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CHANGES OF NITRIDES CHARACTERISTICS  
IN Li–N SYSTEM SYNTHESIZED  
AT DIFFERENT PRESSURES

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Изменение характеристик нитридов в системе Li–N при различном давлении синтеза

При давлении азота от 1 до 10 атм были получены образцы нитрида лития в системе Li–N. Энергодисперсионные рентгеновские спектры образцов Li–N, подвергнутых разложению, показали, что нитрид лития превращается в карбонат с преобладающим содержанием углерода и кислорода. Во время получения нитрида лития при избыточном давлении азота образуется  $\beta$ -модификация, которая могла быть достигнута при давлении в 500 раз выше, что позволяет сделать предположение о создании минимального давления, необходимого для получения фазы высокого давления. Увеличение содержания углерода с ростом давления синтеза нитрида лития подтверждает изменение в стехиометрии его структуры, сформированной с высоким содержанием азота.

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Changes of Nitrides Characteristics in Li–N System Synthesized at Different Pressures

Lithium nitride samples were obtained in Li–N system at nitrogen pressure 1–10 atm. Energy-dispersive X-ray (EDX) spectrum of Li–N samples subjected to decomposition demonstrates that lithium nitride is converted into carbonate revealing predominant content of carbon and oxygen. When lithium nitride is being synthesized at positive pressure of nitrogen,  $\beta$ -modification, which can be achieved at pressure 500 times higher, is formed; this allows one to hypothesize the minimum pressure required to create a high-pressure phase. The increase in carbon content with increasing synthesis pressure of lithium nitride confirms the change in stoichiometry of its structure formed with high nitrogen content.

The investigation has been performed at the Frank Laboratory of Neutron Physics, JINR.

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## INTRODUCTION

Lithium nitride is the only nitride, which is formed in interaction with nitrogen at room temperature; the increase in pressure and temperature accelerates the reaction [1]. The phase diagram of the Li–N system (Fig. 1), known from the literature data [2], indicates the presence of only one compound, namely  $\text{Li}_3\text{N}$ .

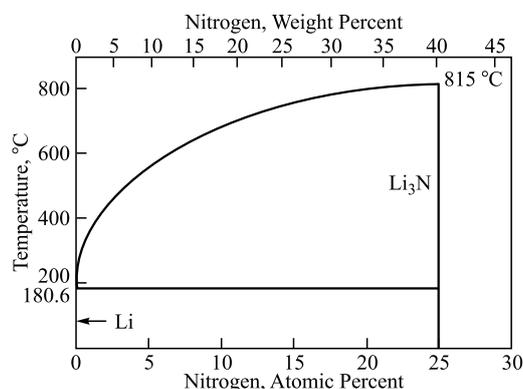


Fig. 1. Phase diagram of the Li–N system [2]

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  $\text{Li}_2\text{N}^-$  and consists of six coordinated Li centers, and another one consists of lithium cations. At a pressure of 0.5–0.6 GPa,  $\alpha$ -modification transforms into  $\beta$ -modification with space group  $P6_3/mmm$  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]. 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 [4].

It should also be noted that lithium nitride serves as a catalyst for the formation of the cubic modification of boron nitride as well as significantly influences

the structure and characteristics of the latter [5,6]. The phase diagram shown in Fig. 1 describes the behavior of the Li–N system at atmospheric pressure. 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.

## EXPERIMENTAL

**Materials and methods.** Lithium nitride was obtained as follows. After the LE-1 grade ingots of lithium metal (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-minute waiting period, the heating was turned on to predetermined temperature. The heating rate varied by 1 to 3 degrees per minute. After being held at this temperature, 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 1 to 10 atm. After being purged with argon, the samples were withdrawn, weighed, and ground down to grain size of less than one millimeter. The obtained samples were investigated by X-ray diffraction analysis.

**EDX Spectra and SEM Imaging.** 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 University Dunarea de Jos 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.

A typical EDX spectrum of Li–N samples subjected to decomposition is shown in Fig.2. It follows from this spectrum that lithium nitride turned into carbonate, as evidenced by the predominant content of carbon and oxygen.

