INTERACTION OF EXCITED F CENTERS WITH LATTICE DEFECTS IN NaCl(Ag) PHOSPHOR

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Theoretical curves are derived for thermal and photothermal bleaching on the basis of an ionic mechanism for F-center destruction.

1. It has been shown [1-4] that the F-center stability to heat and light is substantially affected by impurities, plastic deformation, conditions of preparation, details of the quenching and annealing, temperature of exposure to X-rays, and so on. It is usually assumed that these alter the spectra of electron and hole-trapping centers, which themselves affect the F-center stability. This explanation encounters difficulties in explaining several features, e.g., the reduction in F-center stability produced by impurities that do not produce the electron trapping centers responsible for color centers more stable than the F centers before introduction of the impurity, so the new trapping centers cannot compete with F centers.

Also, thermal destruction of F-centers in undoped crystals occurs via a first-order reaction and corresponds to a low probability of repeated electron capture at F centers. Hence, formation of trapping centers deeper than F centers cannot lead to a substantial further reduction in the probability of repeated trapping at the F centers, and thus to reduced thermal stability of the F centers.

It is also difficult to explain in this way the increase in F-center thermal stability after plastic deformation, since F-center destruction should be a second-order reaction if there is a high probability of multiple capture, but it is not found that the increase in thermal stability is accompanied by a change in the order.

These various factors also produce no appreciable changes in the F-center absorption band, so the F-centers are not appreciably affected. Even if the probability of primary destruction of F centers were altered, it would be difficult to explain in terms of the usual mechanism for ionization of these centers. Therefore the processes producing optical and thermal destruction of F centers are more complex than the usually assumed direct thermal ionization, alone or after optical excitation. We have for some time considered that thermal destruction in alkali halides occurs via ionic processes [5-8, 10-12], which convert the F centers to other (less stable) centers, which in turn undergo direct thermal ionization. This view has been adopted by others for various processes in alkali halides [9, 13-17]. Here we consider the photothermal destruction from this viewpoint, namely interaction of ions with excited F-centers. Thermal activation amounts not to thermal ionization of the excited centers but to activation of the motion of ions in the lattice, the interaction with these converting the F-centers to another type of center. As for thermal ionic disrup-

\[ \frac{dN}{dT} = \frac{P_v}{\beta} n_v - \frac{1}{\beta} \frac{e^{-Q_v/kT}}{N} = 0. \]  

in which \( P_v \) is the probability of thermal release of ions; \( \frac{N}{N_v} \) is the effective cross section for ion interaction with excited F centers, and \( N_{eff} \) is the steady-state concentration of those centers. If \( N \) and \( N_v \) do not change during photothermal bleaching, while the other parameters are the following functions of T

\[ z_p = z_{0p} \cdot e^{-Q_p/kT}, \quad P_v = P_{0v} \cdot e^{-Q_v/kT}, \quad S_p = z_{0p} \cdot e^{-Q_p/kT}. \]

in which \( Q_p \) is the activation energy for interaction of an ion with an excited F center, then

\[ \frac{dN}{dT} = \frac{P_v}{\beta} n_v - \frac{1}{\beta} \frac{e^{-Q_v/kT}}{N} = 0. \]  

Finally, we consider the photothermal bleaching of F centers by ions. The kinetic equation is

\[ \frac{dP_v}{dT} = \frac{1}{\beta} \frac{e^{-Q_v/kT}}{N} \]  

in which \( Q_v \) is the activation energy for interaction of an ion with an excited F center, then
In the case of interest, 
\[ \frac{d n_F^*}{dt} = \frac{P_{0v} n_F^* c n_0}{\beta N^*} e^{-\frac{Q_v + Q_\beta - Q_3}{kT}}. \] 
we have

\[ \frac{dn_F}{dt} = \frac{P_{0v} n_F^* c n_0}{\beta N^*} e^{-\frac{Q_v + Q_\beta - Q_3}{kT}}. \] 

