University of Latvia
Institute of Solid State Physics

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SWIFT-ION-INDUCED MODIFICATIONS OF STRUCTURE AND MICROMECHANICAL PROPERTIES IN WIDE-GAP IONIC CRYSTALS

Summary of doctoral thesis

Submitted for the degree of Doctor of Physics
Subfield: solid state physics

Riga, 2015

The doctoral thesis has been developed in the Institute of Solid State Physics, University of Latvia during period from 2010 to 2014.

EIROPAS SOCIĀLAIS FONDS
EIROPAS SAVIENĪBA
IEGULDĪJUMS TAVĀ NĀKOTNĒ
LATVIJAS UNIVERSITĀTE ANNO 1919

This work has been supported by the European Social Fund within the project 2009/0138/1DP/1.1.2.1.2/09/IPIA/VIAA/004 («Support for Doctoral Studies at University of Latvia»).

The thesis contains introduction, three chapters, conclusions and defendable thesis, references, list of author's publications.
Form of thesis: set of publications in physics, in the subfield of solid state physics.
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The doctoral thesis will be defended at a public session of the Specialized Doctoral Committee of Physics, Astronomy and Mechanics of University of Latvia on May the 22nd, 2015 in the conference hall of the Institute of Solid State Physics at 8 Kengaraga Street, Riga.

The doctoral thesis and its summary are available at the Library of the University of Latvia, 19 Raina Blvd., Riga.

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ISBN 978-9984-45-991-2

Annotation

One of the main areas for the development of modern technologies is utilization of swift heavy ions for improvements of optical, electronic, mechanical etc. properties of materials, for nanostructuring of materials and other tasks of material sciences. Irradiation in the regime of ion tracks opens perspectives for local modifications which are important in fields of nanotechnologies, microelectronics, medicine etc. The doctoral theses are devoted to the investigation of swift-heavy-ion caused changes of structure and micro-mechanical properties in wide-gap ionic crystals, mainly in LiF as a widely used model material in studies of radiation defects as well as in studies of dislocation processes. In the investigation of structure besides AFM, SEM and X-ray diffraction methods instrumented nanoindentation, which is sensitive to defect aggregates and is characterized by the locality of measurements, has been widely used.

The Formation and evolution of dislocation structure caused by GeV energy heavy ions (U, Au, Kr) in LiF crystals has been investigated. It has been shown that tiny dislocation loops and their nuclei are created already in individual tracks but the intensive formation of dislocation structure occurs in the stage of ion track overlapping. It has been found that when certain irradiation parameters are met, formation of nanostructure consisting of columnar blocks oriented in the direction of ion beam occurs. It has been established that, in contrast to heavy ions, light ions (S, C) with a similar specific energy (~11 MeV per nucleon) cause dislocation-rich structure without formation of nanostructure. Both – nanostructure and dislocation-rich structure exhibit high hardness. At high irradiation doses the saturation at 3.5-4.5 GPa is reached which by a factor of 3 exceeds the hardness of unirradiated crystal. It has been cleared up that the saturation of hardness is caused by the transition from plastic deformation *via* dislocation mechanism to shear banding, which is similar to one observed in metallic glasses and is based on atomic rearrangement processes within localized shear bands.

Swift ion caused changes of structure and micro-mechanical properties in few materials (MgO, graphite) for applications in nuclear technologies have been investigated. Results from the standpoint of micro-mechanical properties characterize these materials as resistant to irradiations with high doses. The results show joint contribution of electronic excitations and nuclear (elastic collision) mechanisms in the ion induced formation of defect aggregates and hardening in MgO.

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Introduction

Motivation

Irradiation with ions is being widely used in modification of materials, especially their surface layer in relation to improvements of optical, electronic, mechanical and other properties. In the ion technologies substantial success has been gained including applications of ion implantation, utilization of ion beams in the production of thin films, in vacuum technologies and analytical techniques for the investigation of surface structure and composition.

With the advent of large ion accelerators new possibilities in modifications of structure and properties of materials have been offered by application of high-energy (MeV-GeV) ion beams. Swift ions can penetrate deep surface layers (up to ~100 μm) of material causing radical changes in the structure and topography, leading to amorphization, phase intermixing, formation of latent tracks and other phenomena [1, 2] in various materials. The mentioned processes effectively occur already at room temperature without a requirement for any additional technological threatments. Thus the investigation of structure modification processes in swift ion irradiated materials is an important task from a fundamental as well as application standpoint.

One of actual directions in applications of swift ions is attempts to use them in formation of nanostructures. Investigations are successful in the field of surface nanostructures in dielectric and semiconducting materials. Ensembles of structural elements like nanometer size hillocks, craters or sputtering figures [3] have been obtained. Nevertheless there is a lack of research in the field of structural changes and nanostructuring possibilities within the bulk of an irradiated material. Structural changes intensively occur at high irradiation doses when the primary radiation defects have accumulated and formation of their aggregates have started.

In order to investigate structural changes caused by swift ions at high irradiation doses, very welcome are objects which do not undergo amorphization. LiF and MgO single crystals suffice this requirement thus they were chosen as research object in this doctoral thesis. LiF is well known and widely used model material in the research of radiation defects. An important thing for the research is that the radiation defects in LiF are stable at room temperature. Additionally LiF is well known as model material in research of mechanical properties, especially of processes concerning dislocations [4]. In the interaction of swift ions with LiF ionizing processes and electronic excitations are dominating. Decay of self-trapped excitons leads to creation of Frenkel pairs [5]. This sets a high sensitivity of LiF to radiation.

MgO is included in the list of research objects as a radiation resistant material. In contrast to LiF the band-gap of MgO is lower than the energy required for creation of Frenkel defects, thus formation of defects in MgO *via* electronic excitations is disrupted and substantial contribution comes from the elastic collisions between swift ions and atoms of the material [6].

Aim and tasks of doctoral study

The aim of doctoral thesis is investigation of structure-formation processes and modification of micro-mechanical properties in swift ion irradiated LiF and MgO crystals in the range of high irradiation doses. The aim includes also establishing the possibility of nanostructure formation.

An evolution of structure at high irradiation doses is characterized by a saturation of concentration of primary radiation defects and formation of defect clusters and aggregates (complex color centers, colloids, vacancy clusters, dislocations, etc.). Transmission electron microscopy (TEM) is widely used in their investigation in irradiated crystals. Nevertheless in materials such as LiF, which are characterized by high sensitivity to radiation, TEM method is not applicable. It is well known that electron beam used in TEM causes numerous dislocations and other defects in LiF [7, 8].

In our experiments nanoindentation as an alternative methodological approach due to its locality and sensitivity to the structure was used to investigate defect aggregates. The previous experience shows that micro- and nanohardness is mainly sensitive to the presence of defect aggregates, but the contribution from primary radiation defects is negligible [9]. The second methodological feature of the study is investigations on profile surfaces of irradiated crystals. These surfaces are obtained by cleaving crystals along the ion beam. It allows tracing the changes of structure and micromechanical properties along the whole ion trajectory and provides opportunity to relate the observations to the calculated electronic and nuclear energy losses in the whole range of swift ions.

A fundamental factor that influences radiation effects in matter is the energy loss (d*E*/d*x*). In the case of LiF crystals an important threshold is the critical electronic energy loss d*E*/d*x*=10 keV above which tracks exhibit core damage (small aggregates of defects in the core of track) already within separate ion tracks [10, 11]. Thus a group of heavy ions, for which electronic energy loss substantially exceeds 10 keV/nm threshold, as well as light ions for which the energy losses are below this threshold have been used in the present study.

Following tasks have been highlighted:

1. Investigation of heavy (Au, U, Kr) and light (S, N, C) ion caused structural and micromechanical changes as well as possibilities for the formation of nanostructure in LiF crystals.
2. Investigation of mechanisms of plastic deformation in LiF crystals irradiated with high doses of swift ions.
3. Investigation of the role of nuclear and electronic energy losses in the modification of structure and micromechanical properties of MgO crystals irradiated with swift ions (U, Au, Kr, N).
4. Adaptation of nanoindentation method for the investigation of micromechanical properties of irradiated crystals and diagnostics of ion-induced aggregates of defects.

Contribution of the author

The list of publications of which the doctoral study is based is formed from 8 publications in pier reviewed journals (see the section List of Author’s publications on the page 60). The total number of publications is 20.

The doctoral study has been developed in the Laboratory of Surface Physics of the Institute of Solid State Physics, University of Latvia. Exceptions are irradiations of samples which have been performed in collaboration with the partners from the GSI (Darmstadt, Germany) and Eurasian National University (Astana, Kazakhstan) by using ion accelerators at their disposal. Also x-ray diffraction (XRD) investigations have been performed in collaboration with the Daugavpils University (Daugavpils, Latvia).

The author has mastered methods of structural investigation of irradiated samples using atomic force microscopy (AFM), scanning electron microscopy (SEM) and optical microscopy as well as utilization of chemical etching required for these tasks. A significant place in the performed research is taken by the method of nanoindentation. The author has mastered and services the unit of instrumented nanoindentation (G200, Agilent, USA) for the measurements of modified surface layers and thin films, he also has supplemented methodological knowledge about measurement methods by participating in series of specialized seminars.

The author has performed the mentioned experiments and processing of the results. The analysis and interpretation of the obtained results has been performed jointly with the supervisor and colleagues from the laboratory. The author owns conclusions formulated in the section of novelties and main thesis. The results of doctoral study have been published in scientific peer-reviewed journals. In several publications duties of a corresponding author have been performed. The author has presented the obtained results at 9 international as well at local conferences.

Scientific novelty

In doctoral study a new knowledge about swift ion caused processes of structural modifications in LiF and MgO has been gained based on the investigation of structure and micromechanical properties. The most important novelties are following:

1. A substantial contribution of irradiation-induced dislocations in the processes of structure formation and modification of micromechanical properties has been shown. It has been established that tiny dislocation loops are formed already in individual tracks, whereas a dislocation structure forms intensively at the stage of track overlapping.
2. By irradiating LiF crystals with high energy heavy ions (U, Au, Kr, Xe) a mosaic-type nanostructure has been obtained. Necessary requirements for it have been determined: (1) fluence ($>10^{12}$ ions/cm^2) corresponding to a stage of track overlapping, (2) electronic energy loss of ions are above 10 keV/nm which is necessary for the formation of tracks with core damage and structure orientation in the direction of ion beam.

   Below the mentioned threshold of 10 keV/nm the dislocation-rich structure is formed.
3. It has been shown that formation of dislocations as well as nanostructuring is accompanied by a substantial increase of hardness, reaching saturation at 3.5-4.5 GPa (~200% effect).

It has been found that this saturation is caused by the change in mechanisms of plastic deformation from the dislocation mechanism to the shear banding mechanism which is based on atomic rearrangements.

4. Joint contribution of the impact and electronic excitation mechanisms in hardening of MgO crystals irradiated with swift ions has been established.

1. Review of the literature

In the review it has been dealt with the interaction of swift (high-energy) ions with LiF and related dielectric materials and with irradiation caused effects in them. A detailed review of processes caused by conventional irradiation sources (photons, electrons, γ- and x-rays, neutrons) hasn't been included.

Objects of investigation – LiF crystals belong to wide-gap ionic crystals (E_g=14.6 eV) with a NaCl type lattice – face centered cubic structure (lattice parameter a=4.028 Å, radius of ions: r(F^-)=1.33 Å, r(Li^+)=0.76 Å). MgO crystals also are ionic crystals with the fcc structure. Their band-gap E_g=7.8 eV and lattice parameter a=4.212 Å, the corresponding radius of ions: r(O^{2-})=1.40 Å, r(Mg^{2+})=0.72 Å.

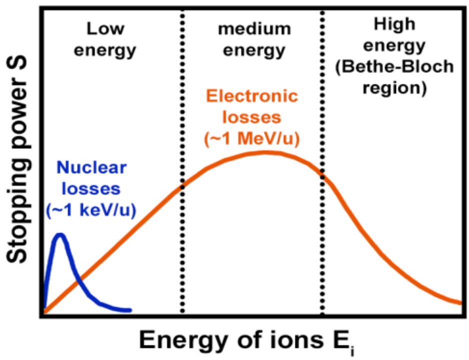

Figure 1. Schematic of stopping power (energy loss) of ions in dependence on their specific energy.

Ions with a specific energy >1 MeV/nucleon are named swift ions. When they penetrate a dielectric material they lose energy and slow down mainly due to two mechanisms: (1) in the result of electronic energy losses which occur by interaction with electrons of material causing the ionization and excitations, (2) in the result of nuclear energy losses in elastic collisions with the atoms and ions of material causing their displacements and displacement cascades (Figure 1). In the case of swift ions electronic energy losses have the dominating role, whereas a contribution from the energy loss caused by collisions with atoms is little [5]. The process of slowdown of swift ions in the matter is well investigated. Electronic and nuclear energy losses as well as a penetration depth of ions in the material under investigation can be calculated by the SRIM code [12]. The active area of research is clearing up the processes of transformation of absorbed dose in structural damage and changes of properties in the explored materials.

The specific of irradiation with swift ions is the localization of radiation defects in ion tracks. By moving through a matter projectiles ionize the central region of tracks and δ – electrons with a wide spectrum of kinetic energies are emitted from it [13]. These electrons cause ionization, electronic excitations and formation of defects (Figure 2) in the halo region surrounding the track. The halo region has a radius of few tens of nanometers and is characteristic to all swift ions (Figure 3b).

