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Microscopic identification of the $F_2{}^+$-O^{2-} center formation in LiF:OH^-

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A model for $F_2{}^+$-O^{2-} formation in irradiated LiF:OH^-, based on a statistical distribution of the defects produced during electron irradiation at −30 °C, has been established. These stabilized centers are formed during the thermal diffusion of the anionic vacancies in competition with the isolated $F_2{}^+$ centers. A critical distance of thirteen lattice parameters suggests that the O^{2-}-α dipole is the precursor entity responsible for $F_2{}^+$-O^{2-} creation.

A great deal of effort has been made by many authors to elucidate the mechanism of $F_2{}^+$-O^{2-} center creation in LiF crystals doped with oxygen or hydroxyl ions.[1] By means of this process one might find a way of increasing its maximum concentration, which is currently on the order of magnitude of 7×10^{16} cm^{-3}.[2] One of the difficulties found in the increase of this maximum level of concentration is the fact that high-energy irradiation primarily produces a high concentration of F centers and electron-trap centers (anionic vacancies, the F center itself, and impurities centers). These electron traps very efficiently promote the formation of isolated $F_2{}^+$ centers, which compete very strongly with the formation of the $F_2{}^+$-O^{2-} centers.

Until now, it was believed that the O^{2-}-α dipole center is the entity responsible for the creation of the $F_2{}^+$-O^{2-} center after the irradiation and diffusion of the anionic vacancies in LiF.[3,4] These dipole centers, O^{2-}-α, are one of the secondary products of the OH^- dissociation as a result of the F-center capture by the substitutional O^- ion. The presence of these dipole centers in γ-irradiated LiF:O and OH^- at 300 K, has been reported.[5] Its absorption bands have maximums at 113 and 190 nm according to Ref. 3. The highest energy absorption band in the near-vacuum ultraviolet is beyond the measurable range of conventional spectrophotometers. The near-uv band overlaps with the intense absorption band of the F centers (with maximum at 250 nm). Considering these facts, these dipole centers are almost impossible to measure by absorption and emission techniques in irradiated crystals.

Besides that, no one has ever before related the production of the $F_2{}^+$-O^{2-} centers with the OH^- doping for a fixed dose and temperature of irradiation. We did that in LiF crystals irradiated with electrons of 1.5 MeV at −30 °C and a fixed dose of 45 Mrad.

Preliminary studies of this center formation as a function of the dose at three different temperatures of irradiation showed that −30 °C and 45 Mrad are the best conditions for the proposed study. Within these experimental conditions, the formation of the $F_2{}^+$-O^{2-} centers can be observed without the presence of F_4 centers whose absorption (maximum at 540 nm) overlaps with the stabilized $F_2{}^+$ center absorption band at 600 nm. For irradiations at higher temperatures and doses one observes an increase of the F_4 concentration.

The minimum dose of radiation should be higher than 12 Mrad in order to break 100% of the initially OH^- ions present in the crystal according to the observation of the absorption band of the OH^- ions at 2.68 μm. The $F_2{}^+$-O^{2-} center concentration was measured 24 h after keeping the samples at room temperature—a lack of time necessary to completely destroy all the unstable $F_2{}^+$ centers produced in competition with the stable ones.

The value of the $F_2{}^+$-O^{2-} concentration in the samples was measured by comparing the $F_2{}^+$-O^{2-} emission intensity at 900 nm with the intensity measured each time for a pattern crystal with a known $F_2{}^+$-O^{2-} concentration. In order to have a normalized signal, we used a mask 0.5 mm wide in contact with the luminescent surface from where the emitted light is collected.

Based on the observation of the optical transparency of the fresh irradiated crystals during the warming up to room temperature, we stated that the electronic irradiation produces only F centers and anionic vacancies. In the first 5 min of thermal treatment the crystal becomes blueish, indicating the formation of $F_2{}^+$ centers. These centers are unstable at this temperature and decay with a half-life of 3.8 h. At the expense of the unstable $F_2{}^+$ centers, the formation of F_2 and $F_3{}^+$ centers makes the crystal greenish, due to the strong absorption band produced at 441 and 458 nm, respectively.

