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The Study of the Influence of γ -Irradiation on LiF Crystals by Optical, Electrical and Mechanical Characteristics

The influence of the dose of γ -irradiation on some physical properties (storage of colour centres, ionic conductivity, microhardness) in LiF crystals differing in oxygen content is studied. It is found out that optical, electrical and mechanical characteristics change nonmonotonously with an increase in dose of γ -irradiation in the range from 10^4 to 10^7 J per kg. Maxima and minima are revealed on all the three dependencies, indicating a periodic construction and redistribution of radiation defects during the change of the absorbed dose. Oxygen impurity enhanced the colouring of LiF crystals, significantly reduced the conductivity, caused mechanical softening and intensified the secondary radiation processes having qualitatively changed the behaviour of electrical and mechanical properties with an increase in irradiation dose.

Изучено влияние дозы γ -облучения на ряд физических свойств (накопление центров окраски, ионную проводимость и микротвердость) кристаллов фтористого лития, отличающихся содержанием кислорода. Обнаружено немонотонное изменение оптических, электрических и механических характеристик с ростом дозы γ -облучения в интервале 10^4 — 10^7 Дж/кг. На всех изученных зависимостях выявлены максимумы и минимумы, свидетельствующие о периодической перестройке и перераспределении радиационных дефектов при изменении поглощенной дозы. Примесь кислорода усилила окрашиваемость LiF при γ -облучении, резко (на 5 порядков) понизила электропроводность, вызвала механическое разупрочнение и интенсифицировала вторичные радиационные процессы, качественно изменив поведение электрических и механических свойств при росте дозы облучения.

1. Introduction

Investigations of the influence of ionizing irradiation on physical properties of LiF crystals are necessary because of the use of LiF crystals containing colour centres as active laser elements as well as passive Q-modulators (PARFIANOVICH et al.; BASIEV et al.; IVANOV et al.). In manufacturing these elements it is essential to determine the optimum absorbed dose which depends on the purity of the specimen.

Optimum absorbed dose can be estimated by studying the dose dependence of physical properties of crystals. Since the behaviour of crystals depend on their original state as well as on irradiation conditions, by the investigation of dose dependences of the properties one should keep in mind these factors (LUTSHIK et al.; SHWARZ et al.; AGULLO-LOPEZ, JAQUE; CATLOW et al.; ELANGO, NURAKHMETOV).

In the present article the results of the experimental investigation of the influence of γ -irradiation dose on some physical properties of LiF crystals differing in impurity (oxygen) content are described for one temperature (room temperature). By comparison of the dose dependencies of a number physical properties one can get an indirect conclusion about the state of the impurities and radiation defects at different irradiation doses and thus to reveal the optimum for certain purposes irradiation doses.

2. Experimental methods

LiF crystals of two types grown from the same raw material (IR type) served as the object of investigation. The concentration of cationic impurities Mg, Ca, Al in crystals of both types was the same — of the order of 10^{-4} — 10^{-5} wt %. Crystals of the first type (LiF I) were grown in vacuum by Stockbarger method. Crystals of the second type (LiF II) were enriched with oxygen and grown in the air by the Kyropoulos method. The content of oxygen was controlled by UV- and IR-absorption spectra. The specimens were irradiated by γ -rays (Co^{60} with power $2 \cdot 10^6$ Rad/h). The absorbed dose varied in wide range of 10^4 — 10^7 J/kg.

The ionic conductivity (σ), measured at direct current by the three-point scheme at $E = 10^5$ V/m and temperatures 300—700 K, was chosen as the electrical characteristic. Absorption spectra were recorded on the spectrometers Specord MPS-501 and UR-20. Mechanical properties were evaluated by microhardness (H) at load 0.4 N.