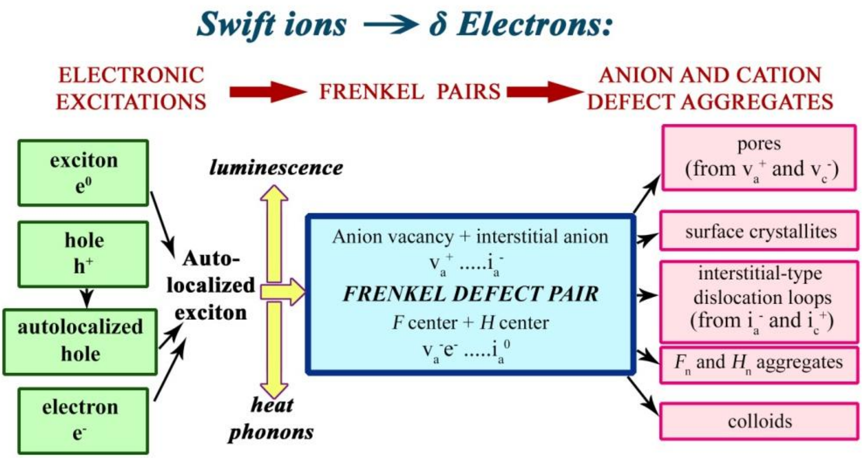

Figure 2. Schematic of swift ion caused processes in ionic crystals.

When ion electronic energy losses in LiF crystals surpass a threshold of 10 keV/nm, complex tracks which contain strongly defected core region with a radius of 1-2 nm (Figure 3a) are formed [10, 11]. The core region has a lower density than an unirradiated crystal [11, 14]. Theoretical estimates show that the core region contains tiny defect aggregates [15]. Such complex tracks with the core region are chemically etchable (Figure 3 c) similar as dislocations [16, 17]. It shows that as dislocations these core-containing tracks have a mechanical stress field around them.

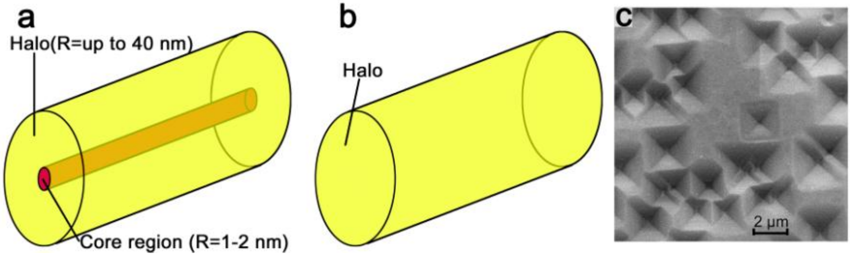

Figure 3. Schematic of heavy ion tracks in LiF single crystal: (a) in the case of heavy ions at energy loss d*E*/dx>10 keV/nm, (b) at d*E*/dx<10 keV/nm. (c) Example showing chemical etching of ion tracks in LiF irradiated with 2.2 GeV Au ions.

For the explanation of processes within ion tracks two theoretical models have been developed. One being used is the model of *Coulomb explosion* [18] in which the evolution of structure begins with an electrostatic repulsion between similar sign (positively charged) ions in the center region causing a reduction of density (Figure 4). After this a relaxation process which partly restores the structure follows. Widely used also is the *Thermal spike* model [19] which is based on the assumption about a substantial but very brief increase of the temperature (even up to the melting) within the core of tracks. It is being used for the description of irradiation induced amorphization, phase transitions and related effects. In the reality the melting process hasn't been observed and calculations show that within a track, not only within the core region, the average increase of temperature is expected up to 250 K [20].

Primary radiation defects in LiF irradiated with swift ions are created by formation of excitons, their autolocalization and decay with the formation of neutral Frenkel *F*-*H* pairs and charged (α-*I*) pairs [5, 21]. The exciton mechanism ensures the high sensitivity of LiF to irradiation (see Figure 2).

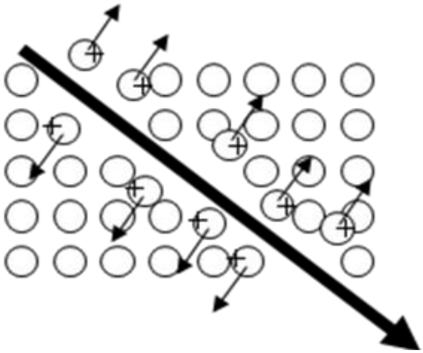

Figure 4. Formation of „Coulomb explosion" in ionic crystals. The swift ion ionizes anions which become positively charged un due to Coulomb repulsion forces they are displaced from their initial positions.

In swift-ion-irradiated LiF crystals optical absorption spectroscopy and luminescence studies as the most prominent defects reveal *F*-centers (electron in an anion vacancy) and F_2 centers as well as F_3^+, F_3, F_4 complex color centers [11, 22, 23]. Together with *F* centers also *H*-centers (interstitial fluorine atoms) and their aggregates in form of fluorine molecules (H+$H$$\rightarrow$$X_2$) and n$X_2$ complexes are formed. The absorption of *H*-centers is well outside the visible part of the spectrum into the UV part. The primary radiation defects and their corresponding optical absorption maximums in LiF are presented in Table 1. Results show that types of primary radiation defects and their formation processes under the influence of swift ions, excluding the specific connected with tracks, are similar to ones observed in alkali halides and related ionic crystals irradiated with electrons, neutrons, x-rays or γ-rays [24, 25].

The concentration of swift ion caused primary radiation defects (F-centers) is dependent on the absorbed energy, which is determined by a dose:

$$E_{\mathrm{abs}} = E_{\mathrm{j}} \times \Phi/\mathrm{R} \qquad (1)$$

where E_{i} is the energy of ions, Φ –fluence and R– the penetration depth of ions. Optical absorption spectroscopy and luminescence measurements show an increase in concentration of *F*-centers with an increased absorbed energy. At the absorbed energy above ~10^{22} eV/cm^3 a saturation of *F*-centers (around 10^{19} cm^{-3}) is reached [23]. The saturation at high doses is explained with the annihilation of defects in conditions of the increased density of excitations, as well as with the formation of defect aggregates, which serve as sinks for different radiation defects. As “high” are considered doses at which overlapping of track halo regions occurs and saturation of primary radiation defects takes place. For the majority of ions the overlapping of tracks occurs at fluences above 10^9- 10^{10} ions/cm^2.

Table 1. Typical color centers in LiF crystals

Center	**Model**	**Maximum of absorption band [nm]**
F	$V_a^+ e^-$	248
F_2	$2V_a^+ 2e^-$	444
F_2^+	$2V_a^+ e^-$	645
F_2^-	$2V_a^+ 3e^-$	950
F_3	$3V_a^+ 3e^-$	317, 377
F_3^+	$3V_a^+ 2e^-$	448
F_3^-	$3V_a^+ 4e^-$	820
F_4	$4V_a^+ 4e^-$	518, 540
H	X_2^-/X^-	~345
Li colloids	nLi	~445
Na colloids	nNa	~520
K colloids	nK	~680
Mg colloids	nMg	275-280

With the saturation of concentration of primary radiation defects significant becomes a role of linear defects (dislocations), various defect aggregates (colloids, vacancy and fluorine clusters, etc.) and planar defects (grain or substructure boundaries) in the modification of structure. Systematic investigations have been performed and theoretical models have been developed for the growth of colloids in alkali halides and related ionic crystals irradiated with conventional sources (electrons, neutrons, etc.) [26, 27, 28 and references within]. Nevertheless, in LiF irradiated with swift ions at room temperature the utilized investigation methods (microscopy, electron spin resonance (ESR), etc.) have not shown the presence of colloids. Colloids haven’t been found also in LiF irradiated at slightly elevated temperature (around 350 K) which can stabilize during a prolonged irradiation with swift ions. A presence of very small colloids, the size of which is below the sensitivity threshold of utilized methods, can be assumed. Mainly it touches the question about defects within the core of tracks, where the formation of clusters consisting of few (4-5) atoms is theoretically supposed [15].

In comparison to LiF MgO crystals are characterized by a substantially higher radiation resistance. It is explained by a fact that the band gap in MgO in contrast to LiF is narrower than the energy required for the formation of Frenkel pairs. This substantially limits the formation of defects *via* electronic excitations and formation of defects in collision cascades caused by swift ions becomes significant. Such behavior is observed for high purity MgO crystals. However, in commercial MgO crystals a joint contribution of electronic excitation and elastic collision mechanisms is observed [6]. The former becomes possible due to presence of impurities in substitution positions of lattice, which ensures autolocalization of excitons and formation of Frenkel pairs.

At conditions of high doses in the formation of defect aggregates a question about the formation of dislocations and their role in ion irradiated crystals protrudes in the foreground. In the doctoral study investigations in this direction take one of the central places. In MgO crystals and spinel compounds TEM results show a formation of numerous prismatic dislocation loops [29]. Ion induced dislocations in LiF crystals have been observed by chemical etching [30]. Generation of dislocations in LiF crystals under influence of electrons is confirmed also by *in-situ* TEM observations [7, 8] whereas theoretical models predict that a growth of dislocations might occur *via* participation of fluorine molecules which are mobile at room temperature [7]. Nevertheless, systematic investigations of ion-induced dislocations in LiF crystals are absent to date. Partly it can be explained by methodological difficulties. Utilization of TEM in the case of LiF crystals is not acceptable because this material is too sensitive to the electron irradiation. A partial solution is utilization of selective chemical etching. Nevertheless, this method is usable only up to intermediate doses.

Due to development of nanoindentation methods new possibilities appear for utilization of this structure-sensitive method for characterization of radiation defect aggregates. The previous experience shows a substantial (up to 200%) hardening effect in LiF crystals irradiated with swift ions [30]. It has been shown that the hardening effect mainly is attributed to the formation of defect aggregates – including formation of dislocations. A substantial advantage for the insight about evolution of defects is the possibility to obtain information about the distribution of defects within the bulk – along the trajectory of ions. It is done by performing indentation measurements on the profile surface of irradiated zone.

From the review of literature if follows that the investigation of structure-formation process at high swift ion doses is an actual task. By solving it, problems regarding the formation of bulk nanostructures and modifications (improvements) of micromechanical properties are touched. Also it allows studying the radiation-resistance of different materials (MgO, etc.) which are candidates for applications in nuclear technologies as well as in the new-generation of ion accelerators.

2. Experimental section

2.1. Investigated samples

For the investigations Korth Kristalle GmbH (Germany) grown LiF single crystals with a purity of 20 ppm have been used. The most notable impurities were Mg and Na. The average density of growth dislocations 5×10^4 cm^{-2}.

In the experiments with MgO MTI, Ca (USA) grown single crystals were used. The most abundant impurities were Ca and Fe.

The investigated samples were 1 – 2 mm thick platelets which were cleaved from a massive block.

2.2. Irradiation

Irradiation of samples have been performed with a help of collaboration partners using ion accelerators at their disposal:

- Irradiation with high energy (MeV-GeV) heavy ions has been performed at the UNILAC linear ion accelerator, GSI Helmholtzzentrum für Schwerionenforschung GmbH, Darmstadt, Germany;
- Irradiation with MeV-energy heavy (Kr, Xe) and light (N) ions have been performed at the DC-60 cyclotron, Astana, Kazakhstan;
- Irradiation with 410 MeV S and C ions has been performed at GANIL accelerator in Caen, France;
- Irradiation with 3-15 MeV-energy gold ions has been performed at the Tanderton accelerator, Porto Alegre, Brazil.

During the irradiation the ion beam was perpendicular to the (001) plane of the sample, except special cases in which samples were irradiated at certain incidence angles in respect to this plane.

For the calculation of a ion penetration range and their nuclear and electronic energy losses in the investigated materials the computer program SRIM Code 2008 [12] was used.

To simplify the characterization of irradiation dose the fluence (Φ) [ions/cm^2] has been used. Correspondingly the ion flux is evaluated as [ions·cm^{-2}·s^{-1}]. The fluence Φ shows the number of ions that have hit the surface area of a sample and it allows to clearly compare the irradiation effects caused by different ions. It is also convenient for the characterization of ion track structure by determining the average distance between tracks and the amount of track overlapping.

The radiation dose in SI system is measured in grays (Gy), the dimension of which is [J/kg]. In order to calculate the dose in grays (Gy), when the fluence is known, the following formula can be used

$$D[Gy] = 1.6\times10^{-10}\,\frac{E_{tot}[MeV]\times\Phi\left[ions/cm^2\right]}{\rho\left[g/cm^3\right]\times R[cm]} \qquad (2)$$

where E_{tot} –the energy of ions, Φ is the fluence – ions per cm^2, ρ is the density of an irradiated material and R is the penetration depth of ions in a material (can be calculated by SRIM program).

2.3. Preparation of irradiated samples for investigation

Investigations have been performed on irradiated surfaces as well as on profile surfaces, which have been obtained by cleaving the irradiated sample along the direction of ion beam. Measurements on profile surfaces are more informative. They allow to obtain data of changes in the structure and mechanical properties along the whole ion trajectory making it possible to see the dependence on depth which is measured as distance from the irradiated surface.