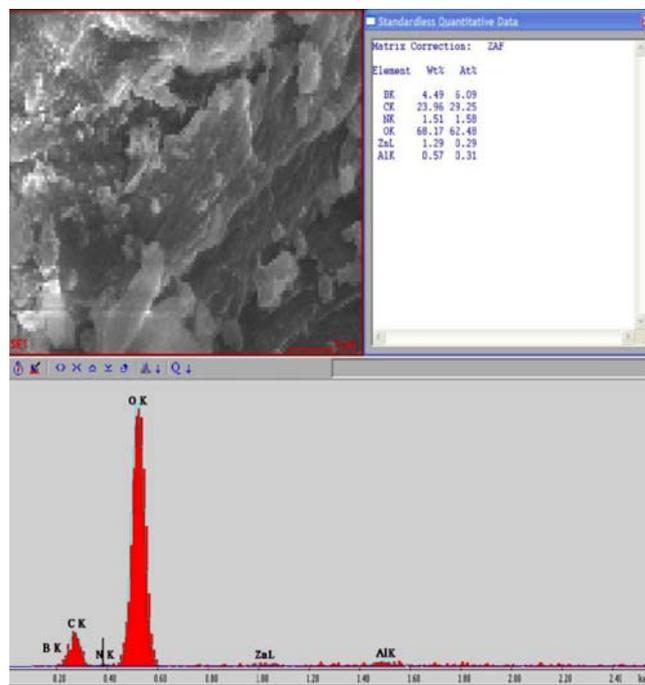


Fig. 2. A typical Li-N EDX spectrum of powder material after decomposition obtained at synthesis pressure of 7 atm

