

SWIFT HEAVY ION IRRADIATION EFFECTS ON DOPED ALKALI HALIDES

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The effects produced by heavy ion irradiation in KBr:Ag and KCl:Ag crystals are investigated using optical spectroscopy. For KCl, the results are compared with the effects obtained in the pure crystals. After irradiation with heavy ions up to 11.2 MeV/u specific energy, the absorption bands suffer a series of changes, related to the structure of defects and also to their dimensions. In the high Ag concentrated samples, the Ag^+ ions are changing their valence to Ag^- while in the samples containing Ag nanoclusters the irradiation induces changes in the nanocluster size.

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1. Introduction

Radiation-induced effects in ionic crystals have been intensively studied by using photons, neutrons, electrons, and α - particles [1] leading to a broad understanding of the exciton-based damage mechanism and of the microstructure of the defects. Various specific damage processes were reported when LiF or other alkali-earth halides are irradiated with energetic heavy-ions [2-4]. Recently, we extended the studies on NaCl and KCl pure crystals irradiated with heavy ions, the formation of primary defects and their distribution around the ion track being investigated [5].

This contribution describes new experiments exposing silver-doped KCl and KBr crystals to a beam of heavy ions and compares the results with those obtained for the irradiation of pure crystals. For pure KCl crystals, a series of results is presented. To test the influence of doping there were used crystals after electrolytical colouring in the cases of both high and low concentration samples, containing either only Ag^- ions or Ag^- ions and $n\text{Ag}^0$ nanoclusters. Comparison with previous results obtained after conversion of Ag^- ions to Ag nanoclusters by means of thermal treatment and UV illumination [6,7] is made. Aggregation phenomena and nanoclusters of silver were investigated by optical spectroscopy.

2. Experimental

2.1. Crystal growth

Crystals were grown by Kyropoulos method in platinum crucible and inert atmosphere (nitrogen). A starting seed is used and the crystals are pulled from melt. The volume of a crystal is $\sim 10 \text{ cm}^3$.

Raw materials (KBr and KCl), usually Merck substances, were purified in the lab and kept at 100°C prior to the growth (to avoid the OH contamination from the air). The silver halides (AgCl and AgBr) were added in the melt in order to obtain different Ag^+ ions concentrations ($10^{16} - 10^{18} \text{ ions/cm}^3$). Due to the segregation coefficients of an impurity, usually any doped crystals have a radial

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distribution of the dopant, and the top of the crystal (near the seed) is less doped than the bottom of the crystal. To minimize this concentration gradient the doped samples were cut perpendicular on the pulling direction and were obtained samples with an uniform distribution of the impurity.

2.2. Irradiation

Single KCl, KBr, KBr:Ag and KCl:Ag crystals were freshly cleaved (100), of size between 0.5 and 1 mm² and thickness between 1 and 1.5mm. The thickness of the crystals was in all cases larger than the projected ion range [8]. The crystals were irradiated with ²³⁸U and ¹⁹⁷Au ions of a specific energy up to 11.2 MeV/u at the linear accelerator UNILAC of the GSI (Darmstadt, Germany), in the fluence range between 5×10⁶ and 10¹² ions/cm².

All irradiations were performed at room temperature and under normal incidence of the ions to the cleavage plane (100) of the crystals. In some cases, thin Al foils of different thickness were placed in front of the samples in order to vary the energy and the energy loss of the ions impinging the sample. For the calibration of the fluence, polycarbonate foils were used. The maximum flux of the ions was limited to 10⁸ s⁻¹cm⁻².

2.3. Optical measurements

The optical absorption measurements after irradiation with heavy ions required fluences between 5×10⁹ and 10¹² ions/cm². For optical microscopy measurements a Nipon optical microscope OPTIPHOT-2 was used.

The color centers were studied using a UV- visible double beam spectrophotometer (ATI Unicam UV4), in the spectral range between 200 and 900 nm where the main absorption bands of the electron (F, F₂), hole (V₃) colour centers and colloidal particles are localized.

As quoted in literature [9], the absorption bands of F and F₂ centers correspond to the maxima at 560 nm and 825 nm for KCl.