For the investigation of micro- un nanomechanical properties the instrumented indentation unit Agilent Nano G200 (USA) has been used. The unit allows performing measurements in standard (BASIC) regime as well as in CSM (Continuous Stiffness Measurement) regime by continuously registering the applied force and displacement of indenter tip. In the case of CSM regime values of hardness and Young's modulus are calculated as functions of displacement into surface. The calculations are based on Oliver-Pharr model [31]. For the calibration the reference samples and methodology recommended by the manufacturer have been used.

The nanoindentation results were also used to evaluate the plasticity by integrating the Load-Displacement (P-h) curves, thus obtaining components of plastic and elastic deformation and the respective work of deformation.

Investigation of structure and surface topography

For the investigations optical microscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM) have been used. For the visualization of dislocations and other defects in the microscopy investigations, irradiated samples were treated by selective chemical etching in the saturated aqueous solution of $FeCl_3 \cdot 6H_2O$.

The method of dislocation mobility used in the doctoral study is also based on selective chemical etching. In it a method of microhardness is combined with chemical etching of a deformation zone around the indent. The measured parameter is the size of a dislocation rosette [32]. Basically this method is probing of material with indentation caused dislocations, the motion of which is hindered by radiation-induced defects – dislocations and defect aggregates.

In addition to microscopy methods x-ray diffractometer SmartLab (Rigaku) was used for the investigation of structure. XRD measurements were performed in collaboration with the Daugavpils University.

3. Results and analysis

3.1. Modification of micro-mechanical properties in LiF and MgO crystals irradiated with swift ions

3.1.1. Investigation of heavy (Au, U, Kr) and light (S, N, C) ion-induced effects using method of nanoindentation

Data from the literature and our previous investigations show that irradiation of LiF crystals with various sources, including swift ions, causes formation and accumulation of radiation defects leading to an increase of hardness [9, 30]. In this section the behavior of hardening effect has been investigated by nanoindentation [33]. To make the comparison of results possible, the energy of swift ions was chosen such as to provide identical specific energy (MeV per nucleon) for all ions. In the experiments performed in this section it was 11 MeV/u.

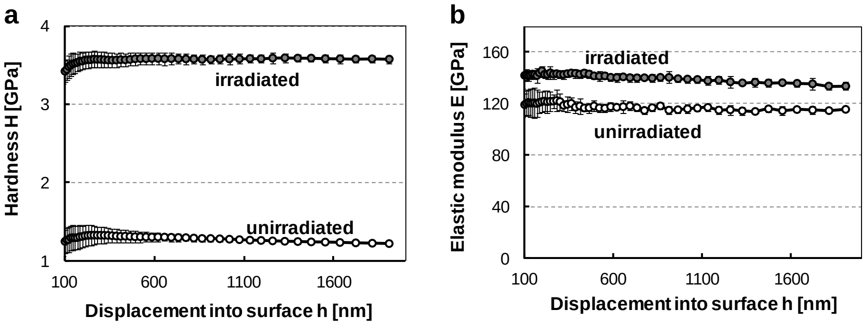

Figure 5. Changes of hardness (a) and Young's modulus (b) in LiF crystals irradiated with 2.6 GeV ^{238}U ions. Measurements were performed on the irradiated surface. Φ=4×10^{11} ions/cm^2.

The results of measurements on irradiated surface (Figure 5) show substantial (up to 170%) hardening effect. Knowing that hardness is sensitive to presence of defect aggregates and linear defects (dislocations) it can be concluded that accumulation of such defects occurs during irradiation. Changes in Young's modulus are small reaching around 20% increase. A modulus maintained around a level characteristic to unirradiated LiF shows that the material doesn't undergo radical structural changes (amorphization, etc.). The small increase of elastic modulus can be attributed to a presence of mechanical stress in irradiated crystals, confirmed by curving of samples. Similar changes of surface hardness and Young's modulus were observed in LiF after high-dose irradiation with different ions.

A detailed investigation of the hardening effect was performed on the profile surfaces of irradiated crystals, which were obtained by cleaving along the ion beam. Nanoindentation tests have been performed on the whole cross-section of the irradiated zone controlling the distance of each measurement point from the irradiated surface (basically depth) using optical microscopy. The characteristic nanoindentation results of a dependence of hardness on the depth are shown in Figure 6. For the comparison, calculated changes of ion electronic energy loss with depth are provided. For the investigated ion energy range electronic energy loss is dominating. The change of ion energy loss in dependence on the depth is called the Bragg curve and the observed maximum on it is correspondingly called the Bragg maximum. By comparing results it can be concluded that overall the data of hardness correlates with the calculated changes of ion energy loss. Especially obvious it is in the case of light ions where the Bragg maximum is clearly pronounced.

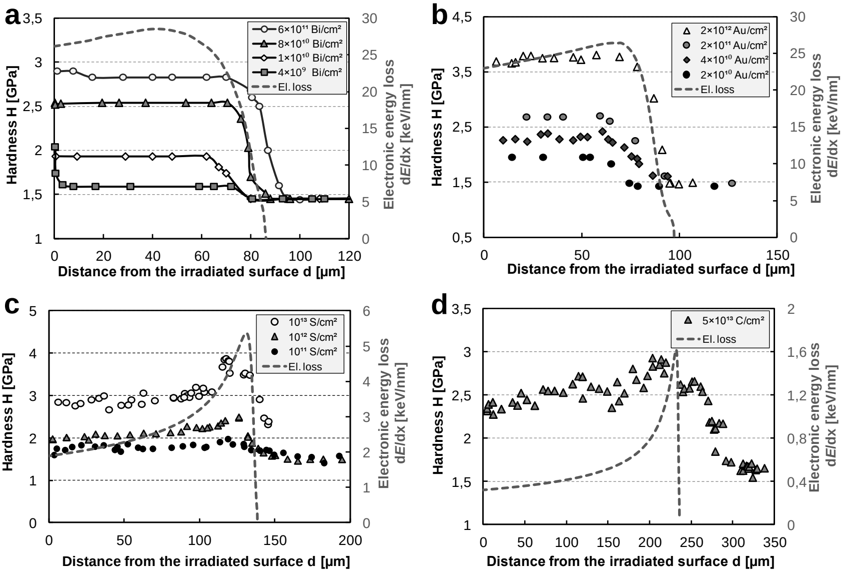

Figure 6. Dependence of hardness and electronic energy loss on depth in LiF samples (profile surface) irradiated with 2.05 GeV ^{209}Bi ions (a), 2.2 GeV ^{197}Au ions (b), 410 MeV ^{36}S ions (c) and 130 MeV ^{12}C ions (d). The depth has been measured on sample cross-sections as distance of each measurement point to the irradiated surface.

The thickness of hardened layer determined by nanoindentation (Figure 6) within error margins coincides with the ion penetration depth obtained from calculated Bragg curves. As a rare exception is LiF irradiated with C ions (Figure 6 d). In this case the zone of hardening substantially surpasses the ion range calculated by SRIM program. In the literature it is mentioned that ^{12}C ions in LiF cause color centers outside the ion irradiated layer [34, 35]. Several possible mechanisms of formation of color centers beyond the range have been analyzed in work [36]. As one of possible causes in the formation of these color centers is the nuclear reaction of ^{12}C ions with Li and formation of ^{14}C isotope [34]. This nuclear reaction is accompanied by β-radiation which in turn creates color centers. The observation made in doctoral study confirms that in irradiation of LiF with C ions not only color centers are formed outside the irradiation zone but also defect aggregates that cause an increase of hardness. An additional credibility for the occurrence of this nuclear reaction is that the penetration depth of β-radiation in LiF crystals (150 μm [34]) is close to depths at which the the hardening was observed.

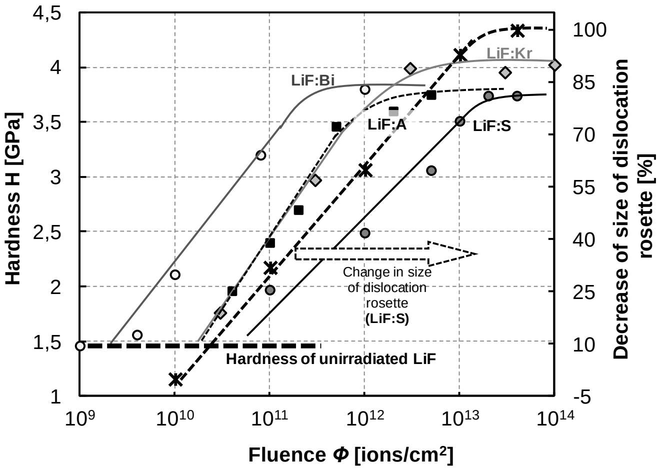

Figure 7. Dependence of hardness on fluence in LiF crystals irradiated with ^{209}Bi, ^{197}Au, ^{84}Kr and ^{36}S ions (left axis) and relative changes in the size of dislocation rosette for LiF irradiated with ^{36}S ions (right axis).

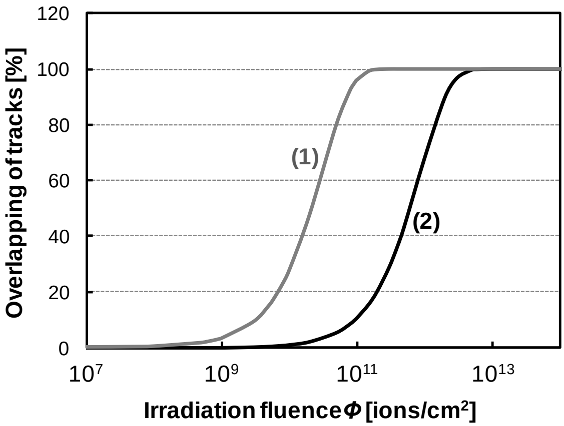

Figure 8. Amount of ion track overlapping in LiF crystals in dependence on ion fluence for uranium (1) and sulfur (2) ions.

In previous investigations it was observed that ion caused hardening in LiF starts to occur in the fluence range above 10^9 – 10^{10} ions/cm^2. The amount of hardening increases with the fluence until the saturation is reached [9]. Such evolution of events is confirmed also by nanoindentation measurements (Figure 7) performed in doctoral study. The threshold fluence at which the hardening can be detected is different for the investigated ions. For the heavy ions (Bi) hardening starts to occur at a fluence around 3×10^9 ions/cm^2 but for the light ions it occurs at fluences about one order of magnitude higher. The difference in threshold fluences can be explained by a fact that the defects responsible for the hardening are formed at the stage of track overlapping but the amount of overlapping for heavy and light ions is different due to differences in track radii. An estimate of track overlapping has been performed for the uranium and sulfur ions (Figure 8). From it a necessary difference of doses can be seen. The overlapping of tracks has been evaluated using Thevenard formula [37]

$$A/A_0 = 1 - \exp(-\pi r_F^2 \times \Phi) \quad (3)$$

where A/A_0 is the ratio between the irradiated surface and the whole nominal surface, r_F is a radius of track and Φ is fluence.

In the actual estimation an average track radius was used which was calculated from optical absorption data of *F*-centers [11, 16, 17]. The evaluation is approximate because the track radius varies along the track trajectory, reaching the highest value at Bragg's maximum [21].

The data in Figure 7 as well as results from numerous other experiments show that the hardness in case of all investigated ions reaches approximately equal saturation values – 3.5-4.5 GPa which approximately three times surpasses the hardness of unirradiated crystal. Causes for the formation of upper boundary of hardness until now were not elucidated. To solve this problem an investigation of deformation zone in samples irradiated with different doses (fluences) was performed.

In unirradiated crystals of LiF and MgO indentation causes a plastic deformation by means of dislocation glide in {110} <100> and <110> system [38]. A zone of plastic deformation, which can be visualized by chemical etching as well-known dislocation rosette, is formed around the indenter imprint on the (001) surface. Rosette consists of dislocation arms oriented in the directions of easy glide of dislocations. Their length represents the mobility of dislocations within the investigated material. It is known that in irradiated crystals the length of dislocation arms decreases because the radiation defects serve as obstacles for the indentation-induced dislocations [9 and references within].

In order to determine the ion-induced changes in the process of deformation, the mobility of dislocations in dependence on irradiation dose (fluence) in LiF was investigated [39]. Figure 7 shows the relative change in the size of a dislocation rosette in LiF irradiated with S ions. As can be seen the size of dislocation rosette gradually decreases with the increasing fluence and above 10^{13} S/cm^2 characteristic features of dislocation glide in directions of easy glide cannot be observed. Also the saturation of hardness is reached at this fluence. At these circumstances the dislocation rosette is replaced by a deformation zone which is not oriented in certain crystallographic directions but follows the distribution of mechanical stresses around the indent which is determined by the geometry of an indenter tip. For the pyramid-shaped intenters maximum shear stresses and maximum plastic deformation occurs towards the center of faces but minimum towards vertexes. The described changes of deformation zone have been clearly shown on LiF crystal irradiated with gold ions (Figure 9). The process of deformation is localized in shear bands around the indenter (Figure 9 c). Fluence for the transition to such a mode of deformation and reaching of hardness saturation (5×10^{13} Au/cm^2) coincides.

The load-displacement curves obtained by nanoindentation do not contain signs of a crack formation. During indentation cracks can be observed only at large loads and their direction doesn't coincide with that characteristic to shear bands. This confirms that shear bands do not have anything common with the formation of cracks.

