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# Changes of nitrides characteristics in Li–N system synthesized at different pressures



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### ABSTRACT

For the Li–N system samples were obtained at pressures of nitrogen from 1 to 10 atm. Energy-dispersive X-ray (EDX) spectrum of a sample of Li–N subjected to degradation shows that lithium nitride turned into carbonate as evidenced by the predominant content of carbon and oxygen. Upon synthesis of lithium nitride at a positive pressure of nitrogen, the  $\beta$ -modification is formed, which can be achieved at a pressure 500 times lower than that described in literature, required to create a high-pressure phase. The increase in carbon content with increasing of synthesis pressure of lithium nitride confirms the change in stoichiometry of its structure formed with high nitrogen content.

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# 1. Introduction

Lithium nitride is the only nitride which is formed in interaction of lithium with nitrogen at room temperature; the increase in pressure and temperature accelerates the reaction [1-3]. The phase diagram of the Li–N system (Fig. 1), known from the literature data [4], indicates the presence of only one compound, namely Li<sub>3</sub>N.

Lithium nitride has two crystalline modifications,  $\alpha$  and  $\beta$ . The former belongs to the space group P6/mmm and has cell parameters a = 0.3655 nm and c = 0.3876 nm. The crystalline structure of this modification consists of two types of layers: one has the composition Li<sub>2</sub>N<sup>-</sup> and consists of six coordinated Li centers, and another one consists of lithium cations [3]. At a pressure of 0.5–0.6 GPa,  $\alpha$ -modification transforms into  $\beta$ -modification [5–8] with space group  $P6_3/mmc$  and cell parameters a = 0.3579 nm and c = 0.6360 nm. The solid lithium nitride is an ion conductor and has the highest conductivity among all inorganic lithium salts. It is studied as a solid electrolyte and anode material and can be used in accumulator batteries [3,9-11]. The solid lithium nitride can be formed by direct reaction of the elements as well as by indirect one, for example, when nitrogen reacts with lithium dissolved in liquid metallic sodium [12]. Due to its high hydrogen uptake capacity, lithium nitride is used as hydrogen storage material [13–15]. It should also be noted that lithium nitride serves as a catalyst for the formation of the cubic modification of boron nitride, significantly influencing the structure and characteristics of the latter [16,17].

The phase diagram shown in Fig. 1 describes the behavior of the Li–N system at atmospheric pressure [4]. To the best of our knowledge, the information on the effect of pressure on the characteristics of this system is missing. In this regard, the study of changes in the characteristics of nitrides in the Li–N system at different pressures of synthesis is of particular interest and represents the aim of the current investigation.

# 2. Experimental

#### 2.1. Materials synthesis

Lithium nitride was obtained as follows. After the LE-1 grade ingots of lithium metal with purity higher than 99.9% (Russian State Standard GOST 8774-75) were placed in a hermetic box, they were purged with high purity argon (Russian State Standard GOST 10157-79). The protective paraffin film was then removed from the surface with the Nefras C2-80 solvent (Russian State Standard GOST 443-76). After that the samples were cut in the form of parallelepipeds with linear dimensions  $1 \times 1 \times 10$ ,  $2 \times 2 \times 10$ , and  $3 \times 3 \times 10$  cm. The fabricated samples were placed in a crucible made of stainless steel, which in turn was placed into the reactor. The reactor was removed from the box and joined to the gas heating system. After being connected, the reactor was purged with high purity nitrogen (Russian State Standard GOST 9293-74); upon completion, the reactor was sealed hermetically, and the injection of pressure was carried out to the required parameters. After 15-min waiting period, the heating was turned onto predetermined temperature. The heating rate varied by  $1-3^{\circ}$  per minute. After being held at this temperature



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Fig. 1. Phase diagram of the system Li-N [4].

both the samples and the reactor were cooled; then the samples were removed and placed in a box. The Li–N system samples were obtained in a nitrogen atmosphere under pressures of 1–10 atm. After being purged with argon, the samples were withdrawn, weighed, and ground down to grain size of less than one millimeter.

#### 2.2. Powder X-ray diffraction

The obtained Li–N powder samples were investigated by X-ray diffraction (XRD) analysis using a DRON-3.0 diffractometer (Cu K $\alpha$  radiation) at Scientific and Practical Materials Research Centre of National Academy of Sciences of Belarus.

#### 2.3. SEM-EDX analysis

The samples were mounted on carbon planchettes as pure crystals. The images and the electron beam-induced X-ray spectra were obtained using the existing research infrastructure at the Dunarea de Jos University of Galati, Romania, consisting of a scanning electron microscope (SEM) of Quanta 200 FEI type, an energy-dispersive X-ray microanalysis (EDX) integrated system, 5 detectors of secondary and backscattered electrons, 1 detector for transmitted electrons, and the software for data processing, quantification of chemical composition using ZAF (Z – atomic number, A – absorption, F – fluorescence) correction algorithm, multipoint chemical analysis with matrix effects corrections, and the analysis of concentration profile along a defined line.

