ACCUMULATION OF IRRADIATION-PRODUCED DEFECTS IN IONIC CRYSTALS LIMITED BY RECOMBINATION

M.E. GLOBUS, B.V. GRINYOV, A.M. RATNER[1], M.A. RATNER[2]

UDC 539.2

Institute for Scintillation Materials, Nat. Acad. Sci. of Ukraine
(60, Lenin Ave., Kharkiv 61001, Ukraine; e-mail: globus@isc.kharkov.com),

[1]**Institute for Low Temperature Physics and Engineering, Nat. Acad. Sci. of Ukraine**
(47, Lenin Ave., Kharkiv 61103, Ukraine),

[2]**Institute for Single Crystals, Nat. Acad. Sci. of Ukraine**
(60, Lenin Ave., Kharkiv 61001, Ukraine)

This paper is dedicated to Victor G. Bar'yakhtar on the occasion of his 75th birthday.

Irradiation-produced defects in ionic crystals (e.g., vacancies and interstitials) usually bear a charge that manifests itself in optical and luminescence properties even at very low concentrations of defects. On the other hand, the Coulomb interaction of charged defects essentially accelerates their recombination, thus diminishing the limiting (stationary) density of defects accumulated under irradiation. The complicated problem of the accumulation of charged defects limited by their recombination has been solved in the present work via numerical statistical modeling. The limiting level of the defect density was obtained as a function of the irradiation intensity. The theoretical results are compared with the traditional idea of the quadratic recombination. It was found that the latter is valid only for a very low concentration of defects (i.e. for a low irradiation intensity) and essentially overestimates the limiting value of the concentration under a strong irradiation. The kinetics of approaching the stationary regime obtained via the numerical statistical modeling is described in a broad dose-rate range in terms of an independent variable comprising the irradiation duration and the dose.

1. Introduction

Irradiation-produced defects in ionic crystals (e.g., vacancies and interstitials) usually bear a charge. Localized charges associated with defects manifest themselves in optical and luminescence properties even at a very low concentration [1—7]. Charged defects diminish the crystal transparency not only through the creation of color centers (e.g., F-centers). The crystal transparency region is narrowed from the side of high frequencies due to an additional absorption related to discrete excitonic levels lying below the band bottom (see, e.g., [1, 6]). Such localized excitons are strongly attracted, due to their large polarizability, by a charged defect resulting in the localization depth of about 1 eV [6]. This is the characteristic red shift of the high-frequency boundary of the transparency region.

Less known is the influence of localized charges on the excitonic luminescence through the interception of excitons, which shifts the luminescence spectrum to the red side and simultaneously enhances the luminescence of excitons via blocking their nonradiative relaxation channels [2—4]. In the case of doped crystals, the localization of excitons near charges diminishes their contribution to the dopant luminescence [4, 5]. Such manifestations of charged defects, due to a strong polarization attraction of excitons, become noticeable even at a low concentration of charges ($\sim 10^{-4}$ mol.%) [2—4,6]. Hence, of interest is the formation of charged defects in a broad interval of their concentration covering several orders of magnitude.

Irradiation-produced defects in ionic crystals, in view of a high sensitivity of optical and luminescence properties to the presence of localized charges, make up a serious difficulty of the scintillation method broadly used in physical researches and facilities. From the applied standpoint of the radiation damage of scintillation crystals, the irradiation-produced defects are extensively studied experimentally. Their influence on the scintillation properties and the possibilities to enhance the radiation stability of scintillators are discussed at all conferences concerned with the scintillation methods and technique (see, e.g., [8]).

However, such an area of research is not always based on the adequate statement of the problem.

The manifestations of radiation defects are examined mostly versus irradiation dose, the effect of the irradiation intensity being considered as less important. This means that photoproduced defects are assumed to be accumulated linearly in dose without a noticeable recombination. However, the experimental dose dependences of the crystal transparency or the luminescence yield indicate the tendency to the saturation of the density of defects caused by their recombination. Nevertheless, up to now, the recombination of localized charged defects has not been adequately analyzed because of a highly complicated character of recombination. The recombination process involves the hopping of localized charges accelerated by the random fluctuation field of all charges (equal on the average to zero), as well as the attraction of opposite-sign charges against the background of their diffusion motion. Solving such a problem analytically is hampered by serious mathematical difficulties.

In the present work, the problem of the accumulation of charged defects limited by their recombination is numerically solved via statistical modeling. The long-range Coulomb interaction of charged defects, strongly influencing their recombination and the saturation level of the charge density, is rigorously taken into account. The method of numerical statistical modeling is described in Sec. 2, and the calculation results are presented in the subsequent sections.