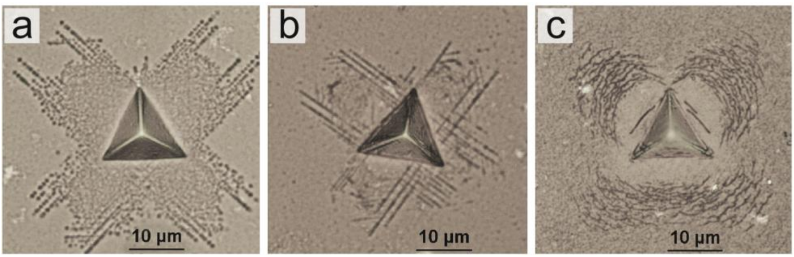

Figure 9. The view of deformation zone for the unirradiated (a) and irradiated with 3 MeV Au ions at 5×10^{12} Au/cm^2 (b) and 5×10^{13} Au/cm^2 (c) fluences LiF crystal. After selective etching.

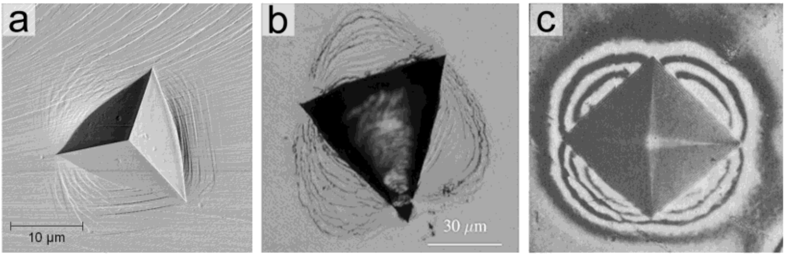

Figure 10. Localized shear bands formed by indentation in LiF crystal irradiated with 2×10^{13} S/cm^2 (AFM image) (a) and in metallic glass [38] (b). A distribution of mechanical stresses around the Vickers indenter (c).

The obtained results show that in irradiated crystals with the increasing fluence the possibility of plastic deformation *via* dislocation glide gradually becomes exhausted and as a replacement other mechanism, in which deformation occurs in localized shear bands, takes over. As it shown in Figure 10 c, maximum shear stress and also maximum deformation is reached towards faces of indenter.

Deformation in form of shear bands has been observed in various materials and can occur *via* different mechanisms. Nevertheless, series of facts show that in irradiated LiF this deformation mechanism is similar to one found in metallic glasses, which is based on deformation *via* atomic rearrangements [40]. For it to occur two requirements have to be met – (1) free volume within the material and (2) high mechanical stresses. Both of these are fulfilled in irradiated LiF. High mechanical stresses are reached within the indentation zone, evidence of which is a threefold increase of hardness. Also the existence of a free volume within irradiated LiF is undoubtful. Macroscopically it is confirmed by expansion of a material known as swelling effect [7] (Figure 11). Also microscopy investigations (RSEM and SAXS) characterize the core of a track as a region with lower density [14]. The visual similarity of shear bands in LiF and metallic glasses (Figure 10 a,b) also points on similarity of mechanisms.

A very characteristic feature of formation of shear bands is that deformation, in contrast to dislocation mechanism, occurs without accumulation of deformation carriers and strain hardening (increase of a stress necessary for a further deformation). Thus a clear upper boundary of hardness can be observed in experiments. After reaching this upper boundary the indentation hardness does not follow further structural changes that occur in the material. Nevertheless, it has to be taken into account that fluences at which this saturation of hardness is reached are close to the radiation caused spontaneous rupture. The formation of shear bands can be considered as the last opportunity for the deformation of material, after exhaustion of which, a brittle rupture *via* formation of cracks follows.

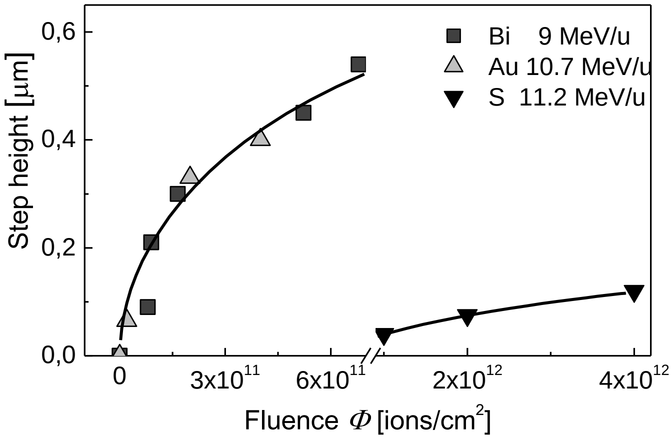

Figure 11. Expansion of LiF crystals (swelling effect) irradiated with swift Bi, U and S ions [17]. The effect has been measured as a step height on the irradiated surface.

In unirradiated LiF crystals the dislocation mechanism of plastic deformation is undoubtfully dominating. Nevertheless, in several works a minute contribution from mechanism related to atomic rearrangements has been observed [41]. Also our observed change in mechanism of plastic deformation is not abrupt. A gradual transitional region, where dislocation mechanism and signs characteristic to the mechanism of atomic rearrangement are simultaneously manifesting, can be outlined.

By summarizing results it can be concluded that the swift-ion-induced upper boundary of hardening effect (approximately threefold increase of hardness) is caused by the transition of a plastic deformation from the dislocation mechanism to the shear banding mechanism, which is based on local atomic rearrangements and is similar to that found in metallic glasses.

3.1.2. Modification of micro-mechanical properties in MgO crystals: contribution of impact and electronic excitation mechanisms

In MgO crystals in contrast to LiF the band gap (E_g =7.8 eV) is narrower than the required energy for the creation of Frenkel defects in anion sublattice (E_{FD}=15.2 eV). Thus in MgO crystals with high purity formation of defects *via* electronic excitations does not occur and their creation can happen by less productive impact (elastic collision) mechanism [6]. This contribution of impact mechanism in the case of MeV-GeV ions is small: more than 90% of the whole energy losses are electronic. Thus MgO belongs to radiation-resistant materials with application perspectives in nuclear and related technologies.

The data from literature shows that in low-purity MgO crystals formation of Frenkel defects under conditions of high density of electronic excitations, typical for irradiation with high-energy ions, nevertheless, occurs [42, 42]. This is due to substituting impurity ions (Ca and others) which are involved in the autolocalization of excitations [6, 42, 43]. Formation of color centers as well as irradiation induced hardening in ion-irradiated MgO has been observed [42-44]. Thus in commercial nominally pure MgO crystals, in which the concentration of impurities is considerable, joint contribution of electronic excitation and impact mechanisms in creation of defects and modification of properties, can be presumed. Estimates from SRIM show that nuclear mechanism reaches the maximum of its contribution at the tail end of the ion range.

In the doctoral study the main attention has been devoted to the clarification of contribution of both mentioned mechanisms in the modification of micromechanical properties by using nanoindentation and measurements of dislocation mobility on profile surfaces of samples. From the list of explored ions (U, Au, Kr, N) for the detailed investigation Kr and N ions were chosen as in their case a relatively higher contribution from nuclear energy loss is to be expected.

Energy losses of ions were calculated by SRIM. For the calculation of nuclear energy loss a standard method was used to obtain linear energy loses [keV/nm]. Also it has been estimated how many oxygen and magnesium vacancies were produced in collision cascades per incident ion. It was taken into account that the energy of secondary ions can be sufficient to produce subsequent defects. These calculations were performed by collaborating partner M. Sorokin.

Results for the sample irradiated with Kr ions shows that the hardening effect can be observed throughout the whole irradiated zone but the distribution of hardness in dependence on depth is variable. The hardness reaches its maximum value at the end of the ion trajectory where the number of created defects *via* elastic collisions dramatically increases (Figure 12). Similar changes in the irradiated zone can be observed in MgO irradiated with N ions (Figure 13).

Results were supplemented with measurements of dislocation mobility. In number of works the possibility of selective chemical etching of dislocations in MgO crystals has been shown [44, 45]. Results show that at the end of the ion range the concentration of defects responsible for impending dislocations is especially high (Figure 12 b). The inserted AFM image shows that the size of dislocation rosettes is sharply decreased in a very narrow depth range (marked with a dashed line). The analysis of dislocation mobility allows concluding that similar to LiF crystals, reduction in size of dislocation rosette with increasing fluence is observed in irradiated MgO as well. Together with it signs of local shear bands are outlined in the structure of indentation zone (Figure 12 b and 13 b). It confirms a substantial contribution of shear banding mechanism in the process of plastic deformation.

For the lowest fluence (5×10^{12} Kr/cm^2) the maximum of hardness does not appear at the end of the irradiation zone, which might indicate on different behavior of both components in dependence on fluence (Figure 12). The contribution of electronic excitation and impact mechanisms in hardening was estimated for all fluences and the results are presented in Figure 14. It can be seen that hardening due to electronic excitations can be observed at fluences above 10^{10} Kr/cm^2 but increase of hardness caused by the mechanism *via* elastic collisions is observable above 10^{12} Kr/cm^2. Such difference can be explained by a substantially larger cross section for the formation of defects in the case of electronic excitations [46]. Taking into account that hardening occurs at the stage of track overlapping, from the obtained data approximate track diameters in the case of electronic and nuclear (impact) mechanisms can be determined. For the electronic mechanism it yields 17 nm whereas for nuclear mechanism only 1.5-2 nm.

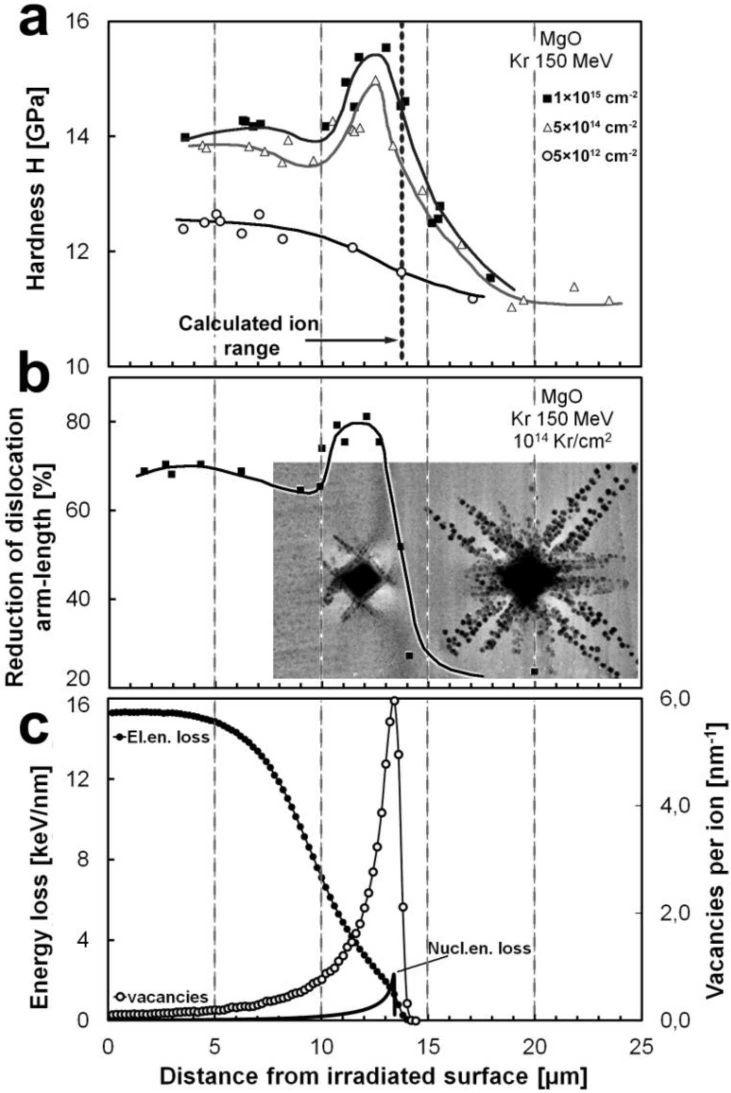

Figure 12. Hardness (a), dislocation mobility* (b) and calculated electronic energy loss (left axis) and number of oxygen and magnesium vacancies produced in elastic collisions per incident Kr ion (right axis) in dependence on depth in MgO irradiated with 150 MeV Kr ions. Φ=5×10^{12}, 5×10^{14} and 5×10^{15} Kr/cm^2.