The concentrations N_F (cm⁻³) of the F centers in KCl crystals can be determined with a Smakula-Dexter formula using oscillator strengths of f~1 ([9] and the references within), according to:

$$N_F(KCl) = 3.6 \times 10^{15} \times \frac{OD}{R} \quad (1)$$

where OD=lg(I₀/I) represents the optical density at the band maximum, and R is the ion range which is practically identical with the thickness of the colored layer.

The electrolytical coloring is used to change the sign of the silver ions from Ag⁺ to Ag⁻. Through the pointed electrode the electrons are injected creating F centers and Ag⁻ ions (Ag⁺ + 2e⁻ → Ag⁻).

Thus we obtained the absorption spectra of the samples that present more resolved bands for the silver ions than in the case of uncolored crystals. Also, the concentration of Ag⁻ ions can be calculated in KCl crystals (in number of Ag⁻ ions/cm³) using a Kleemann relation [10]:

$$N_{Ag^-} = 0.36 \times 10^{16} \times \alpha_{\max} (cm^{-1}) \quad (2)$$

where α_{max} is the optical-absorption coefficient at the wavelength of the Ag⁻ ion peak.

The changes in the number of ions in the case of Ag⁻ are easily observed during various treatments of the crystals. The method has the advantage that the centers formed are very stable. In the case of high concentrated samples, Ag clusters are formed directly by electrolytical coloring.

2.4. Chemical etching

For the etching experiments along the tracks (perpendicular to the sample surface) fluences up to 10^{12} ions/cm² were used.

Several etchants were analyzed for the KCl crystals and the best results were obtained using the receipt indicated by [11], a mixture of 95% solution of ethanol 25% saturated with BaBr₂ and 5% solution of 100g BaBr₂/1l methanol. The etching was performed at room temperature for 1 minute by immersing the samples into the mentioned above solution. After etching on (001) of the samples irradiated through a hexagonal structured grid, successful track etching could be easily discovered due to the characteristic pattern of the irradiated and non-irradiated regions, similar to those obtained for NaCl [5]. Owing the cubic structure of the KCl lattice, the ion tracks and dislocations etch pits have a pyramidal shape.

To determine the range of the etchable damage along the tracks, the samples were cleaved prior to the etching perpendicular to the sample surface, i.e. parallel to the ions trajectories. For more detailed observations, crossed sections of crystals along the ion path were studied with a scanning electron microscope (SEM).

3. Results and discussions

3.1. Optical absorption spectroscopy

The optical study for the pure crystals was carried through for the irradiation with ¹⁹⁷Au of a 10.5 MeV/u energy and fluences between 8×10^9 and 4×10^{11} ions/cm².

Typical spectra are shown in Fig. 1 for KCl crystals irradiated with Au ions at different fluences. For the lower fluence, 8×10^9 ions/cm², the spectra exhibit only three main bands, corresponding to V₃, F and F₂ centers, with the maxima at 212 nm, 560 nm and 825 nm [9]. As it can be observed, at higher fluences the spectrum becomes more complex for both of the crystals, exhibiting peak shoulders at around 360 nm, 425 nm, 680 nm and 735 nm for KCl. These bands can be assigned to more complex color centers such as F₃ or F₄, F centers aggregates, or even to K colloids. The positions of the colloidal bands are expected to appear in the 730-740 nm range for KCl. The absorption bands of these color centers overlap and it is impossible to estimate their concentration.

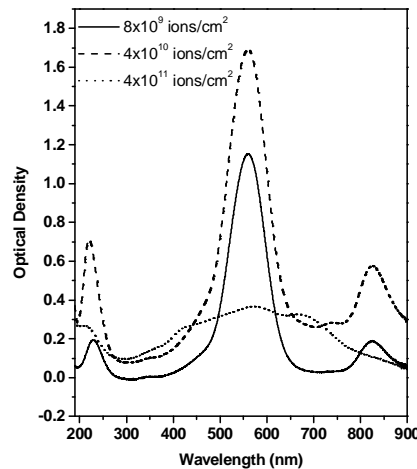


Fig. 1. Absorption spectra of KCl crystals irradiated with Au (10.5 MeV/u) at different fluences.