3. Experimental results

3.1. Absorption spectra

In Figure 1 are shown the absorption spectra of LiF I and LiF II crystals obtained in UV-visible and IR-ranges. The absence of distinctly defined absorption band in the whole wave length range is typical for LiF I. In the absorption spectra of LiF II in IR-range there is a band at $\nu = 3720 \text{ cm}^{-1}$ due to local vibrations of OH⁻-ions (STOEBE). A small rising of the curve at 3500 — 3600 cm^{-1} evidences the presence of complexes of Mg²⁺-ions with OH-groups (STOEBE, a). For LiF II crystals in the visible and UV-regions of the spectrum the bands corresponding to oxygen impurity are observed (LOBANOV et al.; SMUSHKOV et al.; VORA et al.). The rising of the absorption curve near the HUV-region (curve 2 in Fig. 1) can be connected with the local Me²⁺O²⁻ (charge compensation complexes influencing the absorption (LOBANOV et al.).

Thus, for LiF I crystals the absence of absorbing centres is typical, whereas a characteristic feature of LiF II crystals is the presence of various oxygen-containing centres.

After γ -irradiation in the absorption spectra of LiF crystals there appear bands corresponding to F-, F₂- and F₃-centres. For LiF I the band at $\lambda = 250 \text{ nm}$ (F-band) could not be measured due to a high intensity (high concentration of F-centres), and, therefore, it is not shown in Figure 3.

3.2. Ionic Conductivity

The conductivity of LiF I and LiF II crystals is shown in Figure 2. In the chosen temperature range there are regions of intrinsic as well as extrinsic conductivity (curves 1 and 2). For LiF I crystals two regions of extrinsic conductivity are seen without associations (503—773 K, the migration energy of free cationic vacancies

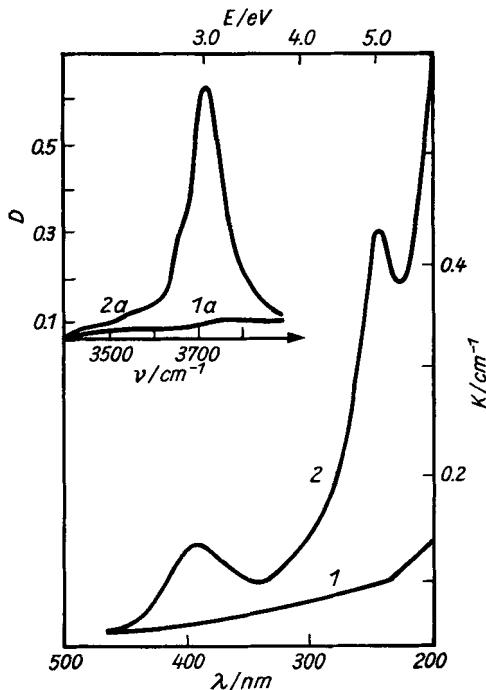


Fig. 1. Absorption spectra of unirradiated LiF I and LiF II, curves 1 and 1a for LiF I, curves 2 and 2a for LiF II. (the specimen thickness is 1 mm)

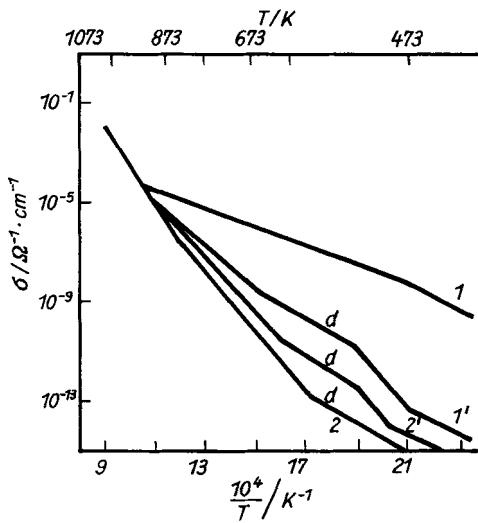


Fig. 2. Temperature dependence of the ionic conductivity for LiF I (1 and 1') and LiF II (2 and 2'). 1, 2 before irradiation, 1', 2' after γ -irradiation (doses are $2.4 \cdot 10^6$ and $1 \cdot 10^6$ J/kg, respectively). The letter "d" denotes a segment with activation energy 1.35 eV

being $E_m = 0.74 \pm 0.03$ eV) and association conductivity (below 503 K, $E = 0.95 \pm 0.03$ eV) (KALMAN et al.). The binding energy of the complex responsible for association conductivity (due to the presence of the impurity-vacancy dipole $\text{Me}^{2+}-\text{V}_c^-$) is equal to 0.4 ± 0.03 eV.