The production of $F_2{}^+$-O^{2-} centers is related to the first step of center aggregation during the diffusion of vacancies. The experimental values of the $F_2{}^+$-O^{2-} concentration as a function of the OH^- concentration is shown in Fig. 1. In this case all the samples were irradiated at the same time with electrons of 1.5 MeV (45 Mrad) at −30 °C. The experimental points could be fitted by using a statistical model involving a critical radius for vacancy capture and the effective OH^- concentration in this process.

Our assumption is that the centers produced by irradiation are statistically distributed in the lattice. Also, we presume that most of the oxygen atoms produced in the OH^- dissociation stay negatively charged in the vacancies as O^- centers because of the small interstitial space available in the lattice. First, let us keep open the structure of the oxygen-type center responsible for the formation of $F_2{}^+$-O^{2-} center by representing it with the symbol X and its concentration by N_x. The vacancies will be represented by the symbol α.

The probability of an α center to have an X center as

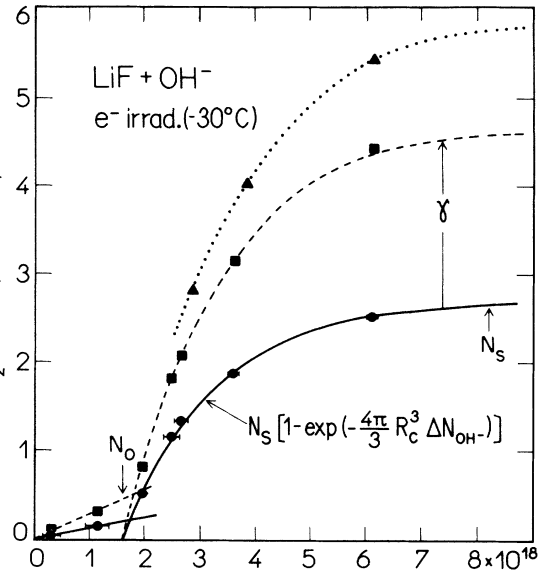

FIG. 1. Formation of $F_2{}^{+}$-O^{2-} in LiF crystals with variable OH^{-} concentration. The solid line represents the formation curve measured after the samples remained for 20 h at 300 K, well after the e^{-} irradiation at −30 °C (45 Mrad). The dashed line shows the effects of the small dose of γ irradiation at 77 K (0.7 Mrad) and the dotted line shows the time effect after eight months at 300 K.

the closest neighbor between the distances R and $R+dR$ is given by

$$p_{x,a}=(1-p)^{(n_1-2)}n_2p\,, \tag{1}$$

where

$$p=\frac{N_x}{N},\quad n_1=\frac{4\pi}{3}\frac{R^3}{R_0^3},\quad n_2=\frac{4\pi R^2}{R_0^3}dR\,,$$

with $R_0^3=a^3/4=1/N$ (a denotes the lattice parameter). p is the occupation probability for the X center in the lattice, n_1 is the total number of anionic sites inside the sphere with radius R, and n_2 the total number of those sites found between the spheres with radius R and $R+dR$.

Let us assume now that the X center captures a vacancy with a constant probability p_0 for pairs (X,a) correlated up to the critical distance R_c producing an $F_2{}^{+}$-O^{2-} center. In this case, the probability of $F_2{}^{+}$-O^{2-} center formation is given by

$$p(F_2{}^{+}\text{-}O^{2-})=p_0\int_{R_i}^{R_c}p_{x,a}\,,\quad R_i=\left[\frac{6}{4\pi}\right]^{1/3}R_0\,, \tag{2}$$

where the integral is

$$\int_{R_i}^{R_c}p_{x,a}=\left[\frac{p(1-p)^{n_1-2}}{\ln(1-p)}\right]_{R=R_i}^{R=R_c}$$

$$\approx\{-\exp[-(n_1-2)p]\}_{R=R_i}^{R=R_c}\,, \tag{3}$$

considering that $\ln(1-p)\approx -p$ once $p\ll 1$ or N_x ($\approx 10^{18}$ cm^{-3})$\ll N$($\approx 10^{22}$ cm^{-3}). So, the total number of $F_2{}^{+}$-O^{2-} centers formed in this process is

$$N(F_2{}^{+}\text{-}O^{2-})=N_a p(F_2{}^{+}\text{-}O^{2-})\,, \tag{4}$$

where N_a represents the initial number of a centers formed during the irradiation. The final expression for $F_2{}^{+}$-O^{2-} center formation was obtained by using Eqs. (2)-(4):

$$N(F_2{}^{+}\text{-}O^{2-})=N_s\{1-\exp[-(4\pi/3)R_c^3N_x]\}\,, \tag{5}$$

where $N_s=p_0N_a$.

