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Faceted pores in a LiF crystal

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Various types of faceted pores, from flat rectangular to club-shaped with a top in the form of a truncated octahedron, found in a LiF crystal are presented, and a mechanism for their formation and directed growth is proposed, mainly along cleavage planes towards a tensile stress gradient

Keywords: pores, cleavage planes, face orientation.

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1. Introduction

Faceted pores observed in a LiF crystal are covered in this paper. The mechanism of pore formation is briefly described in Refs. [1], the main provisions of which are given below. Currently, a concept based on the concepts of the formation of pore nuclei from gas vacancies formed under the impact of an applied load has gained currency, the description of this concept is provided in Refs. [2–6]. It says that an excess of vacancies occurs in the crystal at the first stage under the impact of a tensile load which leads to the onset of the formation of pore nuclei. The growth stage begins after nucleation — the pore size increases because of the influx of vacancies from the crystal volume. Their coalescence and coagulation take place at the next stage, as a result of which micropores, absorbing each other, merge into macropores. But these papers mainly cover spherical pores. It is well known that growing spherical pores can become faceted over time under low loads for minimizing the surface energy [7,8]. The classical Barton-Cabrera-Frank [9] mechanism may be one of their growth mechanisms in this case, in which vacancies enter a terrace on the surface of the pore, diffuse through it, and penetrate into steps and fractures on its surface. The movement of steps and the growth of pores is limited not by volumetric diffusion, but by surface diffusion. Since the steps are located along the intersection of the planes with the pore surface, vacancies emerge along these planes, eliminating some and forming new steps on them. The process is the reverse of the crystal growth process. Absorption of vacancies by steps — the mechanism of expansion of the surface of the pore faces. The study of the vacancy growth of a faceted pore in a crystal is covered in Ref. [10]. It is assumed that the growth is attributable to the diffusion of excess vacancies that occur in the crystal volume under the impact of mechanical tensile stresses. The distribution of vacancies in a crystal near a step and the velocity of its movement are found in the paper. A relationship has been established between the normal pore growth rate and the applied mechanical stress. In the case of intensive emergence of vacancies on the pore surface, they do not have time to diffuse over the pore surface, they become embedded into steps and fractures on their surface due to different rates of volumetric and surface diffusion, which results in the formation of spherical or elliptical pores. The embedding of vacancies in the fractures on the pore surface causes the movement of steps and a gradual increase of the pore volume.

2. Crystal orientation along cleavage planes

A sample of crystal LiF with size of $\varnothing 40 \times 5$ mm, was cut along the plane (001), as can be seen from the cracking lines intersecting at right angles on its input surface in the area of its irradiation with nanosecond laser pulses (Figure 1). Vertical and horizontal thin cracks were formed along the cleavage planes along the planes (100) and (010) due to inhomogeneous heating of the sample by laser radiation. Moreover, diagonal cross-shaped cracking is observed around the two formed craters shown on the left side of Figure 1, which is also observed on the right side of Figure 1 and occurs in the depth of the sample along the lines of intersection of the planes 111, which is rotated at the angle of 45° relative to the planes (100) and (010).

Since this cracking does not occur along a plane, but along the intersection of planes, cracks formed at different depths can shift relative to each other, which makes the cracking lines more blurred. The right picture corresponds to the case of focusing deep into the crystal. Simultaneous cracking occurs in the transverse plane (001) in addition to cracking along the planes (100) and (010) on the surface in the form of thin cross-shaped lines, and diagonal cracking in the depth of the sample along the intersection of the planes $\{111\}$. The emergence of vacancies on the surface of these transverse cracks increases the gap between their surfaces, and thereby increases the reflectance from them.