The concentration of the F centers per cm² (n_F) in KCl crystals was calculated using the equation (1). The absorbed dose D was calculated according to:

$$D[\text{Gy}] = 1.6 \times 10^{10} \frac{E_{\text{tot}}[\text{MeV}] \times \Phi[\text{ions}/\text{cm}^2]}{\rho[\text{g}/\text{cm}^3] \times R[\text{cm}]} \quad (3)$$

where E is the total energy of the ion, Φ is the fluence, ρ is the density of the crystal and R is the length of the ion range which is practically identical with the thickness of the colored layer.

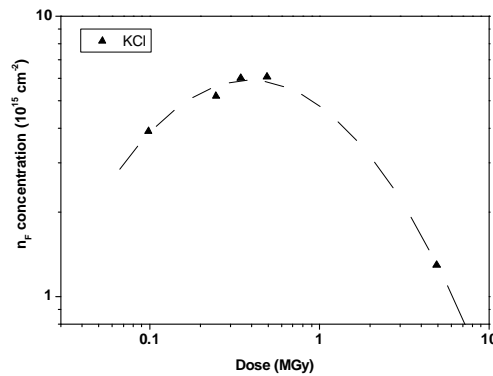


Fig. 2. The concentration of F centers as a function of the irradiation dose for samples of KCl irradiated with Au (10.5 MeV/u). The data are fitted with polynomial functions.

Fig. 2 shows the concentration per cm^2 of the F centers as a function of the irradiation dose for KCl. As in the case of LiF and NaCl, n_F increases with the irradiation dose (fluence) up to saturation and by further irradiation decreases. For KCl the saturation takes place at lower dose and the decrease is larger than that for LiF. Although a saturation value of the F centers concentration appears, the number of single F centers per track ($n_F/\text{fluence}$) is permanently decreasing with the increasing of the fluence, as shown in Fig. 3.

At the saturation, the mean distance between two F centers of the order of about 207\AA for KCl, close to the value of 178\AA for NaCl and different from the case of LiF where the distance between two F centers is only of 73\AA (17 lattice constants). Note that the creation of color centers takes place not uniformly in the crystal. The defects present before irradiation can influence the spatial distribution of the Frenkel pair created by the decay of excitons. This process can be enhanced by fluences (doses) where track halo overlaps [1,2]. The large difference between the values found in LiF, in NaCl and KCl for the distance between the F centers at the saturation level might be explained by the thermal annealing of the primary Frenkel pairs, which in NaCl are not stable at room temperature.

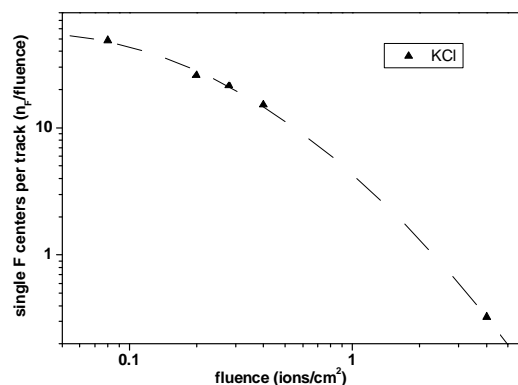


Fig. 3. The concentration of single F centers per track as a function of the fluence for samples of KCl irradiated with Au (10.5 MeV/u). Polynomial fit is included to guide the eye.

The saturation concentration of F centers in KCl (Table 1) is in a good agreement with the results found by Young for irradiation with fission fragments [12].

Table 1. Irradiation parameters and track characteristics for KCl crystals and values of parameters at the saturation level for the irradiation with Au (10.5 MeV/u).

Crystal	Ion	Specific energy (MeV/u)	Total energy E_{tot} (MeV)	Mean energy loss E_{tot}/R (keV/nm)	Range TRIM R (μm)	Saturation concentration of F centers (10^{15} cm^{-2})	Saturation fluence ($10^{10} \text{ ions/cm}^2$)	Lattice constant d (\AA)	Distance between F centers in d
KCl	^{197}Au	10.5	2070	15.3	135.4	6.05	3.8	6.285	33d

In the case of doped crystals, when as-grown samples of KCl:Ag and KBr:Ag are irradiated with energetic heavy ions, primary defects appear (electron centers F, F_2 and complementary hole centers V_3) and takes place the conversion Ag^+ ions \rightarrow Ag^- ions.