2. Numerical Statistical Modeling of the Defect Production and Recombination

The statistical modeling is carried out in the following way. Point lattice defects with positive and negative charges are created with equal probabilities at random points of the simple cubic lattice (the lattice type is of no importance, so far the average distance between defects is very large as compared to the lattice period a). Defects move via hopping over lattice sites, their coordinates being multiple of a. In the absence of electric field, any defect hops from its site to an adjacent site along the x, y, z-axes with a rate $1/\tau_0$ and passes with equal probabilities to one of the six nearest sites. Such a diffusion motion of defects is characterized by the diffusion coefficient

$$D_0 = a^2/2\tau_0. \tag{1}$$

The values of τ_0 and D related to opposite-sign defects are the same (the calculation results can be extended to the opposite limiting case where all the charges of a chosen sign are immovable, via multiplying τ_0 by 2).

The total density of both-sign charges, n, is defined as the averaged number of defects per unit cell of the volume a^3.

For every charge positioned at the site $\mathbf{r}$, the applied electric field $\mathbf{F}(\mathbf{r})$ is calculated by summing over all the rest of charges placed at sites $\mathbf{r}'$ [10]:

$$\mathbf{F}(\mathbf{r}) = \sum_{\mathbf{r}'} \frac{e(2+\varepsilon)}{3\varepsilon} \frac{\mathbf{r}' - \mathbf{r}}{|\mathbf{r}' - \mathbf{r}|^3}. \tag{2}$$

The calculations are carried out with the use of a base crystal in the form of a cube with edge length La. The infinite space used in the summation in (2) is reproduced via the periodic extension of the base crystal (it was numerically checked that the period L does not influence the calculation results in the region $L{>}15n^{-1/3}$). In order to reduce the fluctuations of the statistical modeling, it was carried out for the base crystal consisting of more than 4000 sites.

In the applied field $\mathbf{F}$, every charge hops independently in the equivalent x, y, z directions with a probability dependent on $\mathbf{F}$. This dependence can be specified irrespective of the nature of charges and potential wells, where they are localized (the charge can be self-trapped or trapped in a well existing irrespective of its population). For definiteness, the consideration is carried out in the latter case for charges attached to ions (e.g., for charged vacancies and interstitials in an ionic crystal). The temperature T is assumed to be much greater than the phonon energy, and the hopping of a heavy ion occurs classically above the potential barrier (the tunneling of heavy ions is neglected). The probability for an ion to hop from the site $\mathbf{r}$ to the equivalent adjacent site $\mathbf{r}{+}\mathbf{a}$ is

$$P_{\text{hop}}(\mathbf{r} \to \mathbf{r} + \mathbf{a}) = \text{const} \exp\left(-\frac{U(\mathbf{u}_0) - e\mathbf{F}\mathbf{u}_0}{T}\right), \tag{3}$$

where $U(\mathbf{u})$ is the lattice potential in the absence of a field as a function of the shift, $\mathbf{u}$, of the hopping ion from its site, and the shift $\mathbf{u}_0 = \mathbf{a}/2$ corresponds to the maximum of the potential barrier.

The hopping probability (3) per unit time can be rewritten as a function of the electric field intensity

$$P_{\text{hop}}(\mathbf{r} \to \mathbf{r} + \mathbf{a}) = \frac{1}{\tau_0} \exp\left(\frac{e\mathbf{F}\mathbf{a}}{2T}\right), \tag{4}$$

where $1/\tau_0$ is the rate of hopping along each of three Cartesian axes in the absence of an electric field.

Equation (4) agrees with the relevant existing notion. In the case of a weak field $\mathbf{F}$, Eq. (4) describes the

drift motion with a velocity proportional to **F** and the mobility connected with the diffusion coefficient (1) by the Einstein relation.

For an arbitrary field intensity **F**, Eq. (4) meets the principle of detailed equilibrium:

$$P_{\rm hop}\left(\mathbf{r}+\mathbf{a}\to\mathbf{r}\right)=P_{\rm hop}\left(\mathbf{r}\to\mathbf{r}+\mathbf{a}\right)\exp\left(-\frac{e\mathbf{Fa}}{T}\right). \quad (5)$$

(the charge potentials at the sites **r** and **r**+**a** differ by $e\mathbf{Fa}$). This confirms that relation (4) is of general character and is valid irrespective of the nature of charges. But the constant multiplier τ_0^{-1} in Eq. (4) can vary, depending on the specific crystal and the nature of charges, within many orders of magnitude (this dependence is beyond the present consideration).

The random motion of charges with the hopping probability (4) in field (2) was statistically reproduced resulting in what follows.

3. Calculation Results. Saturation Level of the Density of Defects as a Function of Irradiation Intensity

The process of the accumulation of charged defects with allowance for their recombination was numerically modeled at room temperature (T = 293 K) at typical values of parameters a = 0.5 nm and ε = 6.3. It was assumed that every defect bears the electron charge with a randomly chosen sign. The modeling was carried out at a fixed irradiation intensity (the dose rate).