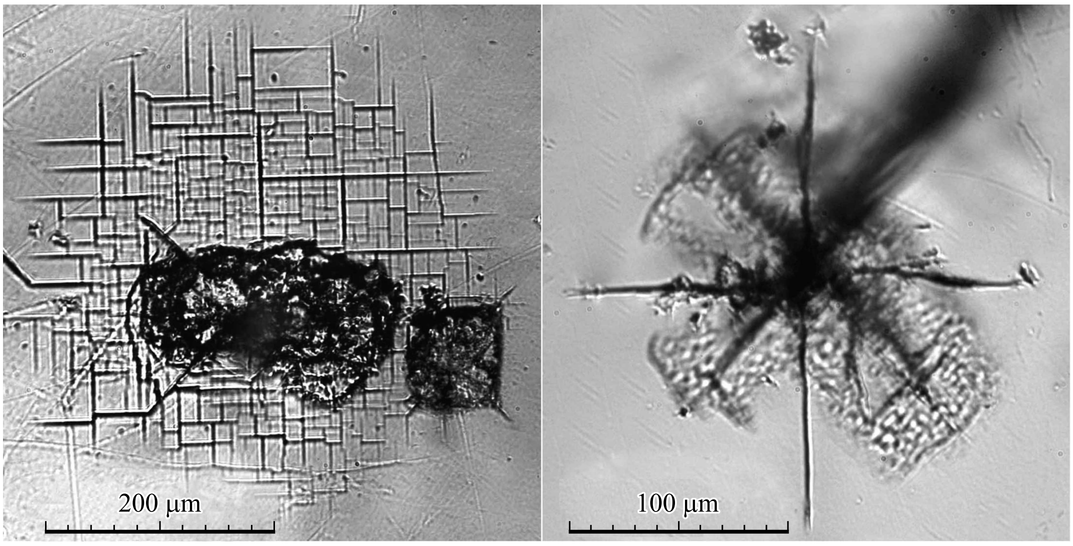

Figure 1. The cracking of the surface of the LiF crystal under the action of a nanosecond laser pulse is shown on the left side, the cracking along the surface is shown by a vertical cross on the right side, and the cracking under the surface is shown by diagonal cross. $I \approx 10^9$ W/cm^2, $\lambda = 920$ nm, $\tau \approx 25$ ns.

A heterogeneous cross-shaped light area is formed as a result, which can be called a flat unfaceted pore. All this indicates that the crystal was cut along the plane (001), and explains to us the location and orientation of the pores formed in it, which will be discussed later.

3. Formation and observation of faceted pores

Accumulations of scattered pores of various kinds and sizes, chains and single pores extending in certain directions and not subjected to laser irradiation were found in some areas in the edges of the sample during its examination (Figure 2). It is unlikely that this is associated with any initial defects of the crystal, since no pores were observed in the rest of the crystal volume.

We do not know the history of previous studies of this sample, so we can assume that the crystal was strongly squeezed in these areas, and negative shear stresses led to the formation of dislocations and Frenkel point defects after stress relief and their localization in the areas of intersection of cleavage planes. It can be assumed that microcracks along the cleavage planes of the crystal acted as seeds for the formation of these pores. These microcracks occurred under the action of tensile stresses along the intersection of the planes (100) and (010) with the plane (001). A whole grid of cracks intersecting at right angles is formed in the case of high stresses as seen in Figure 1. Cracking in the plane (001) instead of cracking in the plane (111) is associated with a lower bond energy between neighboring planes $\{100\}$, the distance between which is a, while the distance between the planes (111) is $a/\sqrt{3}$. Sessile dislocations (partial Frank dislocations) are concentrated

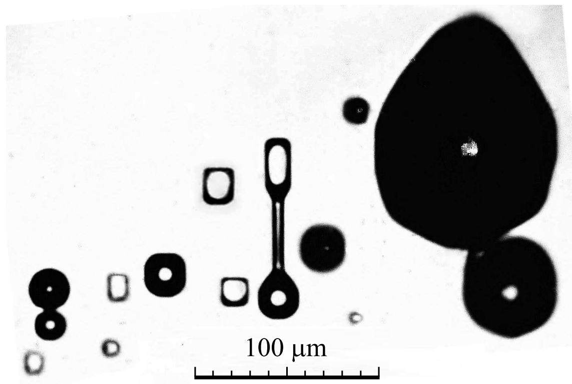

Figure 2. Accumulation of various types of faceted pores found in LiF crystal.