***The inserted AFM image shows dislocation rosettes at the corresponding depth.**

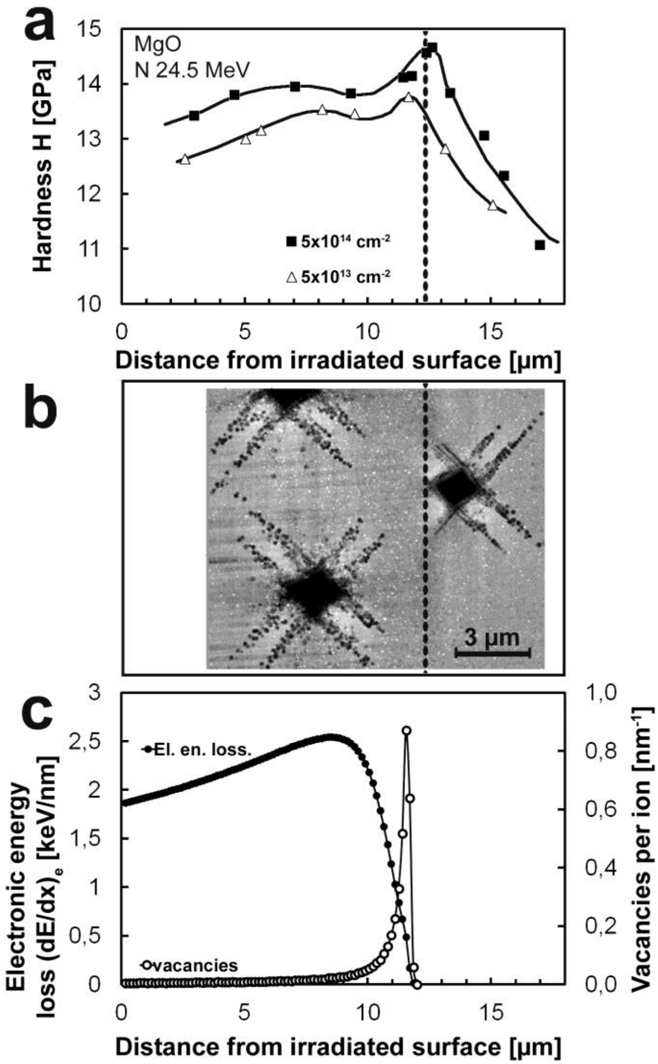

Figure 13. Hardness (a), dislocation mobility (b) and calculated electronic energy loss (left axis) and number of oxygen and magnesium vacancies produced in elastic collisions per incident N ion (right axis) in dependence on depth in MgO irradiated with 24.5 MeV ^{14}N ions. Φ=5×10^{15} and 5×10^{14} N/cm^2.

***The inserted AFM image shows dislocation rosettes at the corresponding depth.**

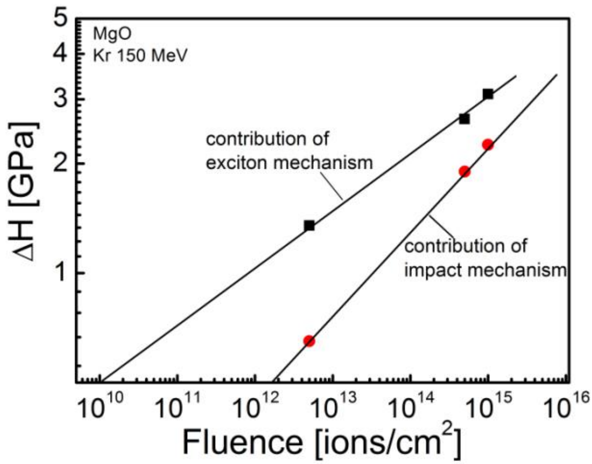

Figure 14. Contribution of electronic excitation and elastic collision components in hardening of MgO crystals irradiated with 150 MeV Kr ions at various fluences.

From the experiments described in this section it can be concluded that in formation of defects and modification of micromechanical properties a contribution comes from mechanism of electronic excitations, which is dominating in the region before the Bragg's maximum, as well as from the mechanism of elastic collisions which is determinant at the tail part of the ion range. The later is found to be high enough to create not only color centers but also aggregates of radiation defects responsible for hardening.

Conclusions about accomplishments presented in section 3.1.

1. A new result is ascertaining a change in the mechanism of plastic deformation in LiF irradiated with high doses of swift ions, where the dislocation mechanism is exhausted and replaced by shear banding mechanism which is based on local atomic rearrangements. The change in mechanisms of plastic deformation determines the upper boundary of irradiation-induced hardening. It has been shown that main requirements for the formation of localized shear bands in irradiated LiF is a high deforming stress and a free volume which is necessary for atomic rearrangements and formation of which is

confirmed by swelling of irradiated materials. Similar change in mechanisms of plastic deformation is apparent also in MgO crystals irradiated with high doses. Results have been published in author's article [39].

2. It has been shown that in MgO irradiated with swift ions additionally to exciton mechanism, which dominates in the region before Bragg's maximum, a contribution in hardening effect also comes from nuclear (collision) mechanism, which becomes dominant at the end of the ion range. The result demonstrates also the possibilities of nanoindentation method to distinguish between these differences. The investigation is summarized in the article #8 in the list of author's publications (March the 30th 2015, accepted for publication in Journal Applied Physics A, DOI: 10.1007/s00339-015-9145-9).

3.2. Formation of dislocations and nanostructuring in LiF irradiated with swift ions

3.2.1. Formation of dislocations in individual ion tracks

Analysis of data in literature confirms that in LiF irradiated with swift ions at room temperature dislocations are considered as the most prominent defect aggregates. This opinion largely has been based on numerous observations of formation of prismatic dislocation loops under electron beam in TEM but also partly because there is a lack of evidence about massive formation of other prominent defect aggregates (colloids, pores, fluorine bubbles). The existing models can explain the growth of dislocations [7, 8] but the formation of dislocations and the role of ion tracks in this process is not investigated.

Based on the TEM observation it has been concluded that during irradiation interstitial type prismatic dislocation loops with a Burgers vector $\boldsymbol{b}=a/2(1\ \bar{1}\ 0)$ are formed. As shown in Figure 15 a, schematically interstitial dislocation can be considered as two disc-type extra planes inserted in normal lattice – one anion plane and other – cation. Equal number of cations and anions is required to retain the charge neutrality. The view of dislocations in electron microscope is shown in Figure 15 b, but on chemically etched surface a schematic representation is given in Figure 15 c. In the result of etching, on the plane which intersects the dislocation loop, a joint pair of etch pits is created.

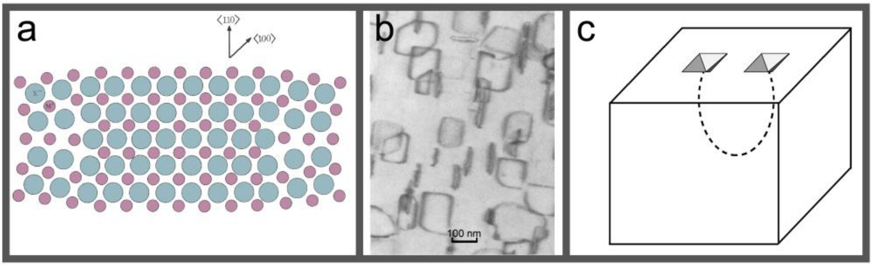

Figure 15. (a) A schematic of interstitial type prismatic dislocation loop in an ionic crystal. Larger circles are anions whereas smaler ones – cations; (b) view of dislocations in TEM [47]; (c) schematic of a dislocation loop on an etched surface.

In the beginning of research a series of experiments on LiF crystals irradiated with heavy ions (Au, Bi, U, Kr), which produce complex ion tracks containing a core region were carried out [48]. A relatively low fluences (10^8 – 5×10^9 ions/cm^2) were used to produce individual well separated tracks or to achieve a low amount of track overlapping. The ion beam was perpendicular to the (001) surface. For the observation of ion tracks the investigated samples were cleaved in the direction of ion beam, after which they were chemically etched in $FeCl_3$ solution for a very short time. Figure 16 shows the overall view of irradiated zone on profile. Due to the fact that in our experiments the direction of irradiation slightly differs from the normal, fragments of incoming tracks on the cleaved profile surface can be seen.

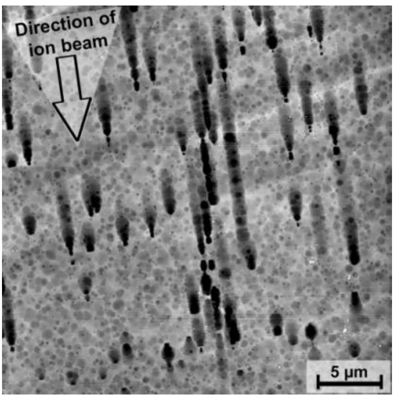

Figure 16. Profile surface of LiF irradiated with U ions. Chemically etched ion tracks and dislocation etch pits in them can be seen. Φ= 10^9 U/cm^2.

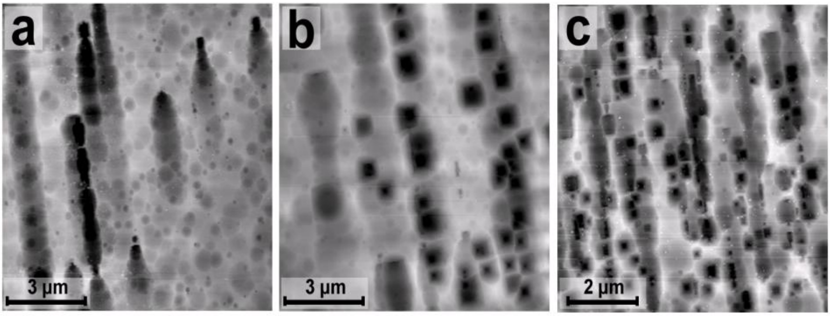

Figure 17. Dislocation etch pits in the trajectory of ions in LiF irradiated with 2.6 GeV U ions at various fluences (a)-10^8, (b)-10^9, (c) -5×10^9 U/cm^2.

At a higher magnification in order of increasing fluence ion tracks are shown in Figure 17. Rows of etch pits are clearly seen in the trajectory of individual tracks. They can be interpreted as either dislocation nuclei or more likely as tiny dislocation loops with the size close to critical (~7-10 nm) for the existence of stable loops. The rounded and not pyramidal shape of etching pits points on the small size of loops. With the beginning of track overlapping, the ordering of etch pits in rows along the trajectory of a track remains but they acquire classic pyramidal shape, which confirms the enlargement of loops in environment saturated with primary color centers. The formation of etch pit pairs also points towards this (Figure 17 b). The ordering of dislocations along the ion trajectory has been observed also in TEM experiments on MgO crystals irradiated with swift ions [49]. The formation of such rows can be explained by the fact that ion tracks which contain core damage as well as dislocations themselves exhibit mechanical stress fields and the interaction of these fields causes self-organized ordering of dislocations.

In order to determine whether formation of dislocation rows is connected with a crystallographic orientation of a sample, series of experiments with irradiation at oblique incidence were conducted [50]. For these experiments GeV Bi ions were used. Results are shown in Figure 18, where irradiation has been performed at 20^o angle in respect to the normal of surface. Two cleavages of the irradiated sample were obtained according to the included schematic (Figure 18 a). The frontal surface is intersected by ion tracks, etching pits corresponding to tracks can be seen (Figure 18 c), the count per area of which coincides well with the fluence. The side-view of the sample is shown in Figure 18 b, in which trajectories of ion tracks oriented in 20^o angle can be clearly seen. Similar to irradiation at normal incidence, dislocation etch pits in the case of irradiation at 20 degrees also are ordered in rows along ion tracks whereas there are very few dislocations in the area between ion tracks. Rows of dislocations are observable only in the region where electronic energy loses remain above 10 keV/nm. After this region a transitional region which contains discontinuous tracks follows. In the further part of ion tracks dislocations are forming only in conditions of track overlapping and their arrangement is chaotic – without indications on the direction of irradiation.

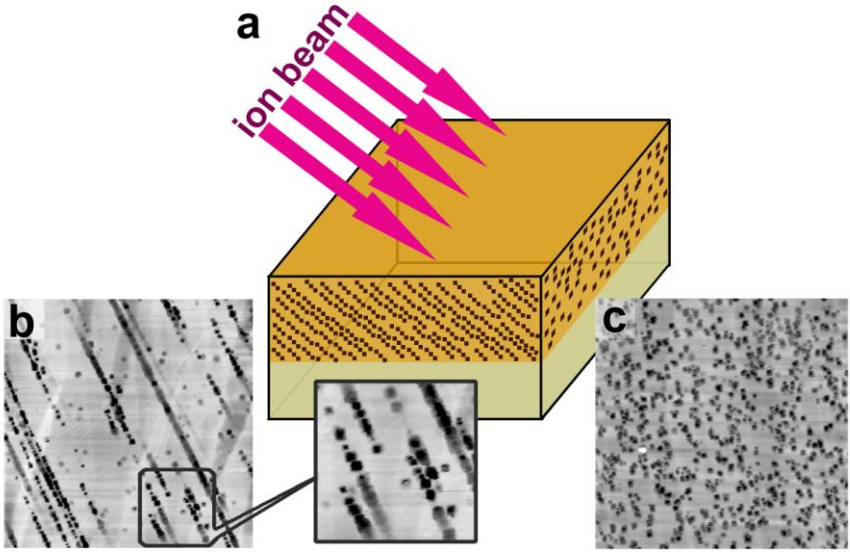

Figure 18. Schematic representation of direction of irradiation and corresponding projections of tracks on cleavage surfaces (a). Track structure on the side surface, AFM image (b). Track structure on the front surface, AFM image (c). Sample is LiF crystal irradiated with 2.38 GeV Bi ions. The incidence angle of ion beam is 20^o in respect to the normal of the surface, Φ= 5×10^9 Bi/cm^2.

The mentioned results confirm that in LiF irradiated with heavy ions dislocation loops are formed within the trajectory of complex tracks which contain core region. Formation of prismatic dislocation loops (emission) in the core region of track supposedly occurs due to

Coulomb forces. With the relaxation of atomic displacements caused by Coulomb forces also dislocation-related processes can occur – including a decrease of distance between interstitial anions and cations [51] and formation of their clusters which can serve as nuclei for the interstitial-type dislocation loops.

In the case of light ions due to low energy losses (d*E*/d*x* <10 keV/nm) ion tracks containing only a halo region are formed. Dislocations within individual tracks were not observed but formation of their nuclei might be considered.

3.2.2. Dislocation structure and nanostructuring at the stage of track overlapping

The substantial role of dislocations on mechanical properties of materials is well known and mechanisms of their mutual interactions as well as interaction with other defects is well investigated [52-54]. Thus investigation of structure evolution in crystals irradiated with swift ion is important and actual.

