Temperature Dependence of Defect Accumulation in Ionic Crystals

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Abstract – The paper presents a model of the description of complicated process the result of which is the defects accumulation in ionic crystals. It is considered the typical calculated temperature dependences of the defects accumulation in these crystals. The performance analysis of suggested model is carried out.

1. Introduction

Radiation defects accumulation in ionic crystals is determined by the totality of consistently developing processes. The primary pair of defects is formed at the disintegration of electronic excitation then the pair is spatially seperated. The primary pair components are transformed into steady defects in the experiment. This process sequence is followed by the disappearance of the created primary pairs. The number of accumulated defects can differ from the number of created ones by the factor of many times. The accumulation efficiency of defects depends on many factors. Therefore, the forecasting of material irradiation results and the change of material properties are complicated problems. In [1, 2] there is a description model of the complicated process the result of which is the defects accumulation. The present paper analyses this model.

2. The temperature dependence model of accumulation efficiency

Radiation creates *e-h* pairs. Then there is an electron trapping on holes of a different self-trapping degree, monohalogenated, bihalogenated. The electron trapping on the hole of any self-trapping degree leads to the exciton totality formation with different excitation degree of electron and hole components.

The relaxation of the exciton created in this way passes through some connected metastable states differing in spatial and energy structure (the position of the exciton nucleus, the degree of oscillatory nucleus excitation, electron excitation level). The relaxation process of any concrete exciton is defined by its initial state. During the relaxation process every concrete exciton passes its metastable state combination. The termination of the relaxation process is the formation of a self-trapped exciton (STE) or F, H – pairs.

The presence of some metastable states has already been proved experimentally. Thus, in paper [3] you can see the probability of α-, I – center existence. The α-center represents a strongly oscillatorily excited V_k – center. The trapping of the electron by such excited V_k – center leads to an I – center creation. The I – center is already a self-trapped exciton with a strongly excited electron and hole system. The center of nucleus fluctuations of such system coincides with the mass center of the two next anions in a lattice. That is the I – center is a central symmetric exciton. As STE is an excited I – center, the spectral position and the band form caused by this center differ from the spectral position of relaxed STE bands.

The result of the relaxation process, the formation of STE or F, H – defect pairs, depends on the initial state of the formed exciton and the ways of its relaxation. For example, in [3] you can see that there are at least 2 channels of exciton disintegration differing in decomposition time: some and more than ten picoseconds. In [4] you can see that the exciton formation efficiency is maximal while optical creation of the exciton by selective excitation in exciton absorption band. In [5, 6, 7] you can see that excitons disintegrate with high efficiency if the optical excitation of the relaxed exciton electron component or its nucleus occurs.

Direct measurements of the temperature dependence of the F, H – defects pair formation efficiency at the excitation by short radiation pulses and measurement with a picosecond time resolution show that at temperatures below 200 K the efficiency almost does not depend on temperature. When the temperature grows, the formation efficiency increases and reaches the maximum value up to 0,8 per one created electronic-hole pair in alkali halide crystals. The existence of such dependence of Frenkel pair formation efficiency means that it is necessary to surmount the energy barrier for a metastable state transformation of disintegrating electron excitation into F, H – pairs. In the range of low temperatures the energy of the electron excitation allocated in the place of disintegration is great enough to surmount this barrier. With the rise in temperature the probability of the barrier surmounting of a metastable state transformation into F, H – pairs grows. The barrier is caused by the necessity of nucleus shift of decomposing electron excitation (H – center being formed) into one knot of the lattice.

The result of the described primary process is the creation of correlated defect pairs. As each concrete self-trapped exciton has its history of relaxation, the pairs of different correlation degree are formed in a

crystal. Hence, the mutual component distribution of the formed primary defect pairs represents some function which is refered to as the function of initial mutual distribution.

The formed primary defect pairs are in _the field of mutual attraction_ which is the consequence of the deformation field interaction around the defects. The presence of the mutual attraction is proved by the existence of a primary defect destruction monomolecular stage. The potential of the interaction between neutral F, H – pair components should be short-ranged, as follows:

$$E = a * exp(- br). \qquad (1)$$

The components of the primary pair of defects _are then separated spatially or annihilate_ as a result of the thermoactivated movements of a mobile pair component. The separation by means of a mobile pair component movement can be effective enough; the probability of the separation can reach the value equal to 0,8 in alkali halides. The spatial separation by means of a thermoactivated movement is possible in a crystal lattice of any kind. The probability of a spatial separation by means of thermoactivated movements increases with temperature growth if pair components are in the region of mutual attraction. The temperature reduces, the cooperating primary genetically connected pairs mainly annihilate at a movement [8, 9].

