Comparison of F- and F_2-centers Production and Stability in NaF Crystals with Ion and Electron Beams [1]

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Abstract – Nominally pure and with impurities of Sc, Cu and Li of different concentrations crystals of NaF were irradiated by electron and ion beams with different doses. Absorption and photoluminescence spectra of initial and irradiated samples were measured. Temperature stability of produced defects (F- and F_2,F_3-centers) was checked. The concentrations of created defects were estimated using Smakula's formula. As a result was carryed out the comparison of F- and F_2,F_3-centers production and stability in NaF crystals irradiated with ion and electron beams.

1. Introduction

Crystals of NaF transparent up to 11 eV are full investigated model objects and perspective optical materials. Irradiation of this crystals by ionizing radiation results in effective generation of single and complex anion vacancies (in particular, F-, F_2- and more complex aggregate colour centers) [1]. Impurity composition of crystals significantly influences on a dynamics of defects production and temperature stability of produced colour centers [2].

There is a possibility to create a reconfigurable lasers on a base of NaF crystals with colour centers [3]. In the recent work [4] there was suggested an idea of optical microcavity creation in green-red spectrum band based on aggregate colour centers produced by charge particles in fluoride crystals. For successful solution of mentioned tasks it is necessary to find optimal colour center concentrations in order to get highest light yield.

The purpose of this work is to compare dynamics of accumulation and temperature stability of F-, F_2-, F_3^+-centers, to establish optimal colour center concentrations in order to get highest luminescence yield in sodium fluoride crystals of various impurity compositions following irradiation by electrons and ions beams.

2. Experimental

Pure and with impurities of Sc, Cu and Li of different concentrations NaF crystals were investigated. Samples were grown in the Institute of Physics, National Academy of Science of Kyrgyzstan using the modified Kiropoulos technique.

Irradiation of samples was carried out with accelerated electrons 10 MeV energy or with accelerated ions of 1 MeV/nucleon energy in Ural State Technical University-UPI. Optical and spectral-luminescence characteristics have been measured using absorption and luminescence excitation methods. Absorption spectra were measured at room temperature using spectrophotometers of types Helios alpha UV-Visible (Ural State Technical University-UPI, Russia) and Lambda 900 UV/VIS/NIR (Lyon University, France). Luminescence and excitation spectra were registered using laboratory equipment in Lyon University, France. Deuterium lamp FL-1039 and double monochromator Gemini-180 were used for excitation. The luminescence spectra from the illuminated face of the crystal were detected with monochromator 320 Triple Imaging Axial and CCD camera.

The project range of accelerated ions in samples was calculated using the TRIM Monte-Carlo simulation code.

Temperature stability was measured using standard method in Ural State Technical University-UPI. Irradiated samples were annealed beginning at 50˚C till 300˚C with the step of 50˚C, so in general there were 6 annealing procedures for each of irradiated samples. After each stage of annealing absorption spectra were measured to observe dynamic of colour centers concentration.

3. Results

Comparison of absorption spectra of the samples irradiated with different charge particle types shows that with increasing of radiation dose the quantity of produced defects (F- and F_2,F_3^+–centers) increase, too, Figures 1–4. It should be noted, that in irradiated by electrons samples F-centers accumulate faster than F_2 and F_3^+–centers (Fig. 1, 3). In contrary, for samples which were irradiated by N^+ ions at beginning fluences there is characteristic approximately equal rate growth of both F- and F_2, F_3^+-centers quantities. However, above fluence equal to 10^{15} cm^{-2} quantity of produced aggregate defects harshly increasing (Fig. 2,4). It

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should be conclude that at high fluences of ions irradiation the processes of effective transformations from single to aggregate colour centers take place.

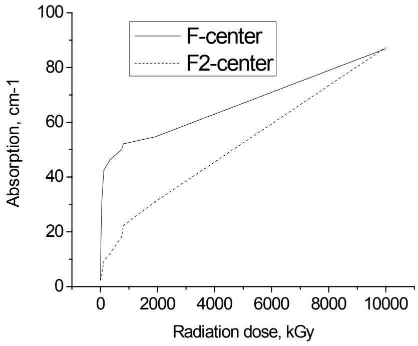

Fig. 1. Absorption of F- and F_2-centers in the bands of 340 nm and 500 nm, consequently, against radiation doses in the sample of pure NaF following electrons irradiation.

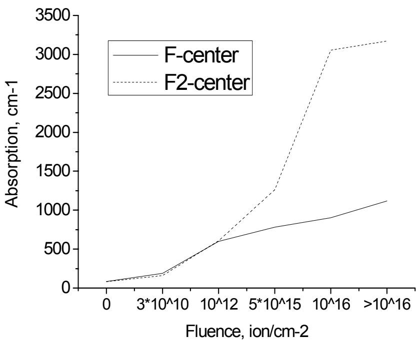

Fig. 2. Absorption of F- and F_2-centers in the bands of 340 nm and 500 nm, consequently, against fluences in sample of pure following N^+ ions radiation.