The conductivity of LiF II crystals was by several orders of magnitude less than that of LiF I. This means that oxygen seems to have cleaned the crystal from part of the defects making a contribution to the conductivity. Below 573 K the segments on the curve $\lg \sigma(1/T)$ with activation energy $E = 1.35 \pm 0.03$ eV are seen due to the freeing of vacancies from dipoles $V_c^- V_a^+$. This conclusion is based on the following. The activation energy of free cationic vacancies in crystals enriched with oxygen is $E_m = 0.95$ eV (STOEBE, b). According to ROZMAN the binding energy of the dipoles $V_c^- V_a^+$ in LiF is equal to $E_g = 0.8 - 0.85$ eV. Taking into account $E = E_m + 1/2E_g$ and substituting the corresponding values of E_m and E_g in this relation one obtains $E = 1.35$ eV.

γ -irradiation changed the conductivity of LiF I and LiF II crystals in different ways. Conductivity in LiF I became lower (cationic vacancies are bound by radiation defects), in LiF II — it became higher (irradiation introduces additional cationic vacancies). Figure 2 shows the presence of a segment corresponding to the freeing of vacancies from the dipoles $V_c^- V_a^+$ on the temperature dependence in $\lg \sigma$ for both crystals (this segment is marked by letter "d"). These dipoles are created by irradiation. The generation of cationic vacancies under irradiation in LiF II crystals is confirmed also by the appearance of a segment with activation energy 0.95 ± 0.03 eV on the curve $\lg \sigma/(1/T)$ for irradiation dose $2.45 \cdot 10^6$ J/kg. This activation energy coincides with the migration energy of free cationic vacancies in oxygen-containing LiF crystals (STOEBE, a).

At low irradiation doses the conductivity of LiF II is almost unchanged, probably because of the balance of processes of radiation generation and joining of the cationic vacancies. It should be noted that at all irradiation doses the conductivity of LiF II was always lower than that of LiF I.

In the present paper the temperature dependence of electroconductivity is considered only briefly as we are interested here only in the change of the crystal perfection with the change in irradiation dose. In plotting the dose¹⁾ dependence of $\lg \sigma$ in the extrinsic conductivity range the conductivity of LiF I was taken at 403 K and of LiF II — at 573 K. The higher temperature in the second case is due to the fact that the conductivity of LiF is drastically reduced after the introduction of oxygen, and the current sensitivity of 10^{-15} A does not permit to make measurements at temperatures below 573 K.

3.3. Microhardness

Microhardness of unirradiated LiF I crystals is equal to $1.50 \cdot 10^3$ N/m² and of LiF II — $1 \cdot 10^3$ N/m², i. e. the introduction of oxygen caused the softening. In alkali halide crystals the most probable cause of the impurity softening is the "scavenging" of background impurities by dopants connecting the unpredicted impurities into complexes (URUSOVSKAYA et al.; BELYAEV et al.). As a result of the interaction of doping anionic impurities and present in raw material cationic ones there appear in the volume of a crystal large regions free from impurities. In our case the softening should be connected with the formation of complexes $Me^{2+}O^{2-}$ revealed by absorption spectra. γ -irradiation significantly changed the microhardness, but at all doses of γ -irradiation the microhardness of LiF II was lower than that of "pure" LiF I.

The softening by oxygen is in accordance with the decrease of conductivity. These facts both are indirect evidence of a possibility of action of a "scavenging" mechanism.