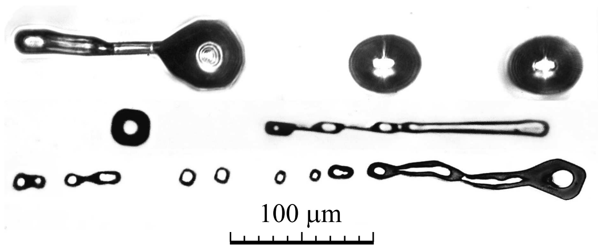

Figure 3. Chains of pores extended in the direction of the stress source.

along these intersection lines. These dislocations can be transformed into the vacancy type prismatic dislocation loops and into a pore in case of a sufficient number of vacancies on them. The process of emergence of vacancies on the pore surface is energetically favorable, since it results in the reduction of the total surface of vacancies and a corresponding decrease of the surface energy. The energy spent on the formation of defects remains in the crystal lattice, and it seeks to minimize internal stresses after removal of external stresses. It seems that such pores are observed in the form of elongated rectangles in Figures 2 and 3. Some of them were flat and had a rectangular shape, and often were lined up along one line or several closely spaced straight lines arranged along the directions [100] and [010].

4. Pore stability

However, it is necessary to ensure the presence of a sufficient number of pore-stabilizing gas atoms for the formation of the pore and its stability. The emergence of vacancies on the pore surface reduces the number of lithium atoms in it in the case of lithium halide, and increases the number of fluorine atoms, which combine into molecules and maintain pressure inside the pore, preventing it from closing. The pores formed in the halides are quite stable, and no changes have been detected in them for several years. Similar spherical pores formed in KCl crystals by the irradiation of the crystal by CO_2 microsecond laser were heated to 700°C for 15 hours in Ref. [11] and their size decreased by less than half. Most likely, this was facilitated by the diffusion of halogen molecules into the crystal volume, accelerated by high temperature.

5. Orientation of pores and their faces

The fact that the pores themselves and their chains extend along certain directions suggests that the stress gradient existed in these particular directions and point defects were formed along this stress gradient and a directed vacancy flux occurred along it. This suggests once again that this sample was once subjected to strong prolonged compression at the edges (perhaps it was squeezed during fastening), and tensile stresses occurred after stress relief contributing to the formation of pore nuclei along the axes of the zone and the flux of vacancies on them. Since vacancies spread along crystallographic planes arranged at different angles, the further away from the stress source, the narrower is the directed the vacancy flux on the growing pore and it grows mainly towards the flux in one plane in the form of rectangles. As the vacancies approach the stress source more and more planes directed at other angles to the pore surface begin to link to the vacancy exit on the pore. This contributes to its growth in other directions, which transforms it into a volumetric pore as it approaches the stress source. But this contributes to the fact that the head growing pore begins to intercept vacancies that could reach further pores, shielding them. As a result, the sequentially arranged pores absorb fewer and fewer vacancies and become thinner as they approach the head. If the sequence of pores merges into one long pore due to emergence of the vacancies on them, in the head of which there is a large volumetric pore, then such a pore becomes like a club, the various variants of which are shown in Figures 2, 3 and 4. The closer to the center of the tensile stresses, the faster is the transformation of a chain of flat rectangular pores into club-shaped or pear-shaped volumetric faceted pores. The tails of the pores (the handles of clubs) are directed towards lower stresses. Since at the first stage the vacancies enter the crack zones stretched along the axis most intensively along planes parallel to these cracks (001), a more intensive emergence of vacancies along other planes transforms them and smaller pores into volumetric, faceted pores at the second stage (their emergence in the longitudinal and the spherical case differs as follows with the same concentration of vacancies in the medium

$$\frac{4\pi r^2}{\pi r^2} = 4,$$

where r is the pore radius). The fact that the tails of the club-shaped pores sometimes experience cracks and extend to the edge of the main head pore suggests that they develop from different seed centers and combine into one composite pore as a result of directed coagulation.

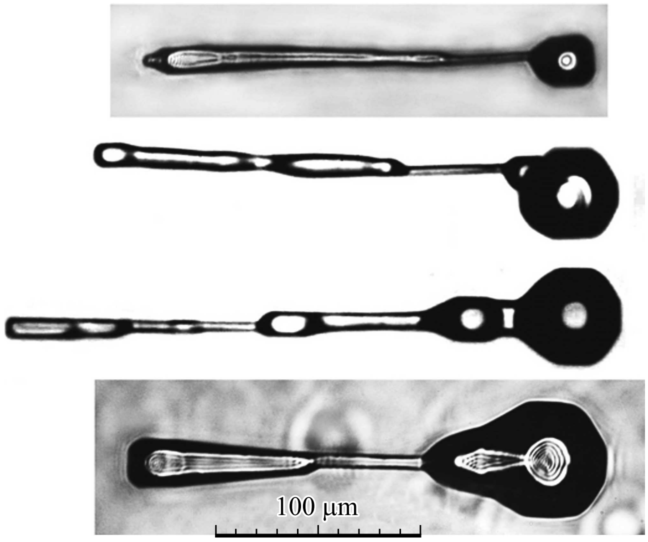

Figure 4. Various variants of club-shaped pores elongated in the direction of the stress source.