The Ag^+ ions in KCl present three bands at approximately 217 nm, 228 nm and 245 nm whereas in KBr the bands appear at approximately 213 nm, 228 nm and 240 nm (Fig. 4).

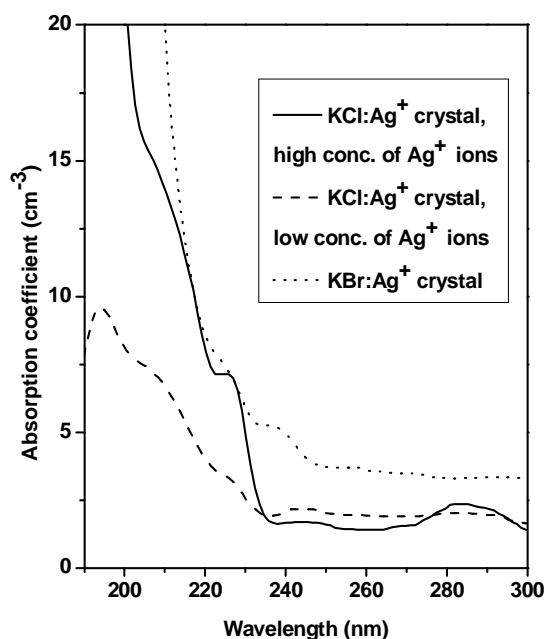


Fig. 4. Absorption spectra of KCl:Ag⁺ as-grown samples with high and low concentration of Ag and of KBr:Ag⁺ as-grown sample, irradiated with U of 11.1 MeV/u specific energy.

In the absorption spectra only one band is usually observed for the Ag^- ions, namely their C band peaking at 290 nm for KCl:Ag⁻ and at 300 nm for KBr:Ag⁻.

Depending on the concentration of silver in the crystal, the absorption spectra of the irradiated crystals show well resolved bands for Ag^+ ions, as it is illustrated in Fig. 4. All the three bands corresponding to the Ag^+ ions can be observed in the spectrum of the highly doped KCl:Ag⁺ sample, along with the appearance of C band of the Ag^- ions.

For the electrolytically colored samples (KCl:Ag⁻+Ag clusters) the differences in the absorption spectra before and after irradiation are more spectacular.

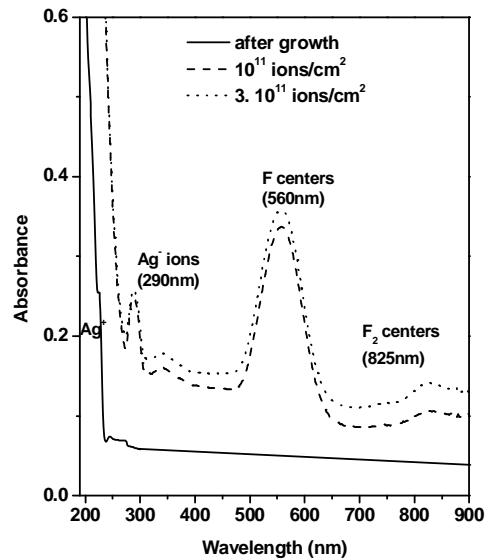


Fig. 5. Absorption spectra of KCl:Ag⁺ as-grown samples irradiated with U ions of 10.5 MeV/u specific energy at different fluences.

When a sample of KCl:Ag is colored electrolytically, Ag⁺ ions are formed and in some cases Ag aggregates give rise to supplementary bands in the absorption spectra. The intensity for the C band (290nm) of Ag⁺ ions is decreasing after irradiation even for medium fluence 10^{10} ions/cm², as it can be observed in Fig. 6. An increasing of the specific energy of the heavy ions produces a stronger diminishing of the intensity of C band. Thus, Ag⁺ ions concentration decreases from the initial value of 1.63×10^{17} ions/cm³ to 3.93×10^{16} ions/cm³ after irradiation with ions of 11.1 MeV/u specific energy, according to equation (2).