As shown in previous section, in the case of heavy ions formation of dislocations begins already within individual tracks. By increasing he fluence, a density of ion tracks and with it also a concentration of dislocations increases within the irradiated material. In the result of track overlapping, not only a number of dislocation loops but also their size increases. As a consequence of interaction between dislocations and due to ordering effect of mechanical stress field in ion tracks, at high fluences self-organized arrangement of dislocations and formation of structure consisting of nano-sized blocks occurs.

The described evolution of structure is also confirmed by the investigations along the ion trajectory in LiF irradiated with 150 MeV Kr ions [55]. For ions with the given energy approximately the first half of trajectory, where d*E*/d*x*>10 keV/nm, formation of nanostructure is observed while in the rest of trajectory freely arranged irradiation caused dislocations can be seen (Figure 19). Between these two zones there is a transitional region. The structure of mentioned zones at larger magnification is presented in Figure 20. The nanostructured part contains elongated in the direction of ion beam blocks with a size 30-90 nm. The density of dislocations in Figure 20 c is around 2×10^9 cm^{-2}. Similar structure in the d*E*/d*x*>10 keV/nm region at fluences above 10^{12} ions/cm^2 has been observed also for other investigated ions (U, Au, Bi).

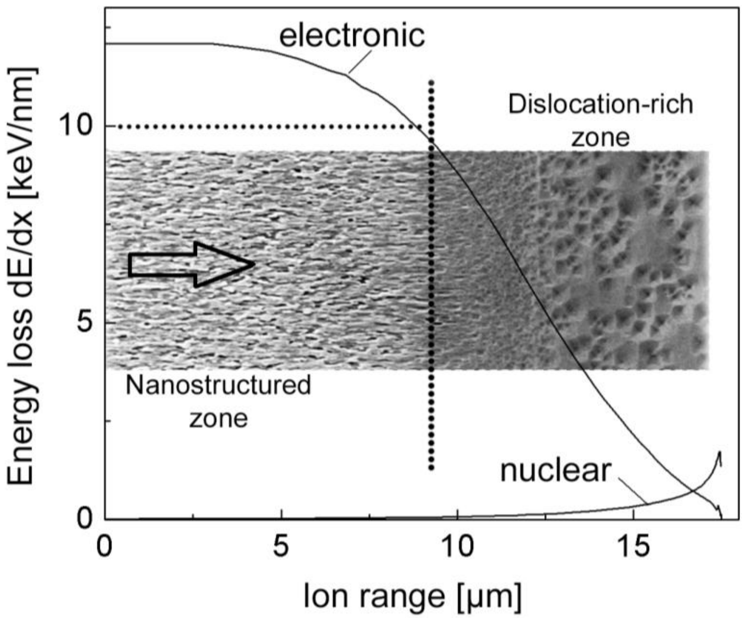

Figure 19. Structural changes and ion energy losses in dependece on ion range in LiF irradiated with 150 MeV Kr ions.
Φ = 6×10^{12} Kr/cm^2, ion flux = 8×10^{10} ions·cm^{-2}·s^{-1}. SEM image shows overall view of a profile surface (after chemical etching). Direction of irradiation shown with an arrow.

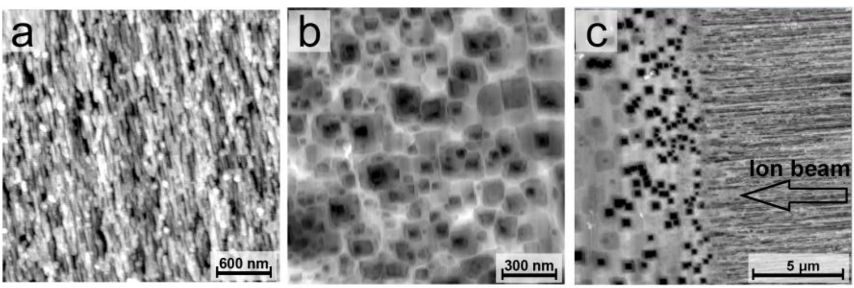

Figure 20. Nanostructured (a), dislocation-rich (b) and transitional region (c) in LiF irradiated with 150 MeV ^{84}Kr ions (AFM images).

X-ray diffraction (Figure 21 d) shows the maintained single crystalline state but with a substantial degree of disordering [33]. In LiF irradiated with U ions high resolution x-ray diffraction shows a structure with presence of elements disoriented by low angles as well as change in interatomic distances (Figure 21 c). The small change of interatomic distances can be explained by a presence of numerous similar linear defects (interstitial prismatic dislocation loops). The investigation of structure in conjunction with the x-ray diffraction data allows interpreting the observed structure as mosaic-type nanostructure with low angle boundaries between blocks, in which dislocations are the most prominent structural elements.

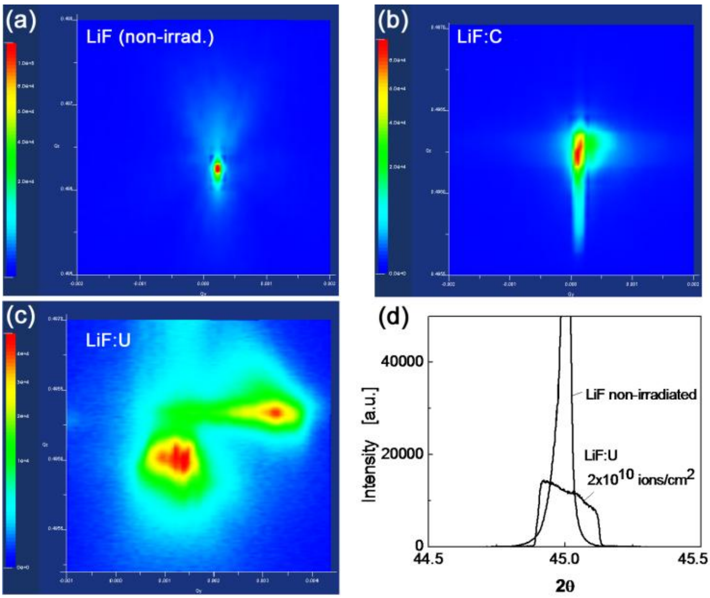

Figure 21. Reciprocal space maps obtained by x-ray diffraction for LiF crystals (a) unirradiated, (b) irradiated with 10^{12} cm^{-2} C ions, (c) nanostructured by irradiation with 4×10^{11} cm^{-2} U ions. (d) X-ray diffraction pattern before and after irradiation with 4×10^{-11} cm^{-2} U ions.

Nanostructure can be expected when electronic energy loss of ions surpasses a threshold of 10 keV/nm and fluence ensures overlapping of tracks. For the majority of heavy ions nanostructuring occurs at fluences above 10^{12} ions/cm^2.

***Thermal stability of nanostructures*.** A thermal stability of the obtained nanostructure and dislocation-rich structure has been investigated in annealing experiments [55]. Structural investigations using AFM and SEM microscopes show that the ion induced nanostructure in LiF crystals is stable up to around 500 K temperature. After annealing above 500 K a transformation of the nanostructure into a structure that is rich in chaotically arranged dislocations occurs. Increasing the annealing temperature even further the density of dislocations gradually decreases and the state of unirradiated crystals is reached at 830 K temperature.

In addition to structural investigations also the influence of annealing on mechanical properties of irradiated LiF crystals has been investigated. A decrease of hardness similar to structural changes occurs at temperatures above 500 K and a full recovery at the level of unirradiated crystal is reached at 830 K. The relative dependence of hardness change on the temperature was plotted in Arrhenius coordinates, from which in the temperature range 530-830 K an activation energy E_{act}=0,2±0,03 eV was determined. This value is close to the activation energy of *H*-center migration in LiF [56]. The activation energy of *F*-center migration is substantially higher (~1.5 eV). This result points towards the substantial role of interstitial fluorine defects in the hardening effect. According to the Hobbs model in the irradiated crystal complex *H*-centers in the form of fluorine molecules are bound to dislocations. Obviously, heating above 500 K temperature leads to a decomposition of these complexes. Free *H*-centers, which can annihilate with less mobile *F*-centers, are released. From what has been said it can be concluded that the disintegration of dislocation structure and recovery of mechanical properties is related to a decomposition of complex *H*-centers and excretion of reaction products from dislocations. The newly formed free *H*-centers can annihilate with less mobile *F*-centers or as an alternative they can exit on the surface of crystal by emitting a neutral fluorine atom.

Further we will look at the formation of dislocations using light ions. AFM data shows that light ions, energy loss of which at a similar specific energy as heavy ions (11 MeV/u) is below the threshold energy loss (<10 keV/nm), at the stage of track overlapping form dislocation seeds as well as numerous dislocations. The arrangement of dislocations in contrast to heavy ions is not related to the direction of ion tracks.

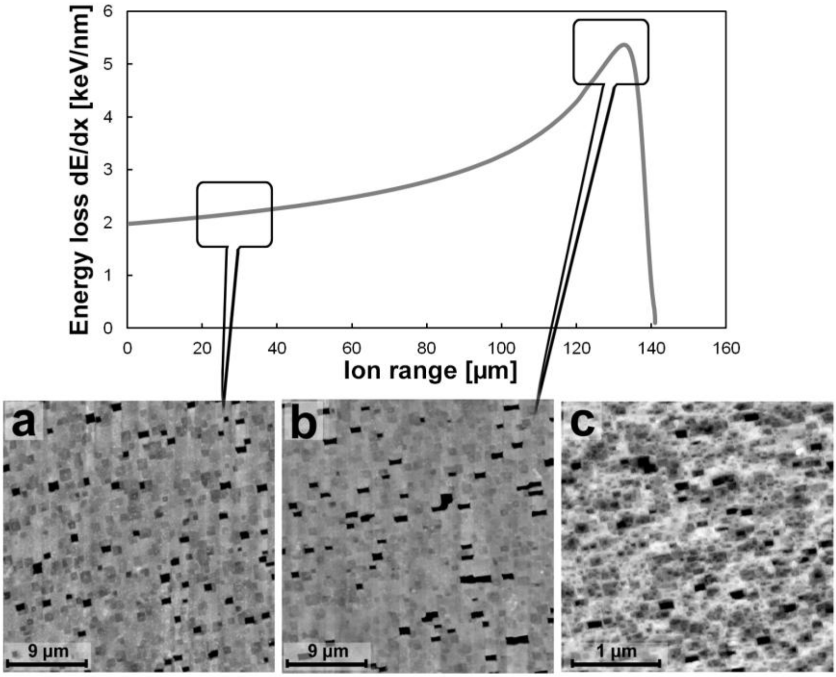

Figure 22. Electronic energy loss and dislocation structure in LiF irradiated with 410 MeV S ions at the fluence of Φ=10^{12} S/cm^2: at the beginning of ion track (a) and at the Bragg's maximum (b). Dislocation structure at Φ=4×10^{13} S/cm^2 (c).

Figure 22 shows dislocation structure in LiF irradiated with 410 MeV S ions. Dislocations can be observed in the whole irradiated zone. Nevertheless, the concentration of dislocation etch pits is not constant along the ion trajectory. It reaches maximum at depth which corresponds to the Bragg's maximum of electronic energy loss. At this maximum (Figure 22 b) the size of dislocation loops is substantially larger than at the vicinity of irradiated surface (Figure 22 a). The elongated shape of dislocation etch pits which forms due to merging of a pair of neighboring etch pits is an evidence for this (see Figure 15 c). Near the surface the size of dislocations loops is so small that both etch pits overlap and are not separately distinguishable with the method of etching. Increasing a fluence leads to an increase of dislocation concentration nearing 10^{10} cm^{-2} while maintaining the chaotic arrangement of dislocations (Figure 22 c). A selectivity of chemical etching decreases and with it also the contrast of AFM images which confirms an increase of chemical activity on the surface.

A similar result to S ions was obtained also in LiF irradiated with other light ions (C, N). Formation of dislocations was observed in the irradiated layer but similar to S ions nanostructuring was not observed even at maximum fluences at which samples still keep their integrity [33]. Also high resolution XRD data do not show a presence of sub-structure and low-angle boundaries in LiF irradiated with C ions (Figure 21 b).

From Figure 22 a and b a concentration of dislocations in LiF irradiated with S ions can be estimated. At the fluence of 10^{12} S/cm^2 (absorbed dose 1.75 MGy) the density of dislocations has been estimated as 9×10^7 cm^{-2}, whereas the average diameter of dislocation loops estimated as 150 nm. From these data it follows that for this fluence the number of dislocated ions contained within dislocations reaches 1.25×10^{18} cm^{-3}. For the comparison it can be mentioned that at the saturation the concentration of *F*-centers reaches 4.5×10^{19} cm^{-3} [57].

At the same absorbed dose (1.75 MGy) the efficiency of dislocation formation in LiF irradiated with heavy (Bi) ions was estimated. For this purpose a number of dislocations within a single track was determined, from which a density of dislocations for the fluence 1.2×10^{11} Bi/cm^{-3} (corresponding to the 1.75 MGy dose) was estimated. Calculations yielded the dislocation density of 1.7×10^{10} cm^{-2}. It confirms that the efficiency of dislocation production is substantially higher in the case of irradiation with heavy ions.