To test this model we plot ΔN defined as $[N(F_2{}^{+}$-$O^{2-})-N_s]/N_s$ in a logarithmic scale as a function of the OH^{-} concentration. The result is presented in Fig. 2. We indeed obtained a very good straight-line dependence yielding, as a fitting parameter, a critical distance of $R_c(13\pm0.1)a$ and $N_s=2.74\times10^{16}$ cm^{-3} (the saturation concentration).

Two mechanisms of $F_2{}^{+}$-O^{2-} formation can be verified: one below and the other above N_0—the starting value of the OH^{-} concentration which validates the proposed model. By using $N_x=N_{OH}-N_0$ in Eq. (5), we plot the predicted curve (solid line in Fig. 1) by the model. The critical radius of thirteen lattice parameters for the distance of vacancy capture by the X center reveals an interaction of the same type as that which exists between two neighboring F centers, one being in the ground state (1s) and the other in the relaxed electronic excited state (2p).[6] This means that the X center must include an anionic vacancy in its structure. Also this center must have an electronic character similar to the F-center ground state in order to trap 2p electrons in a metastable state as an F' center (F center with two electrons) and capture the correlationed vacancy to form the $F_2{}^{+}$-O^{2-} center.

Considering these attributed qualities to the X center, we conclude that it must be the O^{2-}-a dipole center. The following mechanism of formation is proposed:

$$a\begin{cases}\longrightarrow\ +F\longrightarrow F_2{}^{+}\\ \longrightarrow\ +e^{-}\longrightarrow \tilde{F}^{*}(2p)\end{cases}$$

$$+O^{2-}\text{-}a\longrightarrow F_2{}^{+}\text{-}O^{2-}\,.$$

We directly conclude from the model that the O^{2-}-a

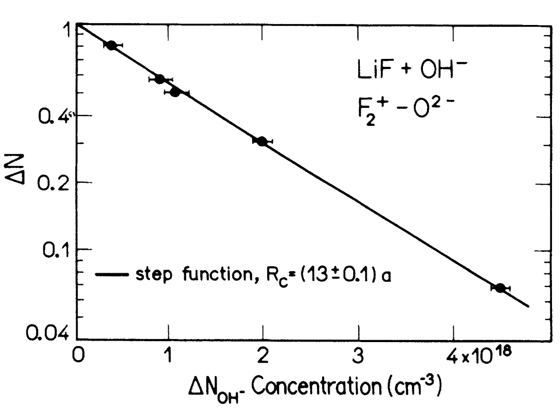

FIG. 2. Logarithmic plot of ΔN defined as $[N(F_2{}^{+}$-$O^{2-})-N_s]/N_s$ as a function of ΔN_{OH^-}, $N_{OH^-}-N_0$, the displaced OH^{-} concentration. The use of a simple step function for the vacancy capture gives a good fit with $R_c=(13\pm0.1)a$.

dipoles concentration is smaller than the OH^- concentration. By computing the necessary O^{2-}-α dipoles concentration to fit the experimental values of $F_2{}^+$-O^{2-} with the use of the fitted parameters R_c and N_s, we could plot $N(O^{2-}\text{-}\alpha)$ vs N_{OH^-} as it is shown in Fig. 3. The results can be explained based on the equilibrium equation between the O^{2-}-α dipole formation (rate A) and destruction (rate B) during the 1.5-MeV electron irradiation. This yields the following rate equation of formation:

$$N(O^{2-}\text{-}\alpha)=N(O^-)\frac{A}{B}\left(1+\frac{A}{B}\right)^{-1}.$$

The values of A/B are 0.086 and 1 for lower and higher OH^- concentrations, respectively. In the last case, the O^{2-}-α dipoles concentration follows the concentration difference $\Delta N = N_{OH^-} - N_0$. These two regions of O^{2-}-α dipole formation indicate that for low N_{OH^-} (consequently low O^- concentration) the dipole center destruction is more efficient than in the case of $N_{OH^-} > N_0$. This may be correlated with the fact that in such high levels of O^- concentration a second O^- ion can capture the unbounded vacancy and electron restoring the O^{2-}-α center.