Prior to presenting the calculation results, a physical scale of irradiation doses should be introduced. Let D be the irradiation dose in units of rad. In the region of small doses, where the recombination is inessential, the density of photoproduced defects n is equal to ηD, where η is the number of defects per unit cell produced by a dose of 1 rad. For estimations, one can put $\eta = 10^{-9}$, which corresponds to the irradiation energy of 50 eV required to create a pair of defects. In the region of large doses, where the dose dependence of n achieves saturation, the saturation value of n is a function of $\eta R_D \tau_0$, where R_D is the dose rate in units of rad/s.

These scales of doses are inherent in the elementary kinetic equation written within the quadratic recombination law:

$$\frac{dn}{dt}\tau_0 = \eta R_D \tau_0 - Kn^2 \quad (\text{for quadratic recombination}). (6)$$

This will be used to compare the results of the statistical modeling with the traditional notion of quadratic recombination law. According to Eq. (6), the saturation value of the defect density is

$$n_{\rm sat} = \left(\frac{\eta R_D \tau_0}{K}\right)^{1/2} (\text{for quadratic recombination}). \quad (7)$$

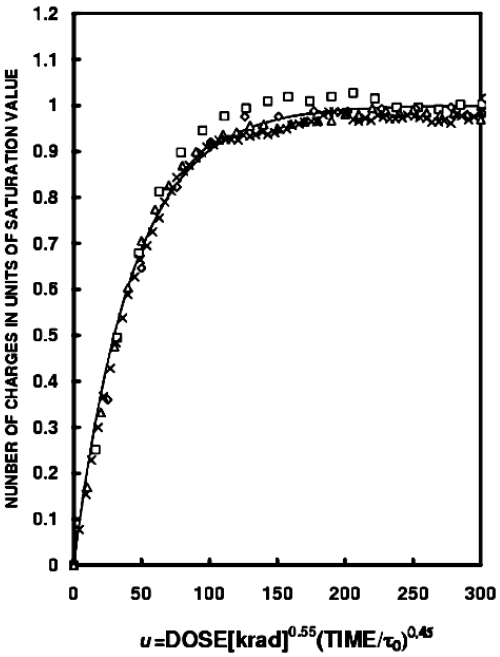

Fig. 1. Density of defects achieved after the long-term irradiation (saturation value) as a function of the dose rate in units rad/τ_0(dose absorbed per time τ_0). The dashed line shows the dose-rate dependence of the defect density according to the traditional notion of quadratic recombination law

Fig. 1 presents the saturation value of the density of defects, $n_{\rm sat}$, as a function of the dose rate R_D multiplied by $\eta\tau_0$ ($\eta = 10^{-9}$). For comparison, the dashed line shows this dependence ($n_{\rm sat} \sim R_D^{1/2}$) within the usual notion of quadratic recombination law. As seen from the figure, the usual notion is applicable at a low density of defects (less than 10^{-5} defects per unit cell, which corresponds to the mean distance exceeding 50 lattice periods). At such distances between charges, the Coulomb interaction becomes inessential, and the statistically independent motion of defects over the lattice is accompanied by a quadratic recombination process. At higher densities, the Coulomb attraction of opposite-sign charges accelerates their recombination essentially, and the factual dependence of $n_{\rm sat}$ on the dose rate deviates from (7) towards the side of low values. At large dose rates R_D, $n_{\rm sat}$ almost ceases to grow with R_D (such a phenomenon was observed experimentally [9,11].

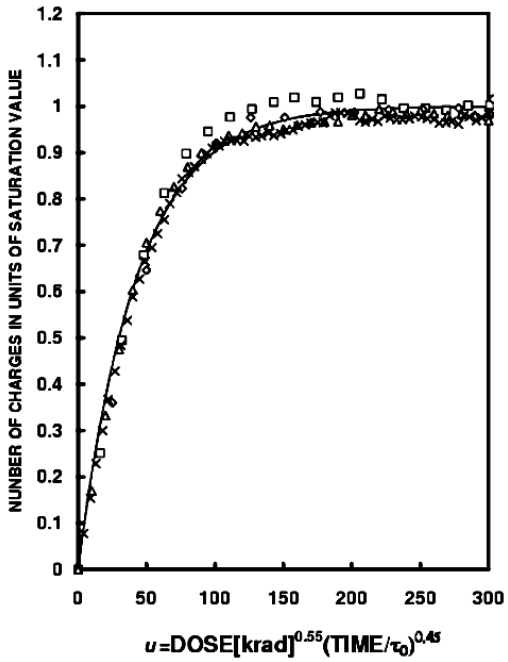

Fig. 2. Kinetics of the defect density expressed in units of its saturation value (shown in Fig. 1) at different values of the dose rate (in units krad/τ_0): 10^{-3} (crosses), 10^0 (triangles), 10^3 (rhombs), 10^4 (squares). The solid line shows the approximation curve (8) at $u_0 = 43$. On the abscissa axis, variable (9) comprising dose and time is plotted