Similar bubbles (pores) with the size up to 45 μm were formed in large quantities in alkali halide crystals of NaCl and KCl in Ref. [11] that were irradiated by microsecond pulses of CO_2 laser ($\tau \sim 5$ ms, $I \sim 10^6 - 10^7$ W/cm^2). However, there were no pores in specially grown crystals with an extremely low content of impurities even with a twofold pumping energy increase which unequivocally links their origin to defects in the crystal lattice [11]. As a rule, the pores observed in the cited paper had a pear-shaped shape that thickened towards the laser radiation. Most likely, this was the result of an optical breakdown initiated by the forced longitudinal-radial scattering [12] on internal microuniformities. A huge number of point defects are formed in the region of their excitation in the case of radial scattering, and the emergence of vacancies into cracks formed as a result of optical breakdown leads to the formation of spherical pores. Since radial scattering, developing from microuniformity, increases its effective radius towards pumping, the diameter of the resulting pores increases as they grow towards pumping, due to the emergence of greater quantity of vacancies on them.

The diameter of pear-shaped pores in LiF, as can be seen from Figures 2, 3, and 4, also increased towards the source of increased stresses in this paper, which also affect the concentration of vacancies.

Vacancies move from an area with a reduced bond energy between atoms to an area with increased energy. The maximum bond energy of atoms in the surface layer increases with the decrease of the radius of curvature of the surface. The surface energy density changes as $\Delta W = \sigma \Delta S$, where ΔS is a change of the surface area. Such a surface is inherent in pores, and the emergence of vacancies on their surface, increasing the pore size, reduces the curvature of their surface along with the bond energy of atoms in the surface layer.

As the size of the pores increases and vacancies occur in them in various crystallographic fields, they increasingly acquire a faceted shape. The number of faces of the formed pores, their shape and orientation are determined by the orientation and number of crystallographic planes along which the vacancies emerge on their surface.

The pore faceting may be asymmetrical depending on the intensity of vacancies on the surface of the pore along various planes. Asymmetry can manifest itself both laterally and longitudinally, due to shielding, making its shape pear-shaped. The dependence of the pore faceting on the rate of vacancy emergence is explained by the fact that the rate of diffusion of vacancies along the steps and fractures on the pore surface is less than along the planes extending onto it, therefore, spherical pores are usually formed in case of an intensive vacancy emergence. The pores formed in the FCC lattice take the form of a truncated octahedron in case of optimal growth conditions and the crystal also takes this form during its growth. This is attributable to the fact that the Brillouin zone has exactly the same shape, which defines the energy boundaries of the crystal cell. Generally, the Brillouin zone is a mathematical model of the electronic structure of a crystal, which determines the position and bond energy of the atoms coming in contact in the crystal, on which the shape of the crystal and the cavities inside it depend.

Vacancies emerge on the surface of the pore along the crystallographic planes extending to its boundaries. In the case of a face-centered cubic lattice, they emerge on the pore surface in eight directions in the planes $\{111\}$ and in six directions in the planes $\{100\}$, which determines its shape.

Figure 4 shows that six quadrangular faces of large faceted pores are directed along the planes $\{100\}$ and eight hexagonal faces are directed along the planes 111. Thus, we obtain an octahedron with clipped vertices as a result — a multiply enlarged copy of the Brillouin zone for this lattice. (Since the pores grew along the plane (001), it is possible to take their image only in profile, perpendicular to the surface.)

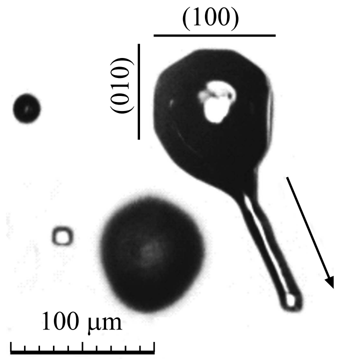

Figure 5. The dependence of the pore faceting on the direction of the crystallographic planes extending onto it and the direction of the vacancy flux.