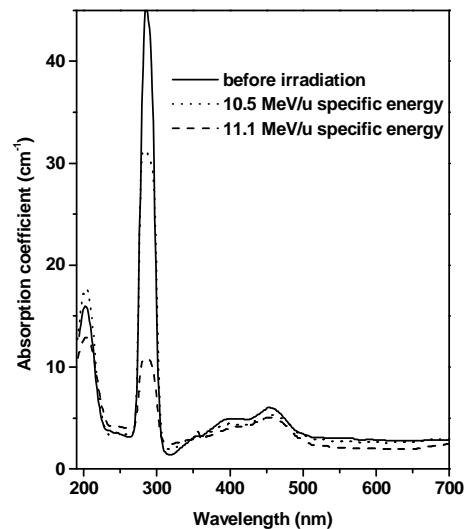


Fig. 6. The absorption spectra of a KCl:Ag⁻ electrolytically colored crystal before and after irradiation with U ions of 10^{10} fluence with different specific energies.

For low doped crystals, the intensity of Ag^- ions absorption band (obtained after electrolytical coloring) is decreasing with the increasing of the fluence. The absorption bands of primary defects (F electron center and their corresponding hole trapped center V_3) are stronger and even F_2 center absorption band appears, as illustrated in Fig. 7.

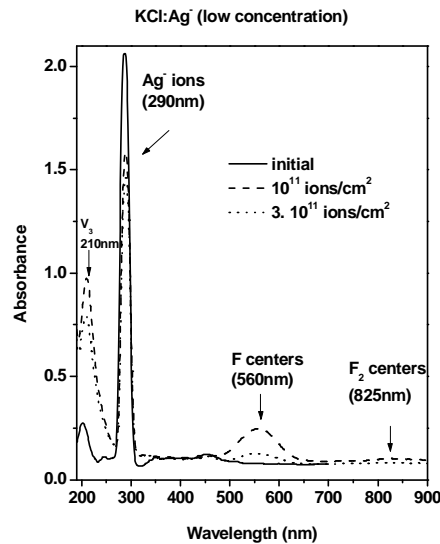


Fig. 7. Absorption spectra of silver doped KCl crystals electrolytically colored irradiated with 10.5 MeV/u U ions at different fluences.

For the highly doped KCl:Ag sample (Ag nanoclusters were formed after electrolytical coloring with an absorption band around 450 nm) the structural changes of the nanoclusters under irradiation are proven by the shift of the colloidal band maximum, Fig. 8. Based on previous measurements and calculations using both absorption spectroscopy and electron microscopy measurements [6, 7] it was proven that a shift of the colloidal band is connected with a change of the nanoparticle dimensions, a shift towards shorter wavelengths corresponding to a decreasing of the particles diameters and to a change in their distribution.

The diminishing of the Ag^- band is suggesting that besides the structural changes appearing on the already formed Ag nanoclusters, new silver nanoclusters are formed during heavy ions irradiation. The number of Ag^- ions is decreasing according to the eq. (2) and the number of colloidal particles is increasing, being directly related with the intensity of the colloidal band [6,7].

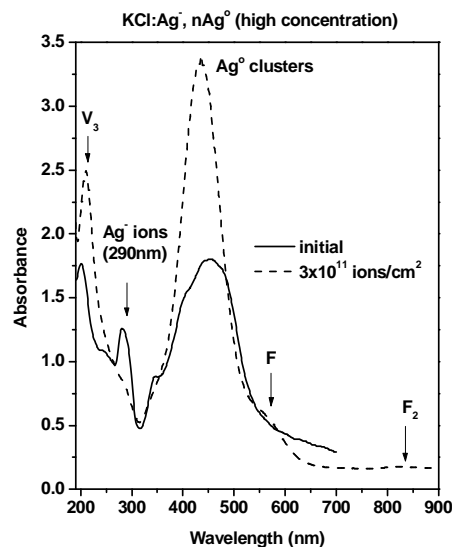


Fig. 8. Absorption spectra of a KCl:Ag⁻, nAg⁰ crystal (high concentration of silver) electrolytically colored before and after irradiation with U ions of 10.5 MeV/u specific energy.

