Plasma technologies application for building materials surface modification

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Abstract. Low-temperature plasma modification of LiYF$_4$ crystal surface in Helium atmosphere caused microhardness decreasing and increasing of roughness of crystal surface. The change of microhardness and morphology is a possible result of Fluorine outgoing from material structure due to heating of surface and plasma chemical reactions and ingoing of Oxygen. As a result of exchange and diffusion processes crystal surface structure become more crumbly, its morphology and mechanical properties change.

1. Introduction
Low-temperature has wide application in different kinds of industry [1-4], including optics, where it is used for surface cleaning, deposition and assisting with deposition of thin functional coatings [5]. Ion’s low energy allows using low-temperature plasma also for modification of some crystals surface, i.e. LiYF$_4$. That crystal is used in laser systems [6], it has relatively high surface microhardness, that prevents its high quality finishing.

The aim of this article is low-temperature plasma modification of LiYF$_4$ crystal surface for increasing of quality of this crystal finishing. To achieve this goal crystal surface was processed by Helium low-temperature RF plasma at atmosphere pressure in the presence of water vapour.

2. Experiments
Experimental unit consists of chamber, RF poser supply, gas supply system. Functional scheme of experimental unit is shown on Fig. 1. The upper and bottom electrodes are situated in chamber vertically and coaxially. The upper electrode is RF power supplied (frequency 13.56 MHz, power up to 50 W) and bottom electrode is grounded. Distance between electrodes was 5 mm. Both electrodes are made from stainless steel and have cylinder form for evenly plasma processing of crystal. The crystal LiYF$_4$ (Fig. 2) was put on the bottom electrode. There was a barrier layer between crystal and bottom electrode. Passive Aluminum radiators was used for electrode cooling and situated outside the chamber. Between RF power supply (“Magniterm LCL”, Russia) and upper electrode there was a matcher. Helium with maximum humidity was supplied through gas inlet.
Atom force microscope NT-MDT Solver P47H was used for measurements of morphology. Microhardness was measured by hardness measuring unit PMT-3. Parameters of experiments of low-temperature plasma processing of LiYF$_4$ crystals are shown in Table 1.

![Functional scheme of experimental unit.](image)

**Table 1. Experiment parameters**

| Parameter               | Value                      |
|-------------------------|----------------------------|
| **Sample**              |                            |
| Material                | monocrystalline LiYF$_4$   |
| Diameter                | 6 mm                       |
| Thickness               | 2 mm                       |
| **Gas**                 |                            |
| Composition             | Helium 100%                |
| Humidity                | 1%                         |
| Rate                    | 1 l/min                    |
| **Supply**              |                            |
| Type                    | RF                         |
| Discharge power         | 20 W                       |
| Frequency               | 13.56 MHz                  |
| Current density (upper electrode) | 7.5 mA/mm$^2$       |
| Processing time         | 15 min, 30 min, 60 min     |
| Chamber pressure        | atmospheric                |
3. Results and discussions

The view of low-temperature plasma within crystal processing is shown in Fig. 3. Wide part of plasma zone is near bottom electrode and sample. Results of AFM measuring is shown in Fig. 4 and 5. Changes of microhardness and roughness of crystal surface are shown in Fig. 6. The microhardness of sample surface decreases with increasing of processing time. The surface roughness increases with increasing of processing time. It could be caused by surface structure changes. Fluorine from crystal material under influence of low-temperature plasma diffuses to the surface and desorbs from it. As a result the stoichiometry of crystal is broken.

Also there is Oxygen in water vapor in Helium and the possibility of plasma chemical treatment of crystal surface is not small. As result in crystal appear Yttrium and Lithium oxides, not only stoichiometry is broken, but chemical composition is changed.

Figure 2. LiYF₄ crystals

Figure 3. The view of low-temperature plasma.
Figure 4. AFM images of the surfaces treated by the helium plasma (a) exposition times 60 min, (b) 30 min, (c) 15 min; (d) is the typical AFM image of the reference virgin sample’s surface.
Figure 5. The roughness of the surfaces processed by helium plasma. AFM image: (a) 60 min, (b) 30 min, (c) 15 min, (d) non-treated.

Figure 6. Dependence of microhardness (■) and roughness (♦) of crystal surface from processing duration.
The difference of crystal surface microhardness from crystal bulk microhardness gives opportunity for next mechanical, chemical or mechanic-chemical polishing of crystal surface and for increasing of finishing quality.

4. Conclusion
The microhardness of LiYF₄ crystal surface decreased in more than 2 times due to low-temperature Helium plasma modification within 1 hour. This result gives an opportunity for increasing of crystal surface finishing quality. Increasing of surface roughness could be caused by fact that crystal surface structure become more crumbly.

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References
[1] Volokitin G.G., Skripnikova N.K., Volokitin O.G., Shehovtzov V.V., Kashapov N.F. Plasma technologies application for building materials surface modification, J. Phys. Conf. Ser. 669 (2016) 012065
[2] Galyautdinov R.T., Luchkin A.G., Luchkin G.S. Low-temperature plasma in processes of deposition of functional coatings. collection of articles IV Republican scientific-technical conference: collection of articles - Kazan : KSTU Publishing house, - 2013, - P. 155-161. (rus)
[3] Galyautdinov R.T., Kashapov N.F., Luchkin G. S. // Applied physics. . - 2005.- № 6.- P. 88-93.
[4] Luchkin A.G., Kashapov N.F. Reactive magnetron sputtering model at making Ti-TiOₓ coatings, J. Phys. Conf. Ser. 567 (2014) 012027
[5] Spravochnik optika tehnologa / M.A. Okatov. – 2-d edition – SPb.: Polytehnika, 2004. – 679 p.
[6] Laser performance of in-band pumped Er : LiYF₄ and Er : LiLuF₄ crystals/ Semashko, V.V. et. al/ Quantum Electronics, Volume 46, Issue 2, 2016, Pages 95-99.
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The article title:

“Plasma technologies application for building materials surface modification”

is incorrect and the correct article title is:

“Low-temperature plasma modification of LiYF4 crystal surface.”