¹⁾ In fact, the dose dependence of normalized conductivity is considered here — the ratios of the conductivities of irradiated and unirradiated specimens.

3.4. Dose dependences of the characteristics under investigation

Experimental results of the dose dependences of the colour centre concentration, change in ionic conductivity and microhardness are presented in Figures 3 and 4 for LiF I and LiF II, respectively. A remarkable feature of these curves is their complicated shape: cyclic changes of the properties and the existence of critical dose values at which there is a drastic change of all the characteristics of the investigated specimens.

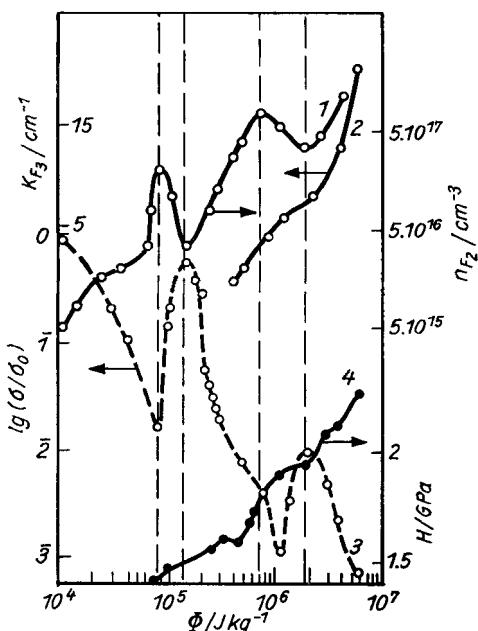


Fig. 3. Dose dependence of the storage of colour centres (2 F_2 -centres, 3 F_3 -centres) of the normalized conductivity $lg(\sigma_{ir}/\sigma_0)$ (4) and microhardness (5) in LiF I crystals

As shown in (DELGADO, ALVARES RIVAS) in LiF crystals after γ -irradiation with dose up to $3 \cdot 10^7$ J/kg there is no evidence of reaching the stationary state of stored energy. It follows from Figures 3 and 4, that, indeed, there is a tendency of increase in number of colour centres with rising dose. On this general tendency of kinetic storage curves behaviour minima and maxima are seen.

The storage kinetics of F - and F -aggregate centres provides information on defects in anionic sublattice, whereas the conductivity measurements permit to judge about changes in cationic sublattice. As to colour centres, both crystals behave similarly but as regards the conductivity, the tendencies in its change with dose for LiF I and LiF II crystals are different. In "pure" lithium fluoride there is total reduction of conductivity with an increase in dose, but in the presence of oxygen σ definitely increases at high doses. Antiphase change in optical and electrical characteristics is typical for LiF I: at doses corresponding to the maxima of anionic vacancies concentration there are minima of conductivity. Thus, there are critical doses when the concentration of anionic vacancies sharply increases and the number of cationic free vacancies, simultaneously, significantly reduces and vice versa. In the case of LiF II both optical and electric characteristics change with dose approximately in phase.

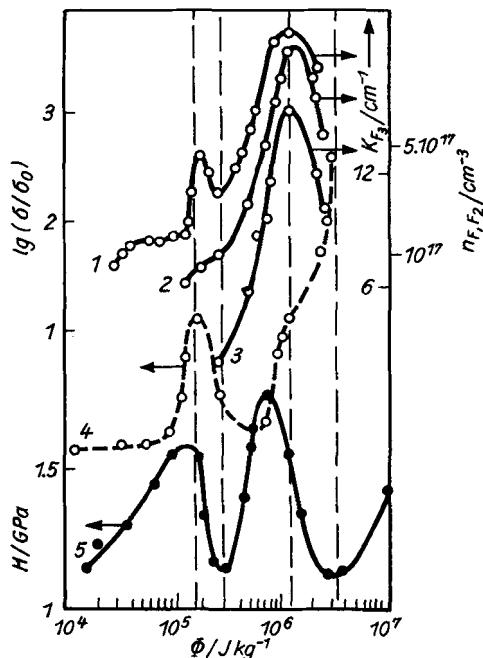


Fig. 4. Dose dependence of the storage of colour centres (1 F-centres, 2 F_s -centres, 3 F_3 -centres), of the mornalized conductivity (4) and microhardness (5) in LiF II