One question still remains about the low efficiency of $F_2{}^+$-O^{2-} formation. This fact may be due to the environmental conditions for the O^{2-}-α centers to capture vacancies in competition with the F centers, which are present in a higher concentration than the O^{2-}-α centers. The probability of vacancy capture p_0 by the O^{2-}-α dipoles can be estimated by the ratio between the initial vacancy concentration (N_a) and the saturation concentration (N_s). N_a was estimated by the summation over all types of F-aggregated centers (F_2, $F_3{}^+$, and $F_2{}^+$-O^{2-} center) produced in the equilibrium at room temperature, given a value of 3×10^{18} cm^{-3}. The estimated value for p_0 was 0.01.

In addition, one may increase the saturation concentration of $F_2{}^+$-O^{2-} centers by the increase of the vacancy concentration before the thermal activation process. This might be possible by bleaching some effective amounts of F centers at low temperature (below 200 K) with an intense laser light.

It was noted that the $F_2{}^+$-O^{2-} centers concentration attained in the equilibrium increased in the samples stored at room temperature for several months. These results are shown in Fig. 1 (dotted line). This effect probably is due to the small thermal diffusion of the O^{2-}-α center at room temperature which remains and reacts with a neighboring F center. Actually, not all the dipole centers can be transformed into stable $F_2{}^+$ centers. Only a small fraction of 1% of these centers were converted after completing the thermal activation process in about eight months. The remaining dipole centers may agglomerate in a more stable configuration inhibiting the $F_2{}^+$-O^{2-} center formation and a possible recovery of the OH^- ions.

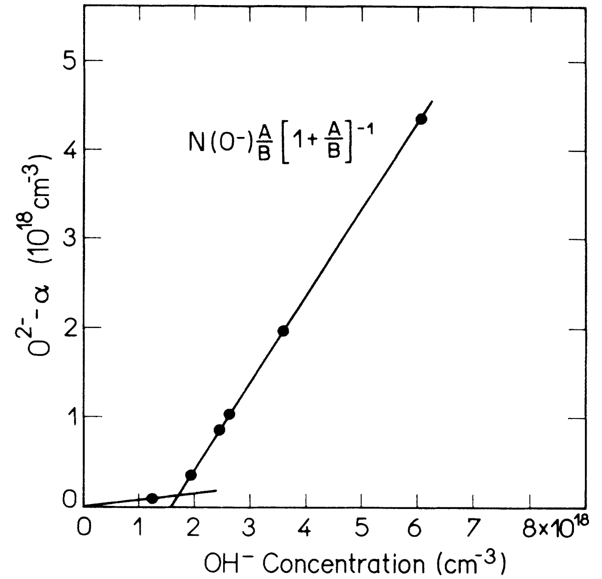

FIG. 3. The predicted O^{2-}-α dipole concentration formed during the e^- irradiation at $-30\,^\circ$C (45 Mrad) by using the fitted parameters R_c and N_s. Towards high OH^- concentration the ratio A/B goes from 0.086 to unity. The A and B represent the rates of formation and destruction of O^{2-}-α centers, respectively.

We found that the saturation concentration (N_s) of stabilized $F_2{}^+$ centers was increased by a factor of 1.7 after the sample reirradiation with a small dose of γ at 77 K. The results are exhibited in Fig. 1 (dashed line). It is clear that the mechanism of $F_2{}^+$-O^{2-} formation still remains unalterable (same R_c) after the γ reirradiation.

The results we presented in this paper clearly demonstrate the microscopic process of $F_2{}^+$-O^{2-} center formation and some improvement for the increase of its final concentration. This study consitutes an important step towards the understanding of the role of the OH^- impurity in the stabilization process of laser-active centers like $F_2{}^+$.

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