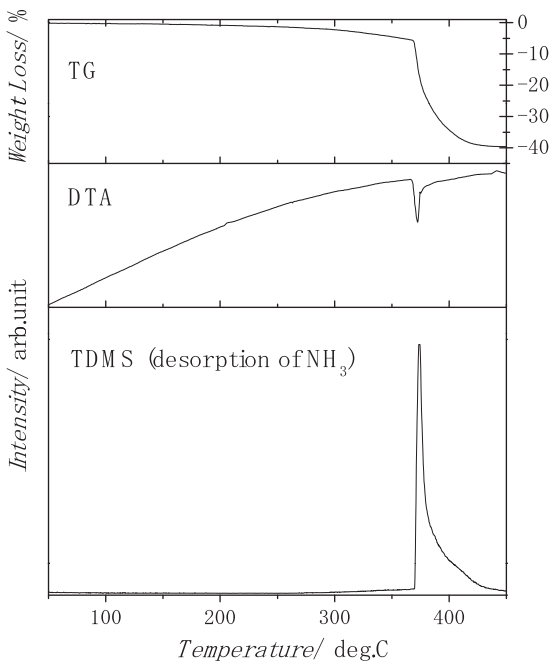

Fig. 2 – Thermal properties (TG, DTA and TDMS with 2 °C/min heating rate) of single crystal $LiNH_2$, which was synthesized from LiH and NH_3 by same method as $LiND_2$.

2. Experimental

Single crystal of $LiND_2$ was prepared by heat–treatment of $LiND_2$ powder. Firstly, we prepared the powder of $LiND_2$ by ball–milling of LiD under 0.5 MPa ND_3 gas in same method

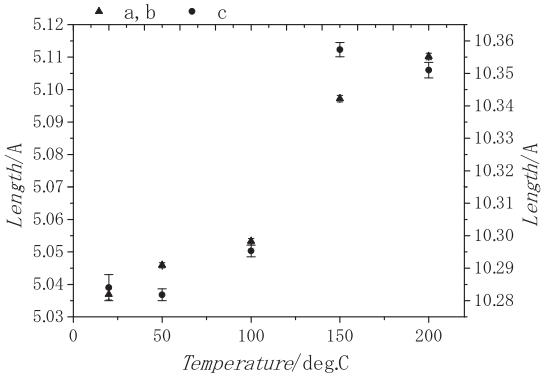

Fig. 3 – Plot of lattice parameters "a, b" and "c" at room temperature, 50 °C, 100 °C, 150 °C and 200 °C.

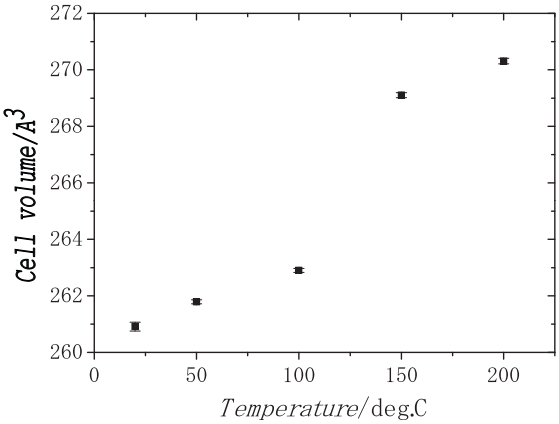

Fig. 4 – Plot of unit cell volume at room temperature, 50 °C, 100 °C, 150 °C and 200 °C.

Table 1 – Structural parameters of single crystal $LiND_2$ 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)