# 3. Results and discussion

Typical EDX spectra of Li–N samples obtained at different synthesis pressures subjected to decomposition are shown in Fig. 2 (for 6 atm) and Fig. 1S (Supplementary Material) (for 8 and 9 atm). It follows from these spectra that lithium nitride turned into carbonate, as evidenced by the predominant content of carbon and oxygen. Also, EDX analysis demonstrates the presence of structures with higher nitrogen content as a function of nitrogen pressure (Fig. 1S).

The SEM images of powder materials of Li–N system obtained at pressures of 1–10 atm are shown in Fig. 3 (for 3, 8 and 10 atm) and Fig. 2S (for 1, 2, 4, 5, 6, 7 and 9 atm) (Supplementary Material). These images show the presence of particles of irregular shape, indicating a high reaction rate of their formation. It should be noted that as the pressure increases, the number of small-sized particles also grows.



Fig. 2. A typical EDX spectrum of powder material of Li–N system obtained at a synthesis pressure of 6 atm after the decomposition.



**Fig. 3.** SEM images of powder materials of Li–N system synthesized at: (a) 3 atm; (b) 8 atm; and (c) 9 atm.

The XRD analysis results are shown in Fig. 4. It should be noted that the obtained lattice parameters are in close agreement with



**Fig. 4.** Dependence of *a* (curve 1) and *c* (curve 2) lattice parameters of  $\beta$ -modification of lithium nitride on the pressure of nitrogen during synthesis at a heating rate of 3° per minute.

the literature values of  $\beta$ -modification [7,8]. Details of XRD patterns with typical peaks used to calculate the lithium nitride lattice parameters obtained at a pressure of 3, 6 and 9 atm are presented in Fig. 5a–c, respectively, showing the structure modification as a function of nitrogen pressure during growing conditions.

As pointed out in [5–7],  $\alpha \rightarrow \beta$  transition in lithium nitride occurs at pressures of 0.5–0.6 GPa, which were not achieved during the process of synthesis (synthesis pressure in this work was of about 1.012 MPa). Thus, one can conclude that the formation of  $\beta$ -structure occurs at lower energy consumption than its transformation. Therefore, it can be assumed that in order to obtain high pressure structures in the process of formation, it is not necessary to use the pressure of the phase transition, but a rather certain minimum pressure, which is 500 times lower.

Moreover, it should be noted that the change in lattice parameters is of linear character, which is similar to the change of the given characteristics in solid solutions.

The increase in pressure most likely leads to the formation of structures which are more saturated with nitrogen.

The decomposition of lithium nitride in air was carried out to measure powder materials content present in reaction products. Chemical composition of the air at the time of decomposition of the samples was the same for all experiments (oxygen 19.1%; nitrogen 77.9%; carbon dioxide 0.1%; inert gases 1%; water – moisture in the air – 1.9%). Fig. 6 shows the dependence of carbon (1) and oxygen (2) contents on the synthesis pressure of these materials.

The standard mechanism of decomposition is as follows:

- 1. Absorption of air moisture.
- 2. Reaction  $Li_3N + 3H_2O \rightarrow 3LiOH + NH_3$ .
- 3. Surface absorption of CO<sub>2</sub>.
- 4. Reaction LiOH +  $CO_2 \rightarrow Li_2CO_3 + H_2O$ .

The obtained results confirm sufficiently the proposed mechanism, taking into consideration that part of the formed water had evaporated, and some of it remained in the crystalline form (the ratio of carbon to oxygen was 1:3.5(4)).

Thus, the increase in carbon content with increasing synthesis pressure of lithium nitride confirms the change in stoichiometry of the structure (the structure is formed with high nitrogen content). The oxygen content reduction may be indicative of structural changes occurring not only in the near-surface layer.



**Fig. 5.** Typical peaks in XRD pattern used to calculate the lithium nitride lattice parameters obtained at a pressure of: (a) 3 atm; (b) 6 atm; and (c) 9 atm. 2θ angles of 55.5° and 70.7° correspond to (112) and (203) reflections, respectively.



Fig. 6. Dependence of carbon (1) and oxygen (2) contents (in %) after the decomposition on the synthesis pressure of nitride in the Li–N system.

# 4. Conclusions

- 1. When lithium nitride is being synthesized at positive pressure of nitrogen,  $\beta$ -modification is formed, which can be achieved at a pressure 500 times higher; this allows one to hypothesize the minimum pressure required to create high-pressure phases.
- The increase in nitrogen pressure during the formation of nitrides results in the formation of structures with higher nitrogen content in the volume and smaller size of crystallite, as shown by EDX analysis and SEM micrographs.

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# Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.jallcom.2013.06. 173.

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