The integration of this requires \( n_F^* \) to be expressed in terms of \( n_F \) as follows: \( n_F^* \) is governed by the optical excitation and spontaneous* radiative decay:

\[ \frac{dn_F^*}{dt} = \frac{n_F^*}{\tau^*} + \frac{N_0}{c} (1 - e^{-2.3\Delta x_m}), \]

in which \( \tau^* \) is the lifetime of the excited state; \( N_0 \) is the number of quanta within the F band incident per second per cm\(^2\); \( c \) is the velocity of light; \( P \) is the probability of absorption by an F center; and \( \Delta x_m \) is the peak absorption coefficient of the F band. If \( \Delta x_m \ll 1 \), we have from (7) that

\[ \frac{dn_F^*}{dt} = \frac{n_F^*}{\tau^*} + \frac{N_0}{c} P \times 2.3 \Delta x_m. \]

At equilibrium, \( \frac{dn_F^*}{dt} = 0 \), so \( n_F^* \) is then

\[ n_F^* = \frac{N_0}{c} 2.3 \Delta x_m \times P \times \tau^*. \]

Radiationless decay reduces \( \tau^* \) to \( \tau (\tau < \tau^*) \), and then

\[ n_F^* = \frac{N_0}{c} \times 2.3 \Delta x_m \times P \times \tau \times d, \]

whereupon we use Dexter's formula [18] for the relation of \( \Delta x_m \) to \( n_F^* \):

\[ n_F = 0.87 \frac{10^{17} n_F}{(n_F^* + 2)^2} \Delta x_m \times \Delta E_\lambda. \] 

Here \( n_0 \) is the refractive index of the crystal, \( f \) is the oscillator strength of an F center, and \( \Delta E_\lambda \) is the half-width of the F band. With (10) the numerical values give

\[ \Delta x_m = 2.2 \times 10^{-16} n_F^* \]

Then (9a) becomes

\[ n_F^* = \frac{N_0}{c} \times 5 \times 10^{-16} n_F^* P \times \tau. \]

Then from (6) we have

\[ \frac{dn_F}{dt} = \frac{P_{0v} n_0 c n_0^*}{\beta N^*} 5 \times 10^{-16} (N_0^* P \times \tau) e^{-\frac{Q_v + Q_\beta - Q_3}{kT}}. \]

We put

\[ \epsilon^* = Q_\beta + Q_\gamma - Q_3, \]

\[ \epsilon^* = \frac{P_{0v} n_0 c n_0^*}{\beta N^*} 5 \times 10^{-16} (N_0^* P \times \tau). \]

Integration of (13) gives

\[ n_F = n_F^* e^{-\epsilon^* \tau}, \]

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Figure 2 shows curves calculated from (14), which show that the rate of photothermal F-center destruction is much reduced as the concentration of ion trapping centers increases.

*Induced emission may be neglected here, in view of the low intensity of the optical excitation.

**Fig. 2.** Theoretical photothermal bleaching curves for: \( \epsilon = 0.10 \) eV, \( F_{0v} = 4 \times 10^{12} \) sec\(^{-1}, \) \( \epsilon = 0.30 \) eV, \( n_F = 10^{16} \) cm\(^{-3}, \) \( \epsilon = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( V_0 = 10^{10} \) cm\(^{-3} \) sec\(^{-1}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}, \) \( f = 0.30 \) sec, \( N = 10^{16} \) cm\(^{-3}. \)

We can derive \( \alpha^* = \frac{P_{0v} n_F}{V_0 \gamma N_0^* \gamma}, \) \( \gamma^* = \gamma \) from experiment if we assume that thermal and photothermal destruction both involve the same types of ion and ion trapping center; then

\[ \frac{\beta_0}{\beta_0^*} = \frac{\gamma_0}{\gamma^*}, \]

\[ \frac{\gamma_0}{\gamma} = \frac{\gamma^*}{\gamma^*}, \]

\[ \beta_0 = \frac{\gamma_0}{\gamma_0^*}, \]

Or, since \( \gamma_0 = \sigma_0 / \sigma_0^* \) and \( \gamma_0^* = \sigma_0^* / \sigma_0^* \),

\[ \frac{\beta_0}{\beta_0^*} = \frac{\gamma_0}{\gamma_0^*}, \]

\[ \frac{\gamma_0}{\gamma} = \frac{\gamma^*}{\gamma^*}, \]

These theoretical relationships allow us to calculate bleaching curves, including some of the major parameters of the processes. A comparison of theory with experiment will be presented in a forthcoming paper.