Nanoindentation measurements show that irradiation with heavy as well as with light ions causes increase of hardness (see section 3.1). In addition to this observation in our experiments we have found that a large hardening effect is observed for the dislocation-rich structure as well as for the nanostructure produced by heavy ions. In both cases at a sufficiently high fluence the upper limit of hardening effect is reached.

The performed investigations confirm the important role of dislocations in the hardening effect. The role of dislocations intensifies in irradiated crystals because they serve as sinks of radiation defects and as seeds for the growth of their clusters. The reduction of dislocation mobility in crystals due to influence of segregation is well known. Such “atmosphere” containing dislocations become immobile and can serve as strong obstacles for the indentation caused dislocations [58].

In crystals irradiated with swift ions the reduction of dislocation mobility with increasing fluence is clearly pronounced. In the case of MgO crystals it is shown in Figures 12 and 13. Thus at high fluences irradiation caused dislocations by losing their mobility become strong obstacles for the indentation produced dislocations.

For the description of interaction between dislocations and strong ensembles of obstacles the Orowan's model [54] can be used. According to this model (Figure 23) the dislocation line bows due to shear stresses between obstacles, it encompasses obstacles and continues its path forward leaving behind dislocation loops around obstacles (Orowan's loops). The mechanical stress required for the dislocation to overcome the obstacle is calculated using Orowan's formula. In the case of hardness the effect related to surmounting obstacles is expressed according to formula (4).

$$H = H_b + \frac{\alpha \cdot G \cdot b}{\lambda} \qquad (4)$$

where H – hardness of material containing obstacles, H_b – hardness of initial material, α – coefficient characterizing the strength of obstacles, G – shear modulus, b –Burgers vector and λ – average distance between obstacles.

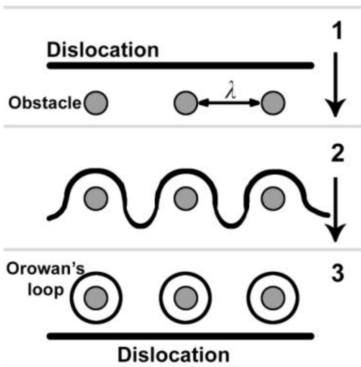

Figure 23. Orowan's bowing model describing the interaction between a dislocation and hindering obstacles.

Taking into account that dislocations are localized in ion tracks, the distance between tracks can be used as a parameter in the Orowan's formula (4) for the hardness calculation of irradiated crystals. The hardness values calculated using this formula were compared against experimentally obtained values. The comparison for LiF irradiated with Bi ions, which produce tracks with a core damage, is given in Figure 24. The calculated and experimental values coincide well. As expected, differences were observed in the region of hardness saturation. A good conformity of experimental data with the Orowan's model was observed also in the case of other heavy ions, which allows using this model for the explanation of swift ion induced hardening mechanism. In the case of light ions experimental data about the concentration of dislocations necessary for estimations were obtainable only up to fluences of 10^{12} ions/cm^2.

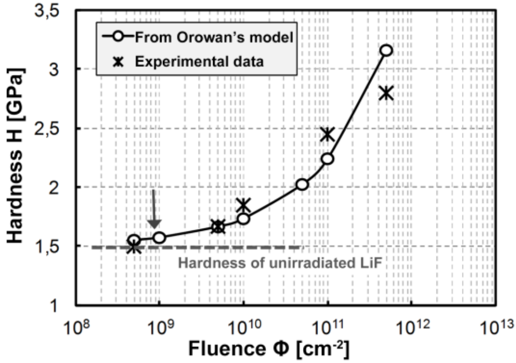

Figure 24. Experimentally obtained and calculated from Orowan's model hardness values (using the average distance between tracks) in dependence on fluence in LiF irradiated with 2.38 GeV ^{209}Bi ions.

3.2.3. Possibilities for nanostructuring by irradiation with low-energy heavy ions

Analysis of literature data about formation of color centers in LiF crystals confirms that in the case of heavy ions, energy of which is in the range of few MeV and energy loss of which is below critical 10 keV/nm threshold, there are peculiarities in respect to GeV energy ions. The most important one is relatively high contribution from nuclear energy losses. This circumstance in addition to a low penetration depth of MeV energy ions within a crystal and a high density of excitations allows obtaining *F*-center concentration on more than one order of magnitude higher than in the case of GeV ions at a similar absorbed energy [42, 43]. It was expected that higher concentration of primary radiation defects by intensifying formation of defect aggregates will bring peculiarities also in processes of structure formation and modification of mechanical properties. In order to determine it the investigation of structure and micromechanical properties in LiF irradiated with 3-15 MeV Au ions was performed [59, 60]. The penetration depth of these ions in LiF is in the range of 0.7-3.5 μm and 50% from the energy loss are contributed by the nuclear mechanism.

Optical absorption spectra for samples irradiated with MeV ions are different from those of GeV ions with relatively more intensive 445 nm band which confirms a more pronounced tendency of color center aggregatization (Figure 25 a).

Nanoindentation tests show clear hardening effect on the irradiated surface (Figure 25). The effect increases at higher fluences. At fluences above 10^{14} Au/cm^2 the upper limit of hardness is reached. The results for all energies of MeV ions are grouped on a single curve which can be linked to a ratio *E*/R (where R is the penetration depth of ions) which in all cases is almost identical.

The comparison between MeV and GeV ions shows that high hardness values are achieved in both cases, only for MeV ions it requires more than one order of magnitude higher fluence.

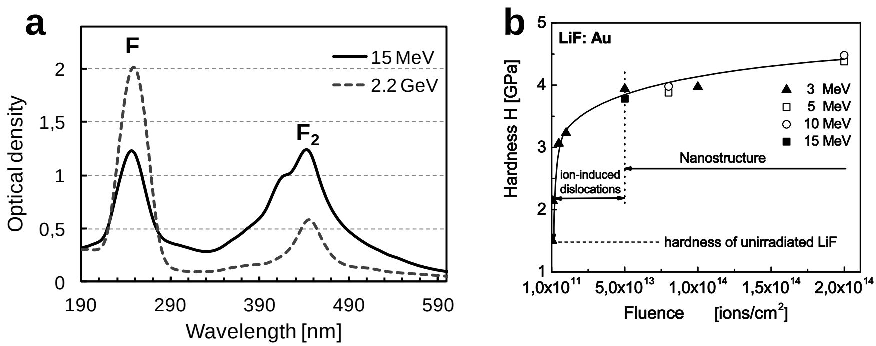

Figure 25. (a) Optical absorption spectra of LiF irradiated with 15 MeV (Φ=5×10^{13} ions/cm^2) and 2.2 GeV (Φ=1×10^{10} ions/cm^2) gold ions. (b) Dependence of hardness on fluence in LiF irradiated with 3-, 5-, 10- and 15- MeV ^{197}Au ions.

Structural investigation of LiF irradiated with MeV ions shows formation of dislocation-rich structure up to fluence of 5×10^{13} Au/cm^2 whereas at higher fluences a formation of nanostructure with a grain size 50-150 nm (Figure 26) has been observed. An evidence for a tendency of fragmentation of structure under swift ion irradiation might be investigations of irradiated LiF thin polycrystalline films [61]. Our results suggest that fragmentation occurs due to an evolution of dislocation system by formation of substructure boundaries.

In the case of MeV ions at the high-dose region a transition from plastic deformation via dislocation mechanism to shear banding, which is described in section 3.1, can be clearly observed in the indentation zone.

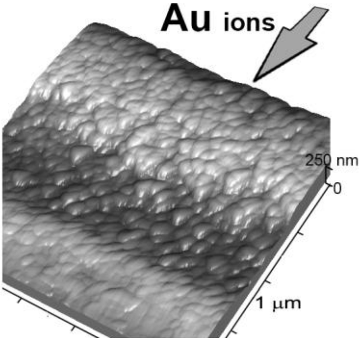

Figure 26. Structure of LiF irradiated with 15-MeV Au ions at fluence Φ = 5×10^{13} Au/cm^2 (3D-AFM image of profile surface after chemical etching).

Figure 27 shows depth profiles of hardness and energy loss (their values along the trajectory of ions). Due to the fact that for the given energy ions electronic and nuclear energy losses are close, contribution of both mechanisms can be observed on hardness curves. The mechanism of electronic excitations dominates in a region up to the Bragg's maximum whereas mechanism of elastic collisions becomes determinant at the tail end of ion tracks. In this respect there is a similarity with the observations in MgO crystals where both mechanisms substantially contribute to the formation of defect aggregates and hardening.

In Figure 27 it can be seen that in the evolution of defects the ion current which determines the ion flux has a substantial role. This problem has been touched in work [42] and the increase of *F*-center concentration at strong currents has been linked to a fact that at conditions of high density of defects, formation of complex *H*-centers intensifies and they are excluded from a recombination with *F*-centers. By matching several factors – low penetration depth of these ions (up to 3.5 μm), intensive ion flux (6.2×10^{10} ions·cm^{-2}s^{-1}) and high fluence (up to 10^{14} Au/cm^2), a concentration of primary radiation defects on one order of magnitude higher than in the case of GeV ions was obtained. A high intensity of irradiation and high concentration of primary radiation defects are favorable factors for the formation of defect aggregates and nanostructuring.

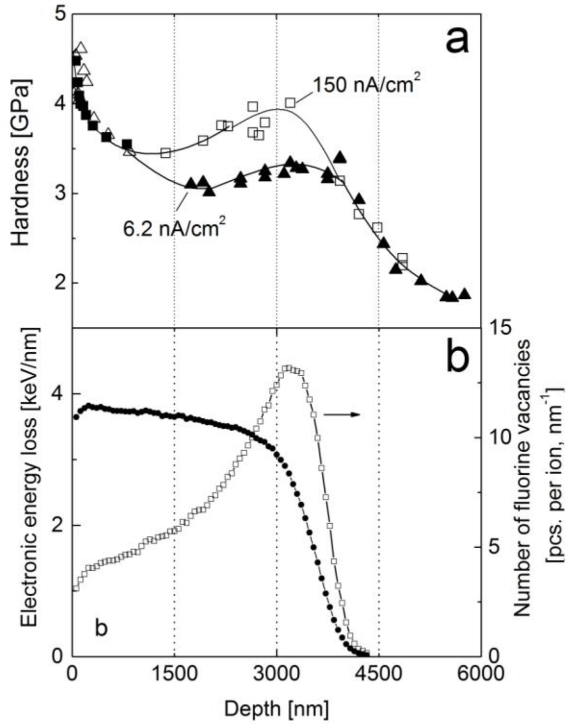

Figure 27. (a) Depth profile of hardness in a LiF crystal irradiated with 15-MeV Au ions at ion beam currents of 6.2 and 150 nA/cm^2. Measurements performed on a profile surface by controlling the distance to the irradiated surface. (b) Calculated depth profile of electronic energy loss (left axis, filled circles) and fluorine vacancies per incident Au ion in collision cascades (right axis).

3.3. Use of micro-mechanical methods for investigation of radiation resistance in materials for practical applications

3.3.1. Influence of GeV energy ^{238}U and ^{197}Au ions on properties of MgO

Due to developments in nuclear technologies and adjacent activities, interest about materials, which are resistant to swift ions, fission fragments and influence of other energetic particles, increases. As one of such candidates is MgO utilization of which in storage of radioactive materials and in other processes linked to radiation is an actual problem. A preservation of integrity and strength of a material in such conditions is one of fundamental requirements for applications.

In our work the influence of irradiation with 2.2 GeV energy U and Au ions on micromechanical properties and structural changes in MgO crystals have been investigated. MgO was irradiated with fluences up to 7×10^{13} ions/cm^2. The work has been performed in collaboration with the GSI, Darmstadt, Germany.

Results are shown in Figures 28-30. Optical absorption spectroscopy shows formation of *F*-type color centers. In nanoindentation measurements on irradiated surface (Figure 28 a) a hardening effect has been found, which at maximum fluence (7×10^{13} ions/cm^2) reaches 55%. From load-displacement data obtained by nanoindentation, calculated work of plastic and elastic deformation shows a slight radiation-induced decrease in microplasticity (from 72% to 67%). In our investigations a similar change in micromechanical properties was observed in related ZnO crystals irradiated with 150 MeV Kr ions.

Overall the results confirm a preservation of most important mechanical properties, in the case of hardness, even a substantial improvement. Nanoindentation, x-ray diffraction, optical absorption as well as results on modifications of a structure confirm accumulation of radiation defects and their aggregates (mainly dislocations), an increase of disordering and formation of radiation caused mechanical stresses within the material. The mentioned changes are not critical regarding micromechanical processes but might influence mechanical properties negatively on a macro scale.

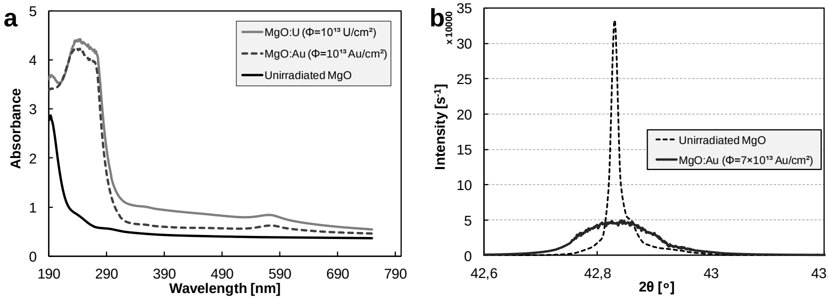

Figure 28. Optical absorption (a) and x-ray diffraction (b) spectra in MgO irradiated with gold and uranium ions.

