METASTABLE $F_2$ CENTER STATES IN LiF CRYSTALS

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Using time-resolved pulsed absorption and luminescence spectroscopy we have studied the creation of $F_2$ centers during electron pulses of nanosecond duration in the temperature range 80 to 300 K. We show that the formation of $F_2$ centers in long-lived metastable states is thermally activated and competes with $F_2$ center relaxation to the singlet state. It is shown that the $S$--$T$ crossing in the set of states which describe the $F_2$ center lies above the $^{1}\Pi_u$ level. We propose that when the crystal is excited with the lowest energy quanta which produce a photocurrent, the formation of triplet $F_2$ centers takes place by localization of a conduction electron on an $F_2^+$ center.

In the present work we have used pulsed and absorption spectroscopy to study $F_2$ center formation in states of different multiplicity by localization of an electron on an $F_2^+$ color center.

The source employed was an electron accelerator with the following parameters: electron energy $2 \cdot 10^5$ eV, volume energy density from 1 to 20 J/cm$^3$-pulse, and a pulse duration of 10 to 20 nsec. We studied the photoluminescence of the $F_2$ centers, the radioluminescence of $F_2^+$ and $F_2$ color centers, and the kinetics of the absorption decay at the maxima of the $F_2^+$ and $F_2$ bands induced by the electron pulse in a crystal which had first been irradiated to produce $F_2^+$ and $F_2$ color centers in a known ratio. The absorption decay measurements covered the time range from 10 nsec to 0.1 s after the end of the electron pulse, for temperatures from 80 to 300 K.

The following processing was employed to create the color centers in the crystals: They were either irradiated with electrons at 300 K or irradiated at 200 K and then heated to 300 K in accord with the method described in [1]. By varying the heating time, the rate of heating, and the radiation dose employed on the crystal, we could obtain crystals with varying ratios and concentrations of $F_2^+$ and $F_2$ centers before a single electron pulse was used.

Specially purified crystals of LiF were used, which were transparent from 110 to 3000 nm, with an oxygen impurity content determined by proton activation analysis to be below $1 \cdot 10^{-5}$ mol. %.

RESULTS

The action of a single electron pulse on a crystal containing $F_2$ color centers causes creation of $F_2^+$ centers, while destroying a portion of the $F_2$ centers during the pulse (Fig. 1, curves 1 and 2). In the millisecond time range after the electron pulse at 300 K a partial restoration of the radiative $F_2$ centers occurs (Fig. 1, curve 2).

The emissions near 910 and 670 nm arise simultaneously with the electron pulse, and its spectral composition is identical to the emission induced by excitation in the $F_2^+$ and $F_2$ bands, respectively.

Lowering the crystal temperature during the electron pulse exposure leads to the following changes between 300 and 80 K: First, the intensity of the radioluminescence of the $F_2$ centers increases (Fig. 2, curve 2), and the processes which lead to $F_2$ center destruction during the pulse become less effective (Fig. 1, curve 3; Fig. 2, curve 3), and the millisecond time stage in which the $F_2$ centers reappear disappears almost entirely (Fig. 2, curve 1). Second, the intensity of the radioluminescence of the $F_2^+$ center increases as the temperature is lowered, while the number of $F_2^+$ centers created by the electron pulse remains nearly constant between 300 and 80 K (Fig. 2, curves 4, 5).

Fig. 1. Kinetics of the optical absorption relaxation at the maximum of the $F_2^+$ band (curves 1, 4) and the $F_2$ band (curves 2, 3, 5, 6), induced by the action of a single electron pulse at 80 K (curves 3, 6) and at 300 K (curves 1, 2, 4, 5), in a crystal containing an initial concentration of $F_2$ centers (1, 2, 3) and $F_2^+$ centers (4, 5, 6).

Fig. 2. Temperature dependence of the efficiency of the processes which take place after an electron pulse acts on a crystal containing an initial concentration of $F_2$ centers: formation of $F_2$ centers in a metastable state (1) and $F_2^+$ centers (5), the destruction of $F_2$ centers (3), the radioluminescence emission from $F_2$ centers (2) and $F_2^+$ centers (4); $F_2(0) = 2 \times 10^{17}$ cm$^{-3}$, $W = 12$ J/cm$^3$.

The presence of $F_2^+$ centers in the crystal initially, along with the $F_2$ centers, leads to the following changes in the effects of an electron pulse at 300 K: First, after the pulse is completed, all the $F_2^+$ centers in the crystal are destroyed (Fig. 1, curve 4). The radioluminescence emission of the $F_2^+$ centers seems independent of the initial concentration of $F_2^+$ centers and is identical to that observed in crystals containing the same $F_2$ concentration before the electron pulse (Fig. 3, curve 1). Second, the efficiency of processes which lead to creation of $F_2$ centers in long-lived metastable states after the electron pulse, increases in direct proportion to the $F_2^+$ center concentration before the pulse (Fig. 3, curve 3). In contrast to the case discussed above ($F_2^+(0) = 0$), the growth of the $F_2$ center concentration in the millisecond stage of the absorption relaxation exceeds the number of $F_2$ centers destroyed by the pulse (see Fig. 1, curves 2, 5). This fact demonstrates conclusively that in LiF crystals in the range 200 to 300 K the formation of $F_2$ centers due to localization of electrons at $F_2^+$ centers proceeds via the creation of $F_2$ centers in a metastable state. Third, the presence of $F_2^+$ centers in the crystal leads to an increase in the radioluminescence intensity of the $F_2$ centers when the starting $F_2$ concentrations in the crystals are the same (Fig. 3, curve 2).

Lowering the temperature of the crystal during the electron pulse irradiation leads to the following changes in the induced radiation processes in a crystal containing an initial concentration of $F_2$ and $F_2^+$ centers. First, the $F_2^+$ radioluminescence intensity increases as the temperature is lowered exactly the same way as in a crystal which does not contain an initial concentration of $F_2^+$ color centers (Fig. 2, curve 4). Second, between 200 and 80 K, a reduction occurs in the efficiency with which $F_2$ center are generated in a metastable state, and the intensity of the $F_2$ center radioluminescence increases (Fig. 4, curve 2). In the temperature range 80 to 100 K the nanosecond component of the absorption relaxation at the peak of the $F_2$ band reverses sign: at the same time that $F_2$ centers are destroyed, they are also created during the electron pulse (Fig. 1, curve 6). If we take into account the temperature dependence of the destruction of the preexisting $F_2$ centers in the crystal caused by the electron beam (Fig. 2, curve 3), the creation of new $F_2$ centers during the electron pulse has the temperature dependence shown in Fig. 4, curve 3, which coincides with the temperature dependence of the $F_2$ radioluminescence induced in the crystal by the same electron pulse. This fact conclusively demonstrates that as the temperature is lowered the creation of new $F_2$ color centers due to localization of electrons at $F_2^+$ centers takes place by creation of $F_2$ centers in a radiative state, with an efficiency which increases as the temperature is lowered.