In NaF samples with impurities of Sc, Cu and Li much more both single and aggregate defects then in pure crystal following electrons and ions irradiation were produced. The character of defects accumulation for impurity crystals is similar to those for pure crystals.

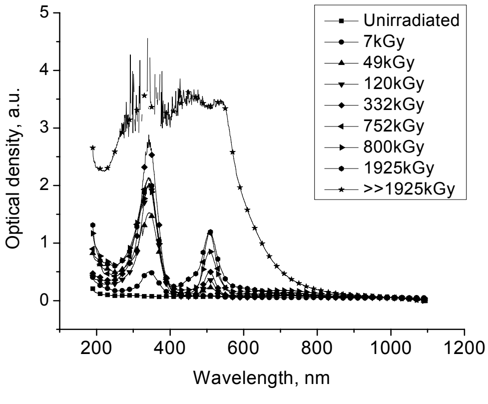

Fig. 3. Absorption spectra of pure NaF irradiated by electrons (energy 10 MeV) with different doses.

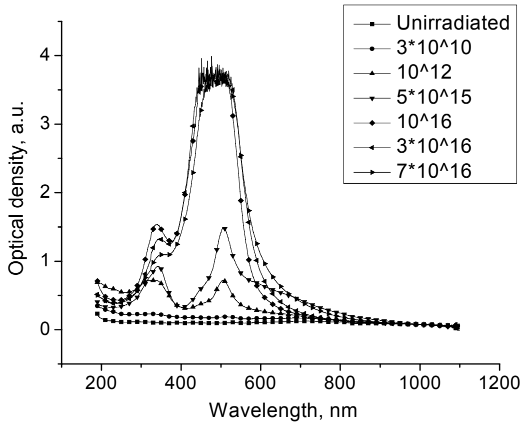

Fig. 4. Absorption spectra of pure NaF irradiated by N^+ ions (energy 16 MeV) with different fluences.

Observed difference in dynamics of single and aggregate defects accumulation at electrons and ions bombardment could be interpreted in following way: heavy charge particles (ions) because of they big masses are inducing much more vacancies then electrons which have much smaller mass.

Calculations using Smakula's formula (1) for quantity estimation of induced defects perfectly confirm this result.

$$N = 0.87 \cdot 10^{17} \cdot \frac{n}{(n^2+2)^2} \cdot f^{-1} \cdot \alpha \cdot H \qquad (1)$$

where N – concentration of colour centers (radiation induced defects) (cm^{-3}), α – absorption in maximum of band (cm^{-1}), H – half-width band spectrum (eV), f – frequency factor (probability of transfer between levels). For our calculations it was taken f=1 for F-, F_2-, F_3^+-centers. Thus, in this way it would be estimated the minima defects concentration.

Quantity of defects was calculated for samples which were irradiated by accelerated electrons with dose 752 kGy and by ions with fluence of 10^{14} cm^{-2}. At these values of radiation the most luminescence yields were obtained in comparison with other values of radiation. The estimations of minima concentrations are:

for electrons radiation treatment

- F-centers – N=3,281*10^{17} $см^{-3}$
- F_2-, F_3^+-centers – N=4,43*10^{16} $см^{-3}$

for ions radiation treatment

- For F-centers – N=0,58*10^{19} $см^{-3}$
- For F_2-, F_3^+-centers – N=0,438*$10^{20}$$см^{-3}$

This estimations show that quantity of defects (colour centers) inducing by ions is in three orders more then quantity of defects induced by electrons.

Investigation of luminescence spectra has shown that by excitation of deuterium lamp luminescence bands of F_2- and F_3-centers are in the green, red and near red spectrum range (Fig. 5).

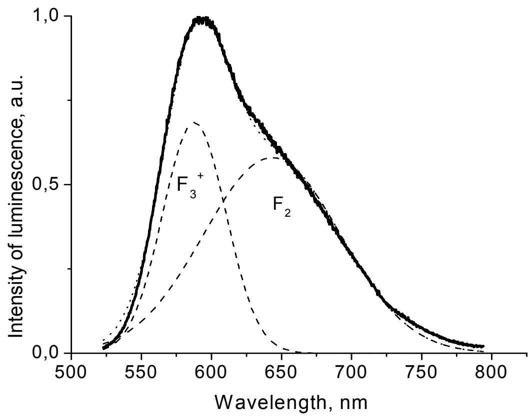

Fig. 5. Luminescence spectrum of pure NaF excitated in 500 nm following electrons irradiation (energy of electrons is 10 MeV, radiation dose is 752 kGy).

At the next step the questions of temperature stability of produced radiation defects were clarified.

In the absorption spectrum of irradiated by electrons NaF pure sample the general bands connected with $O^{2-}V_a^+$ – centers (230, 311 nm), F – centers (340 nm), F_2, F_3^+ – centers (510 nm) were obtained (Fig. 6). During annealing we observed particular transformation of F– centers into $O^{2-}V_a^+$ – centers. Simultaneously, F_2, F_3^+ – centers dissociated into single vacancies at T<200°C.