The presence of oxygen changed radically the dose dependence of microhardness. If in "pure" crystals the microhardness at doses up to $8 \cdot 10^4 \text{ J/kg}$ is practically constant and then rises monotonously with irradiation dose, in LiF II containing oxygen there are sharp changes of microhardness, its maxima almost coinciding with these of the curves for colour centres and conductivity. The cyclic changes in microhardness mean a periodical change with concentration of radiation defects of the state of dislocation obstacles, when complexes from vacancies, interstitials and impurities are formed and destroyed succesively.

4. Discussion

There are numerous experimental data showing that as a result of the action of ionizing irradiation on alkali halide crystals, besides the primary processes of the creation of Frenkel pairs, secondary processes take place, which, on the one hand, cause the recombination of the complementary pairs and the lattice restoration, but, on the other hand, stimulate the storage of radiation defects. It is known that with increasing of the radiation dose more and more complex electron colour centres up to the colloidal particles are created (SHWARZ et al.). Simultaneously there occurs the enlargening of the defects of interstitial type: the aggregates of H-centres are formed (CATLOW et al.) hole centres are coagulated (BELOVA et al.), dislocation loops are created (HOBBS et al.) as well as cavities (METREVELI), the halogen is removed from the crystal, crystallites grow on the surface (TSAL, PAVLYK).

The account of the spatial distribution of the radiolysis products, reverse reactions in the case of tunneling and diffusion-controlled recombinations of radiation defects demonstrates the possibility not only of stabilizing these defects, but also of destroy-

ing those already stabilized at the earlier stages of irradiation (MILLERS et al.). So, the competition of the creation and destroying of the radiation defects can be the cause of the oscillating change in physical properties of γ -irradiated LiF crystals, revealed in present work.

The oscillating change in colouring with dose in alkali halides was observed earlier after neutron (ANDRONIKASHVILI et al.) and X-ray (BOYARSKAYA et al.) irradiation. The authors (ANDRONIKASHVILI et al.) compared optical data with corresponding change of electrical properties and came to the conclusion that these changes can be caused by the periodic production and destroying of dislocation loops under irradiation. This explanation can not be valid in the case of X-irradiation, when the production of dislocations is not revealed. Authors (BOYARSKAYA et al.), revealing the parallel oscillation of optical and mechanical (microhardness) properties with dose of soft (Cu) irradiation believe that this periodicity is due to participating of two processes—creation and recovery of some radiation defects.

Experimental data presented here, obtained on γ -irradiated LiF crystals, include the dose dependencies of three physical characteristics for two crystals differing in impurity content. According to our data one should agree with point of view of (BOYARSKAYA et al.) about the origin of the oscillation in physical properties. We must add only that on the processes occurring by irradiation very significant influence have oxygen.

5. Conclusion

As a result of complex investigation of the change of several physical properties of LiF crystals under the influence of ionizing irradiation with different doses a rather complicated periodic character of the change is revealed. Such behaviour reflects the periodicity in the formation and reconstruction of radiation defects and impurity centers (cationic and anionic). Different character of dose dependencies of the optical, mechanical and electrical properties for crystals differing in oxygen content indicates the interaction between radiation defects (primary and secondary) with impurities and mutual their influence on their state. Oxygen is found to accelerate the secondary radiation processes, radiation defects in their turn reduce the influence of oxygen on all physical properties, studied in this work. For understanding the nature of the change in impurity and radiation centers occurring by increase in dose of irradiation, the application of other methods especially direct microscopic one is necessary.

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