In the initial spectrum presented in Fig. 8 can also be observed that the Ag nanoclusters band is in fact an overlapping of absorption bands, indicating that we have more than one predominant dimension and that the particle size distribution is broad. The irradiation is inducing a tightening of the Ag particle distribution, in the spectrum after irradiation the colloidal band appears to be well resolved indicating one predominant dimension of the particles.

For the electrolytically colored doped KBr:Ag crystals similar behavior was observed. The sample of KBr:Ag⁻+Ag nanoclusters after irradiation show an increasing of the Ag-ions C band (~300 nm) and a decreasing of the colloidal band (~420 nm), as it can be observed in Fig. 9. This is probably due to the fact that after coloring some of the Ag⁻ ions formed aggregates of Ag⁻ ions (the colloidal band is overlapping the Ag⁻ aggregates band). Ag⁻ aggregates are known to be thermally and optically unstable. Moreover, the colloidal band is shifting towards longer wavelengths (~440 nm) and this means that the Ag particles are increasing their sizes.

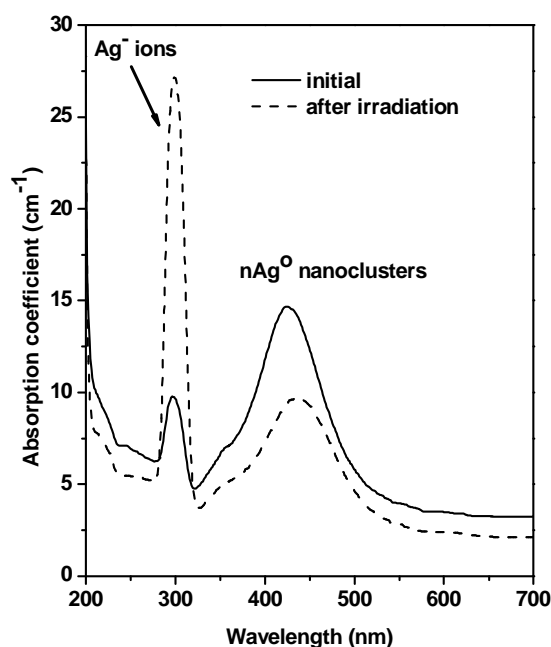


Fig. 9. Absorption spectra of a highly doped KBr:Ag crystal before and after irradiation with U ions of 10.5 MeV/u specific energy with a 10^{10} ions/cm² fluence.

3.2. Track etching measurements

KCl crystals were etched along the tracks in the solution described above after the irradiation with Au ions of 10.5 MeV/u specific energy. The damage along the ion trajectories becomes visible as long striated structures, as shown in Fig. 10.

The damage along the ion path is revealed as a strip in the upper part of the images, darker in the optical microscopy image, lighter for the electron microscopy image. For all irradiations the etched tracks were continuous.

For the irradiation with Au ions, the length of the etched track was 127 μm , shorter than the range according to the TRIM code [8] which was 135.4 μm . There is no difference in the aspect of the crystals when doped and pure crystals are studied by microscopy means.