Another temperature behaviour of colour centers annealing one can see for samples irradiated with N^+ ion beams (Fig. 7). Firstly, more temperature stability of aggregate F_2, F_3^+ – centers were observed. Secondly, the process of thermal transformation F – centers into aggregate centers were registered.

Thus, the temperature stability of color centers in the samples irradiated by ions and electrons significantly differs.

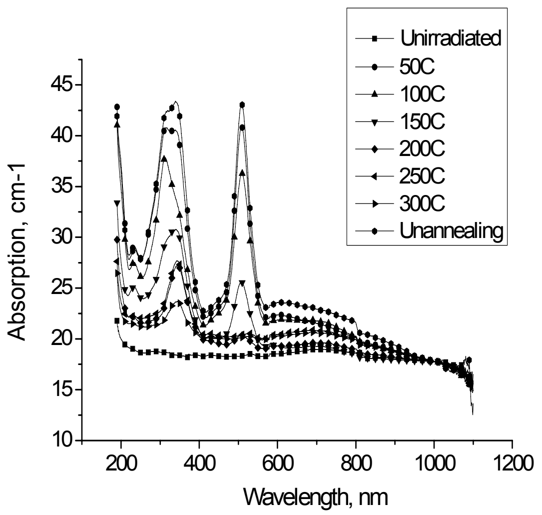

Fig. 6. Absorption spectra of pure NaF irradiated by electrons (energy 10 MeV) with radiation dose 752 kGy following annealing.

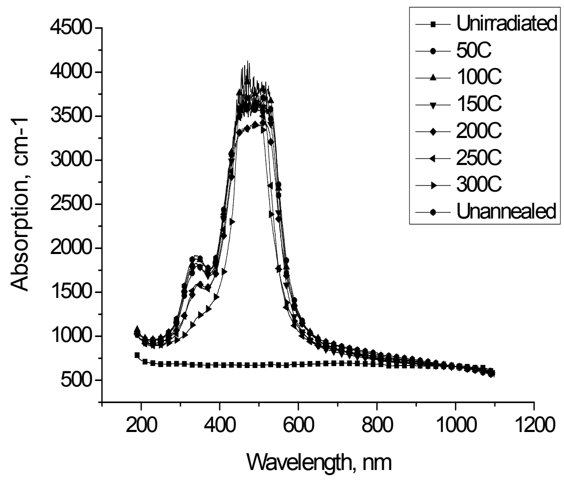

Fig. 7. Absorption spectra of pure NaF irradiated by N^+ ions (energy 16MeV) with radiation fluence 10^{16} cm^{-2} following annealing.

Mott-Seitz formalism (2) can be used to describe dependence of quantum yield from temperature which is caused by intrinsic temperature decay [5]:

$$\eta(T)=\frac{I(T)}{I_0}=\frac{1}{1+\omega\cdot\exp(-\frac{W}{kT})} \qquad (2)$$

where η(T) – luminescence efficiency, I_0 – initial intensity of the luminescence, k – Boltzmann constant, T – annealing temperature, ω – constant which is intrinsic characteristic present colour center, W – activation energy of internal extinguishing (eV). Factors ω and W are selective parameters with the values for F-centers of $\omega=0.64*10^6$ и W=0.451 eV and for F_2, F_3^+-centers $\omega=0.14*10^4$ и W=0.251 eV.

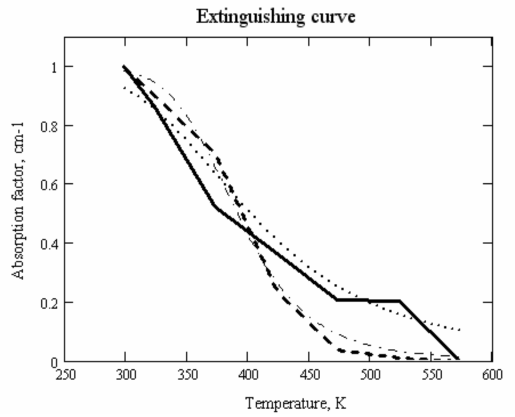

Fig. 8. Experimental and theoretical curves of temperature decay of F- (solid line) and F_2, F_3^+-centers (dotted line) for pure crystal NaF irradiated with electron beams (radiation dose 752 kGy).

Figure 8 shows that activation energy of temperature decay of F_2, F_3^+-centers is smaller than those for F-centers for electrons irradiated crystals. In contrary, for ions irradiated crystals the activation energy of temperature decay of aggregate centers is bigger.

4. Conclusion

There was carried out comparison of accumulation effectiveness of single and aggregate colour centers inducing by different kinds of corpuscular radiation (ion and electron beams) in pure and with impurities of Sc, Cu and Li NaF crystals. The temperature stability of produced defects were investigated. The aggregate defects induced by ions are more temperature stable. Thus for creation optical active planar structures it's predominantly to use beams of accelerated ions.

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