The pore faces grow perpendicular to the planes extending onto it, while the pore itself grows along the stresses created in the crystal. This is clearly visible in Figure 5, where thin lines show the orientation of the planes along which the perpendicular faces of the pore line up. The third such plane (001) is the plane of the drawing. The thick arrow shows the direction of the stress gradient. The same can be seen on the lower pore in Figure 3, where the rectangular faces of the pores do not coincide with the direction of their growth. Thus, the asymmetric output of vacancies to the surface of the pores is manifested in distortions of their shape. The size of the formed pores increases in the direction of high stresses in this case. The size of faceted pores in the transverse and longitudinal directions is determined by the rate of diffusion of vacancies in these directions, which depends on the distribution of their concentration, which in turn depends on the tensile stresses in these directions. Figure 2 shows various types of faceted pores formed in the area of uneven tensile stresses.

The smaller the pores, the shorter is the length of the terraces through which vacancies emerge, and the weaker is their faceting.

Since the cleavage planes are the faces of the crystal lattice, the sequential access to the vacancy stages formed in the pores mainly along these planes contributes to the growth of faceted pores. Naturally, the higher is the cleavage of the crystal lattice, the more clearly the pore faceting is manifested. The cleavage of a crystal is determined by the difference of atoms bonds within their uniform layer (plane), and the energy of atom bond between these layers.

The greatest intensity of vacancy rate was observed along the plane (001) in this paper. But the problem of pore growth itself remains quite relevant. The rate of emergence of vacancies is studied in a recent paper [13] in which the pore growth rate was modeled based on significant differences in atomic displacements along different crystallographic directions for various crystallographic directions, taking into account the elastic deformation field in aluminum, which also has a FCC lattice, and it was shown that it significantly differs in the direction [100] from directions [110] and [111].

6. Conclusion

An attempt is made in this paper to explain the mechanism of formation and growth of various types of faceted pores observed in a LiF crystal. The proposed mechanism explains the dynamics of their growth from a sequence of flat rectangular pores to club-shaped pores with a top in the form of a truncated octahedron. It is shown that the pore faceting is distorted when the vector of tensile stresses does not match the orientation of the crystallographic planes.

Conflict of interest

The author declares that he has no conflict of interest.

References

[1] A.V. Redkov, FTT **61**, *12*, 2385 (2019). (in Russian). DOI: 10.21883/FTT.2019.12.48559.41ks [Translated version: 10.1134/S1063783419120448]
[2] P.G. Cheremskoy, V.P. Betekhin, V.V. Slezov. Mikropory v tviordom tele. Energoatomizdat, M. (1990) / 376 p. (in Russian).
[3] S.A. Kukushkin Uspekhi mekhaniki *2*, 24 (2003). (in Russian).
[4] S.A. Kukushkin. J. Appl. Phys. **98**, 033503 (2005). doi.org/10.1063/1.1957131
[5] A.A. Vakulenko, A.A. Kukushkin. FTT **40**, 1259 (1998). (in Russian).
[6] S.A. Kukushkin, S.V. Kuzmichev. FTT **50**, 1390 (2008). (in Russian).
[7] M. Kitayama, A.M. Glaeser. J. Mater. Synthesis Proc. **6**, 161 (1998).
[8] A.V. Redkov, A.S. Graschenko, S.A. Kukushkin, A.V. Osipov, K.P. Kotlyar, A.I. Likhachev, A.V. Nashchekin, I.P. Soshnikov. FTT **61**, 433 (2019). (in Russian). DOI: 10.21883/FTT.2019.03.47232.265, translated version: 10.1134/S1063783419030272]
[9] W.K. Burton, N. Cabrera, F.C. Frank. Philos. Trans. R.. Soc. A **243**, 299 (1951).
[10] S.A. Kukushkin, A.V. Osipov, A.V. Redkov. Izv. RAN. MTT. *1*, 94 (2020. (in Russian). DOI: 10.31857/S0572329920010158
[11] V.E. Rogalin. Lazerno-opticheskie sistemy i tekhnologii, FGUP „NPO Astrofizika“, M., 2009, p. 70–77.
[12] N.E. Bykovskii Optics and Spectroscopy, **129** (7), 876 (2021). DOI: 10.1134/S0030400X21070043
[13] A.V. Nazarov, A.P. Melnikov, A.A. Mikheev. Fizika metallov i metallovedenie **124**, *9*, 785 (2023). (in Russian).

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