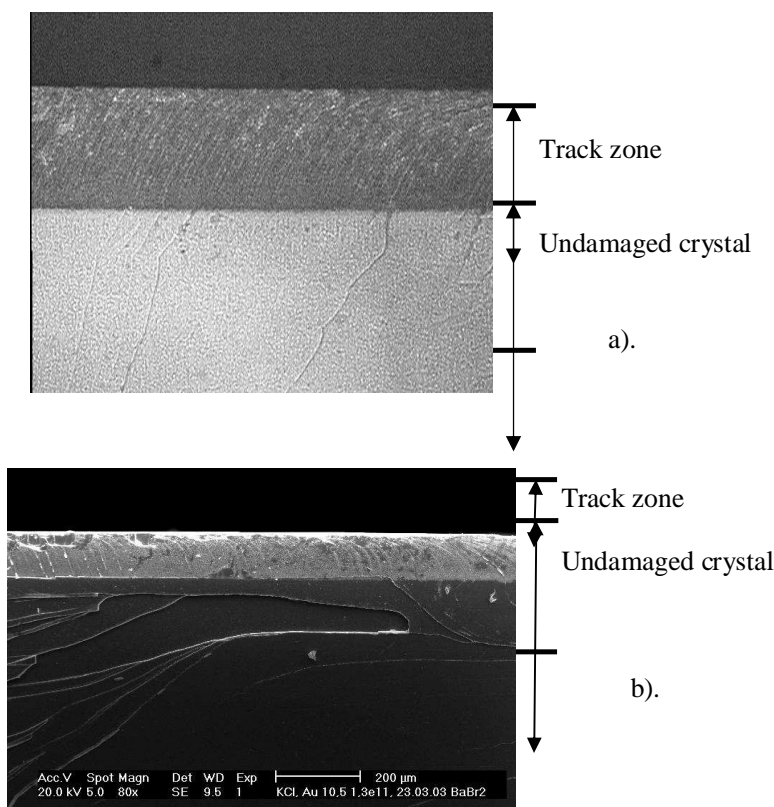


Fig. 10. The images of the damages produced along the ion tracks in a KCl crystal by the irradiation with Au ions of 10.5 MeV/u specific energy: a) optical microscopy and b) electron microscopy.

4. Conclusions

In conclusion, for the colored samples the irradiation produces changes of the Ag-ions absorption bands, the Ag⁺ aggregates and structural changes of the already formed silver nanoclusters. However, further irradiations at higher energies should be performed in order to increase the penetration depth.

When irradiating silver doped crystals with heavy ions, similar processes take place as during thermal treatment or UV illumination, indicating that the formation of Ag nanostructures is possible by irradiation for highly doped crystals.

While the thermal treatment and UV illumination take place in the entire crystal (usually 1×1×2 cm³) the heavy ions irradiation takes place in a surface layer up to 150 μm thickness. The appearance of Ag⁺ ions (intensity of C band dependent of fluence), the decreasing of Ag⁺ ion band intensity with ion fluence and the change of size and distribution of Ag nanoclusters demonstrates that the heavy ion irradiation is a strong enough driving force able to form nanostructures in doped alkali halides, its effects being measurable by both optic and microscopic means even on a thin layer above the surface of the crystals.

References

- [1] N. Itoh, A.M. Stoneham, *Materials Modification by Electronic Excitations*, Cambridge Univ. Press, (2001).
- [2] C. Trautmann, K. Schwartz, O. Geiß, *J. Appl. Phys.* **83**, 3560 (1998).
- [3] K. Schwartz, A. Benyagoub, M. Toulemonde, C. Trautmann, *Radiat. Eff. Def. Solids* **155**, 127 (2001).

- [4] I. Manika, J. Maniks, K. Schwartz, C. Trautmann, Nucl. Instr. Meth. B **196**, 299 (2002).
- [5] M. Enculescu, K. Schwartz, C. Trautmann, Nucl. Instr. Meth. B, **229**(3-4), 397 (2005).
- [6] E. Vasile, M. Datcu, S. Polosan, E. Apostol, V. Topa, J. Cryst. Growth **198/199**, 806 (1999).
- [7] M. Enculescu, V. Topa, E. Vasile, Nucl. Instr. Meth. B, **191**(1-4), 433 (2002).
- [8] J. F. Ziegler, P. Biersack, U. Littmark, The Stopping and Ranges of Ions in Matter, Pergamon, New York, (1985).
- [9] Ch. B. Lushchik, A. Ch. Lushchik, Decay of electronic excitation with defect formation in solids, Nauka, Moscow, (1989).
- [10] W. Kleemann, Z. Phys. **214**, 285 (1968).
- [11] K. Sangwal, Etching of Crystals. Theory, Experiment, and Applications, North-Holland, Amsterdam, (1987), 405
- [12] D. A. Young, Radiation Measurements, **34**, 139 (1995).