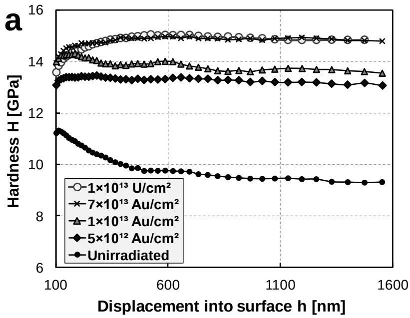

Figure 29. Dependence of hardness (a) and Young's modulus (b) on indentation depth in MgO irradiated with various fluences of ions. Measurements performed on the irradiated surface.

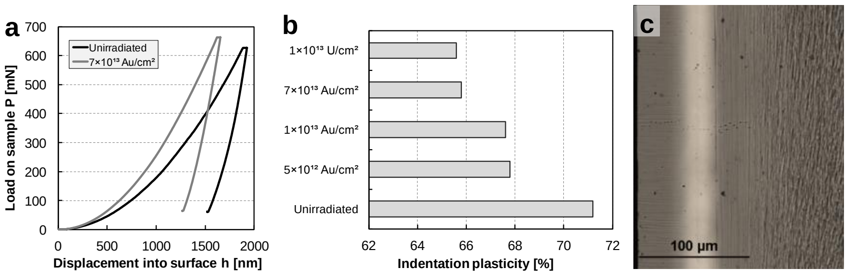

Figure 30. (a) Load-displacement curves obtained by nanoindentation, (b) indentation plasticity calculated from load-displacement curves, (c) irradiation caused region of mechanical stresses behind the irradiated MgO layer.

3.3.2. Influence of GeV energy ^{238}U ions on mechanical properties and structure of isotropic polycrystalline graphite

Characterization of persistence of micromechanical properties in graphite under influence of GeV energy ions is actual due to potential application of graphite in nuclear technologies, including modern ion accelerators. From a fundamental standpoint processes in swift ion tracks in graphite, where a short-term thermal impact and impulse loads are acting, are interesting due to a possibility for a formation of various carbon forms (diamond-like carbon, fullerenes, nanotubes, etc.).

Single crystalline graphite is very fragile and anisotropic material thus in technology fine-grained isotropic graphite is preferred. In our work modifications of mechanical properties and structure of graphite irradiated with 2.6 GeV energy U ions have been investigated [62]. The maximum fluence 10^{13} U/cm^2 used for irradiation corresponds to 250 MGy dose.

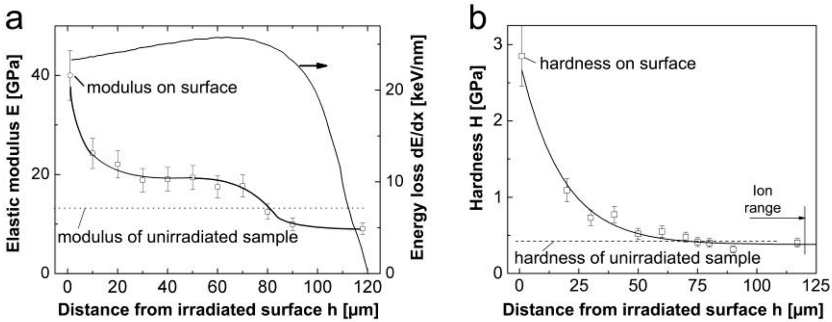

Figure 31. (a) – Depth profiles of Young's modulus and electronic energy loss, (b) Depth profile of hardness in R6650 grade fine-grained graphite irradiated with 2.6 GeV ^{238}U ions. Fluence 10^{13} U/cm^2.

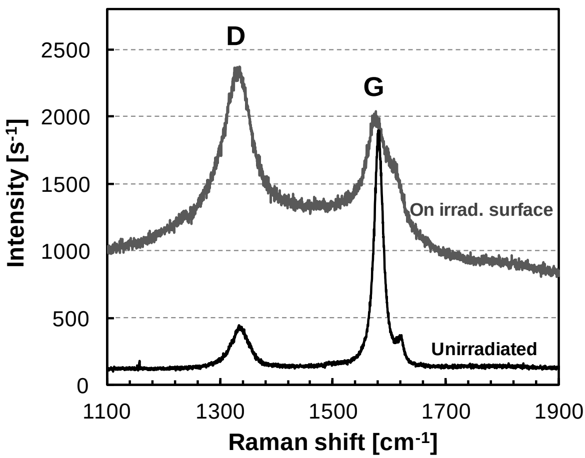

Figure 32. Raman spectra for unirradiated and irradiated with 2.6 GeV U ions isotropic polycrystalline graphite (R6650), fluence Φ=1×10^{13} U/cm^2.

The obtained results show that very soft graphite in the result of irradiation becomes a material with high hardness and Young's modulus (Figure 31). It confirms a formation of a hard form of graphite. The mentioned changes affect the surface layer the most but are observable also in a layer up to several tens of micrometers. In order to determine to which carbon form this material belongs spectra of Raman shift have been obtained. Results showed Raman spectra characteristic to amorphous (glassy) carbon with G band at 1580 cm^{-1}, D band at 1350 cm^{-1} and wide plateau between these bands (Figure 32) [63]. Glassy carbon is unusual in a way that sp^2 bonds are dominating in it whereas material has high hardness [64]. It is explained by a fact that glassy carbon possesses traits characteristic to curved arcuated configurations of graphite [65].

Overall graphite withstands irradiation very well. Micromechanical properties and microplasticity doesn't show significant signs of degradation. Nevertheless, the unequal distribution of hardness with depth can be a cause of long-range mechanical stresses which might stimulate macroscopic damage processes.

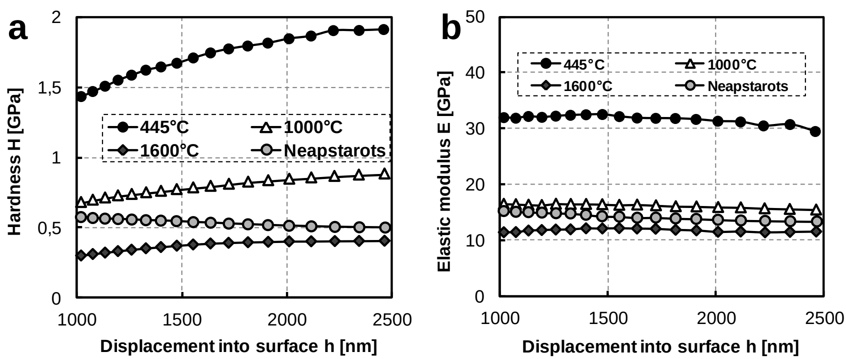

Figure 33. Dependence of hardness (a) and Young's modulus (b) on temperature.

In this case a favorable observation is that in real conditions of a severe irradiation partial recovery of micromechanical properties and structure occurs due to intensification of diffusion and recombination of defects (Figure 33).

Conclusions and main results

The doctoral study has been devoted to investigation of micro-mechanical properties and structure-formation processes in LiF and MgO crystals under high-dose irradiation with swift ions at room temperature. Irradiation doses for the light ions reach up to 90 MGy but for heavy – up to 250 MGy.

It has been shown that irradiation with MeV-GeV energy ions creates prismatic interstitial-type dislocation loops in LiF crystals, similar as it has been observed by irradiation with high-energy electrons [7, 47]. By using AFM, SEM and methods of chemical etching it has been determined that dislocations occur already in individual ion tracks forming rows of dislocations in the trajectory of a track. Dislocation structure intensively forms at the stage of track overlapping. Dislocation rows have been observed in the trajectory of all heavy ion tracks in a wide range of irradiation angles. It can be concluded that dislocations is a characteristic structural feature of complex track structure caused by heavy ions.

It has been shown that irradiation caused dislocations substantially contribute in processes of a structure formation and modification of micromechanical properties. The most prominent examples are formation of nanostructure and the observed hardening effect caused by swift ions.

By irradiating LiF crystals with high-energy heavy ions (U, Au, Kr, Xe) a mosaic-type nanostructure with block size 30-90 nm and low angle boundaries between them have been obtained. The requirements necessary for it have been determined: (1) irradiation fluence ($\geq 10^{12}$ ions/cm^2) ensuring overlapping of tracks, (2) a sufficiently high energy of ions, for which the electronic energy loss surpasses the critical threshold ($dE/dx \geq 10$ keV/nm), which is required for the formation of tracks containing core damage. Tracks with such structure have a mechanical stress field which by interacting with the stress fields of dislocations serves for the formation of a nanostructure oriented in the direction of ion tracks.

By irradiating LiF crystals with ions for which the energy losses are below the mentioned threshold ($dE/dx \geq 10$ keV/nm), in the case of heavy as well as light ions a structure rich of freely arranged dislocations was usually observed.

Nevertheless, at specific circumstances nanostructuring has been achieved by irradiating LiF crystals with relatively low-energy heavy ions. For these experiments 3 MeV – 15 MeV energy Au ions were used. By matching several factors – strong contribution of impact processes in the radiation damage, low penetration depth of these ions (up to 3.5 μm), intensive ion flux (6.2×10^{10} ions·cm^{-2}s^{-1}) and high fluence (up to 10^{14} Au/cm^2), a concentration of primary radiation defects on one order of magnitude higher than in the case of GeV ions was obtained. In such circumstances nanostructuring was achieved due to an intensive formation and self-organization of dislocations. The unusually high observed concentration of *F*-centers can be linked to an intensive formation of complex *H* centers which become excluded from the recombination with *F* centers [43].

The obtained results show that dislocation-rich structure as well as nanostructure is characterized by a substantial increase of hardness, at high fluences reaching saturation values of 3.5-4.5 GPa. It has been found that the saturation of hardness is caused by a transition in mechanism of plastic deformation from dislocation slip to formation of localized shear bands, which are similar to ones observed in metallic glasses and and occur *via* local atomic rearrangements under high applied stress.

Nanoindentation method has been successfully used in investigations. By complementing it with measurements of dislocation mobility, a contribution from electronic excitations and collision mechanisms in the hardening effect of swift ion irradiated LiF and MgO crystals has been evaluated.

Nanoindentation with an orientation towards applications has been used for the investigation of structure and micromechanical properties in MgO and related oxides (ZnO) as well as other radiation-resistant materials (graphite). A high resistance of MgO to irradiation with GeV-energy U and Au ions has been observed. Maintained crystallinity and microplasticity in irradiated MgO crystals and substantial increase (55%) of hardness has been shown.

An influence of GeV energy heavy ions (U, Au) on properties of graphite has been investigated. A novelty is the result that irradiation causes transformation of graphite into a sp^2 form of glassy carbon which is characterized by high hardness and Young's modulus values. Nanoindentation and AFM methods have been successfully used for the characterization of ZnO nanocomposites and ceramics as well as carbon DLC films [67-70].

In the field of structural investigation a research connected with the dislocation processes, which requires a detailed continuation, has been solved successfully. For the following research interests touch structural modification processes in functional materials which are caused by low-energy, especially slow, but highly charged (charge +30 up to +90) ions. In contrast to GeV ions, which are characterized by very high kinetic energy, highly charged ions have a considerable potential energy (used for the ionization). The data from literature shows that slow highly charged ions are surprisingly efficient in formation of surface nanostructures [66]. The interest concerns a possibility for the formation of volume nanostructures.

Main thesis

1. Formation of swift-ion-induced dislocations in LiF crystals has been studied. It has been established, that small dislocation loops and their nuclei appear already in individual tracks while an intense growth and ordering of dislocations occurs in the stage of track overlapping. In complex ion tracks exhibiting core damage dislocations are arranged in a row along the ion trajectory.
2. A mosaic-type nanostructure has been obtained in LiF crystals by irradiation with high energy heavy (U, Au, Kr, Xe) ions. The necessary conditions for nanostructuring have been determined: (1) fluence ensuring the overlapping of tracks (10^{11} - 10^{12} ions/cm^2) and (2) electronic energy loss of ions above 10 keV/nm.
   When energy loss of ions is below 10 keV/nm, swift ions create a dislocation-rich structure consisting of randomly distributed dislocations.
3. It has been found that nanostructure as well as dislocation-rich structure exhibit increased hardness which at high doses reaches saturation (3.5-4.5 GPa, 200% hardening effect). It has been shown that the effect saturates due to transition from plastic deformation *via* dislocation mechanism to shear banding mechanism which is based on local atomic rearrangements.
4. It has been shown that in LiF and MgO crystals irradiated by swift ions the contribution in the observed hardening effect comes from exciton mechanism as well as from nuclear (collision) mechanism. The exciton mechanism is dominating in LiF crystals, whereas in commercial MgO crystals which contain impurities the contribution of both mechanisms is substantial.

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   (March the 30th 2015 – the article has been accepted for publication in Journal *Applied physics A.*)

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Acknowledgements

The author expresses sincere gratitude to the supervisor of doctoral study Janis Maniks and to colleagues from the Laboratory of Surface Physics – Ilze Manika, Faina Muktepavela and Rolands Grants for the support and valuable consultations during the preparation of thesis.

Gratitude expressed to collaboration partner Prof. Kurt Schwartz for the contribution in discussions regarding results, for valuable consultations and performance of irradiation experiments. The author wants to acknowledge also collaborator Michael Sorokin for the participation in theoretical calculations.

Acknowledgment to the ESF project «Support for Doctoral Studies at University of Latvia» for the financial support during preparation of this study.