4. Kinetics of Accumulation of Radiation Defects after Switching on Irradiation

The analysis of the calculation results shows that the defect density kinetics after switching on the irradiation can be presented in the following way:

$$\frac{n}{n_{\rm sat}} = 1 - \exp\left(-\frac{u}{u_0}\right). \qquad (8)$$

Here, $n_{\rm sat}$ is the saturation value of the density of defects shown in Fig. 1, and

$$u = D^{0.55}\left(\frac{t}{\tau_0}\right)^{0.45} \qquad (9)$$

is a variable comprising the irradiation duration t and dose D expressed in krad.

Fig. 2 presents the density of defects, calculated at different fixed dose rates, versus the variable u. The solid line shows approximation (8) with a value $u_0 = 43$ related to the set of parameters given at the beginning of Sec. 3.

As seen from Fig. 2, the calculated kinetics of the defect density related to dose rates differing within 7 orders of magnitude is described by the approximation curve (8). This means that the degree of approaching the stationary regime with $n = n_{\rm sat}$ depends on the dose and irradiation duration almost in the same degree.

1. *Zhu R.Y.* // Proc. Intern. Conf. "Heavy scintillators", Chamonix (France).— 1992.
2. *Shpilinskaya L.N., Zaslavsky B.G., Kovaleva L.V. et al.* // Semicond. Physics, Quantum Electronics & Optoelectronics.— 2000. — **3**.— P. 178.
3. *Ogurtsov A.N., Ratner A.M., Savchenko E.V. et al.* // J. Phys: Condens. Matter.— 2000.— **12**.— P. 2769.
4. *Ratner M., Grinyov B., Ratner A.* // Radiat. Measurem.— 2004. —**38**.— P. 627.
5. *Renker D.* // CERN # 89-10. ECFA Study Week Instrument Technology. — 1989.— P. 601.
6. *Ratner A.M.* // Phys. Lett. A.— **265**.— 2000.— P. 411.
7. *Globus M.E., Grinyov B.V.* Inorganic Scintillators.— Kharkiv: Acta, 2000 (in Russian).
8. *Book* of abstracts of IEEE Conference, Nuclear Science Symposium, Portland, USA, 2003; Rome, Italy, 2004.
9. *Eremenko V.V., Gnatchenko S.L., Kachur I.S. et al.* // Low Temp. Physics.— 2001.— **27**.— P. 22.
10. *Fröhlich H.* Theory of Dielectrics.— Oxford: Clarendon Press, 1958.
11. *Eremenko V.V., Gnatchenko S.L., Kachur I.S. et al.* // Phys. Rev. B.— 2000.— **61**.— P. 10670.

Received 25.05.05

ОБМЕЖЕНЕ РЕКОМБІНАЦІЄЮ НАКОПИЧЕННЯ ДЕФЕКТІВ У ІОННИХ КРИСТАЛАХ ПІД ОПРОМІНЮВАННЯМ

М.Є. Глобус, Б.В. Гриньов, А.М. Ратнер, М.А. Ратнер

Р е з ю м е

Фотоіндуковані дефекти в іонних кристалах (наприклад, вакансії та міжвузловинні атоми) звичайно несуть заряд, що проявляється в оптичних властивостях та люмінесценції навіть при дуже низькій концентрації дефектів. З іншого боку, кулонівська взаємодія заряджених дефектів суттєво прискорює їх рекомбінацію, що знижує максимальну (стаціонарну) щільність дефектів, накопичуваних під опромінюванням. Складну задачу про накопичення заряджених дефектів, обмежене їх рекомбінацією, в цій роботі розв'язано шляхом чисельного статистичного моделювання. Стаціонарна щільність дефектів знайдена як функція інтенсивності опромінювання. Результати обчислень порівнено з традиційним уявленням про швидкість рекомбінації, яка квадратично залежить від щільності дефектів. Показано, что традиційне уявлення адекватне тільки при дуже низькій концентрації дефектів (тобто при відповідно низькій інтенсивності опромінювання), а для умов інтенсивнішого опромінювання дає істотно завищене значення стаціонарної щільності дефектів. Кінетика наближення до стаціонарного режиму, розрахована шляхом чисельного статистичного моделювання, описана в широкому интервалі інтенсивностей з використанням незалежної змінної, що враховує дозу і час опромінювання у вигляді деякої їх комбінації.