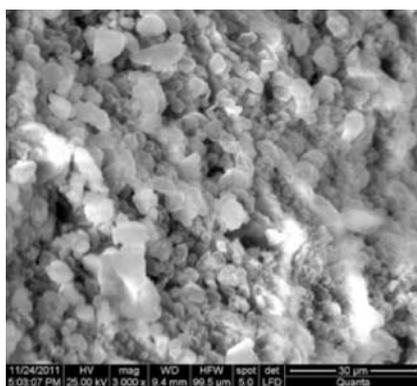


Fig. 3. Powder materials of Li-N system synthesized at 1 atm

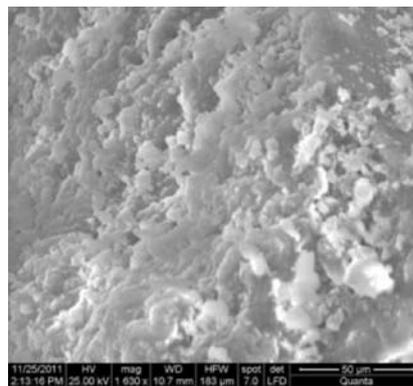


Fig. 4. Powder materials of Li-N system synthesized at 2 atm

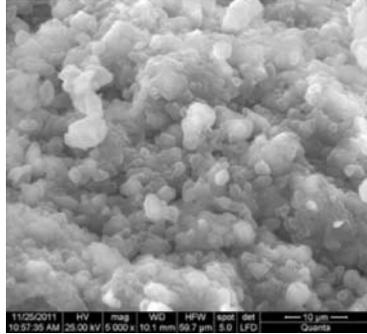


Fig. 5. Powder materials of Li-N system synthesized at 3 atm

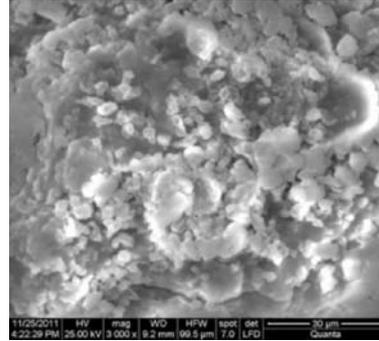


Fig. 6. Powder materials of Li-N system synthesized at 4 atm

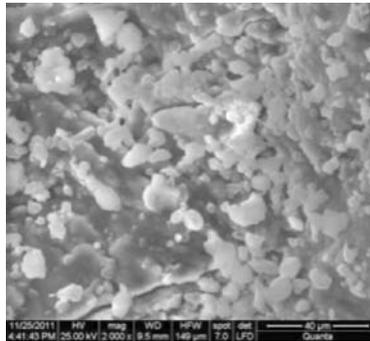


Fig. 7. Powder materials of Li-N system synthesized at 5 atm

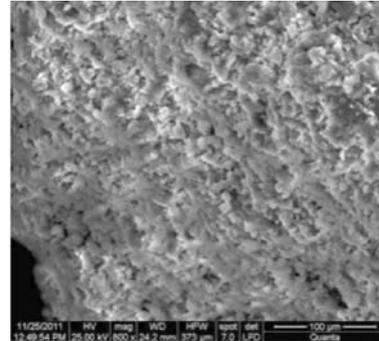


Fig. 8. Powder materials of Li-N system synthesized at 6 atm

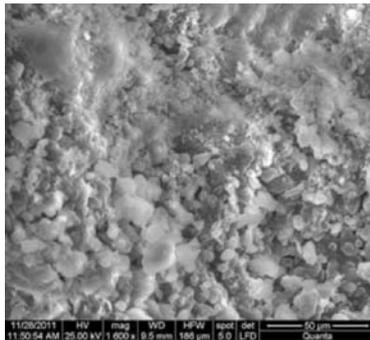


Fig. 9. Powder materials of Li-N system synthesized at 7 atm

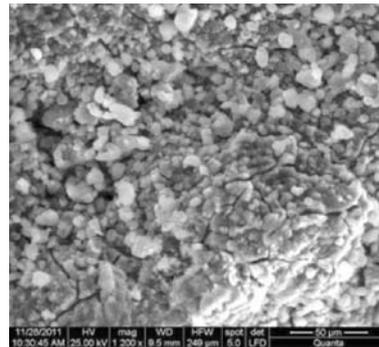


Fig. 10. Powder materials of Li-N system synthesized at 8 atm

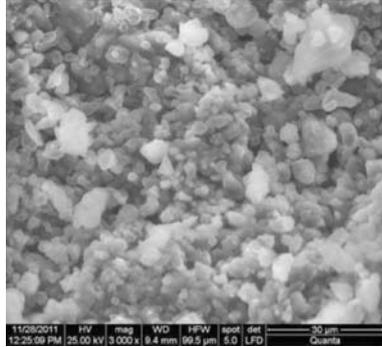


Fig. 11. Powder materials of Li-N system synthesized at 9 atm

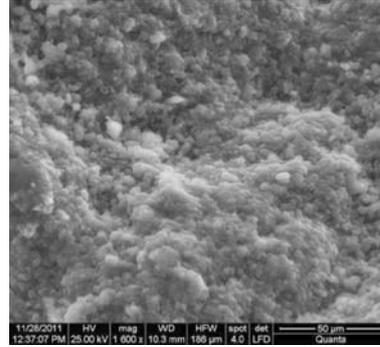


Fig. 12. Powder materials of Li-N system synthesized at 10 atm

The powder materials of Li-N system obtained at pressures of 1–10 atm are shown in Figs. 3–12.

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.

**X-Ray Diffraction Analysis.** The X-ray diffraction analysis results obtained with a DRON-3.0 diffractometer are shown in Fig. 13.

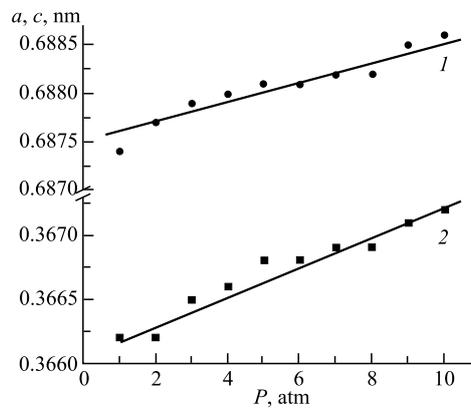


Fig. 13. The dependence of  $a$  and  $c$  lattice parameters of lithium nitride on the pressure of nitrogen during synthesis at a heating rate of 3 degrees per minute (curves 1 and 2)

It should be noted that the obtained lattice parameters are in close agreement with the literature values of  $\beta$ -modification. As pointed out in [3],  $\alpha \rightarrow \beta$  transition in lithium nitride occurs at pressures of 0.5–0.6 GPa, which were not achieved during the process of synthesis (synthesis pressure was about 1.012 MPa).

Thus, one can conclude that the formation of  $\beta$ -structure occurs at lower energy consumption than its transformation. Therefore, one can assume 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 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. Fig. 14 shows the dependence of carbon (1) and oxygen (2) contents on the synthesis pressure of these materials.

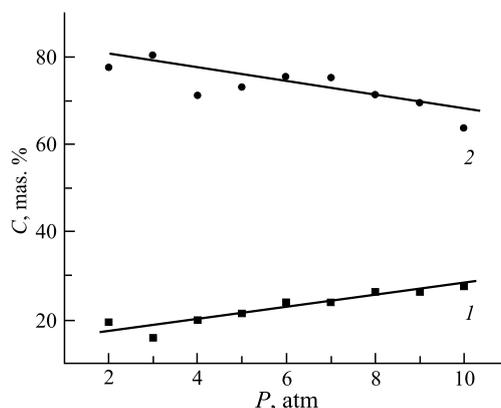


Fig. 14. The dependence of carbon (1) and oxygen (2) contents after decomposition on the synthesis pressure of nitride in the Li-N system

The standard mechanism of decomposition is as follows:

1. absorption of air moisture
2. reaction  $\text{Li}_3\text{N} + 3\text{H}_2\text{O} \rightarrow 3\text{LiOH} + \text{NH}_3$
3. surface absorption of  $\text{CO}_2$
4. reaction  $\text{LiOH} + \text{CO}_2 \rightarrow \text{Li}_2\text{CO}_3 + \text{H}_2\text{O}$

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.



## CONCLUSION

1. When lithium nitride is being synthesized at positive pressure of nitrogen,  $\beta$ -modification, which can be achieved at pressure 500 times higher, is formed; this allows one to hypothesize the minimum pressure required to create high-pressure phases.

2. 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.

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