Spatially separated primary F, H – pair components can recombine with other primary defects which are not connected with them genetically. It leads to the concentration reduction of the formed separated centers. The part of primary pair mobile components can be trapped by lattice defects which existed before irradiation or were created by radiation. The steady defects are formed under conditions of the experiment,

e. g. V- centers in alkali halides. The accumulated defects concentration is proportional to the concentration of the separated genetically connected pairs. The created steady defects can destroy if the conditions of the experiment change. For example, when the temperature rises the defects can be transformed into new steadier ones. The probability of primary defect transformation into steady and, hence, accumulated defects depends on the kind of the material and its initial deficiency. In alkali halides the transformation of a mobile H-centre into V- center occurs when it is trapped by cationic vacancy. In MgF_2 the defects in a cationic sublattice can't be formed, as their formation energy is high. The stabilization of the created H- centers in MgF_2 is possible only by means of the reaction between them resulting in the creation of fluorine molecules in interstices. Since the cross-section of this reaction is small, the probability of mobile component stabilization in MgF_2 is low. Therefore, the accumulation defect efficiency in MgF_2 is low, whereas the efficiency of the primary pair formation into alkali halides and MgF_2 is comparable.

The following process definitions for mathematical model construction are to be used:

Primary pair formation is the totality of the following processes:

● – zone electron and hole (or exciton) relaxation up to a metastable exciton state capable of transforming into a pair of defects _(predefective condition);_

● – the origin of the primary pair from a predefective state as a result of a nucleus shift of a decaying exciton into one of the nearest lattice knots due to the energy released in the place of pair's origin at the relaxation of an electronic excitation or due to the thermal energy of the lattice.
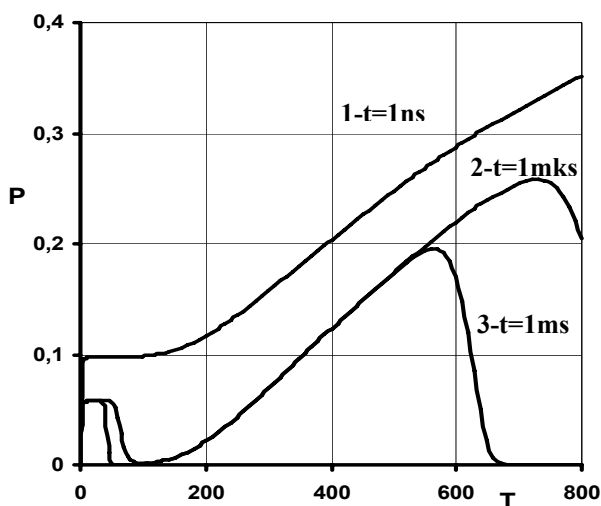

Fig. 1. Temperature dependence of the defect survival probability by the moment of time equal to 1 nanosecond, 1 microsecond and 1millisecond after its creation
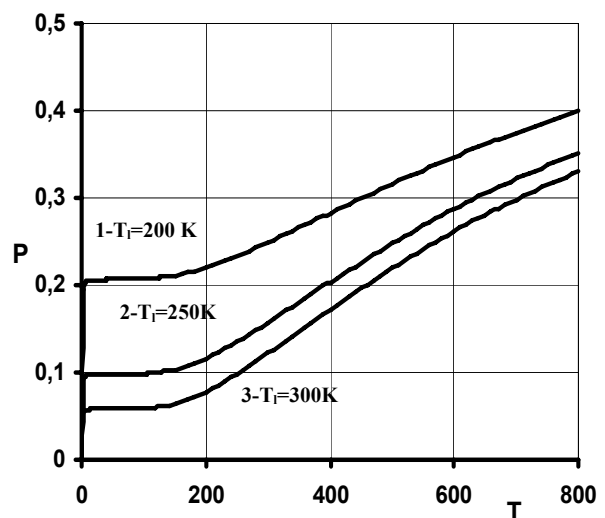

Fig. 2. Temperature dependence of the defect formation probability when the local temperature values in the region of the defect origin are equal to 200, 250, 300 K
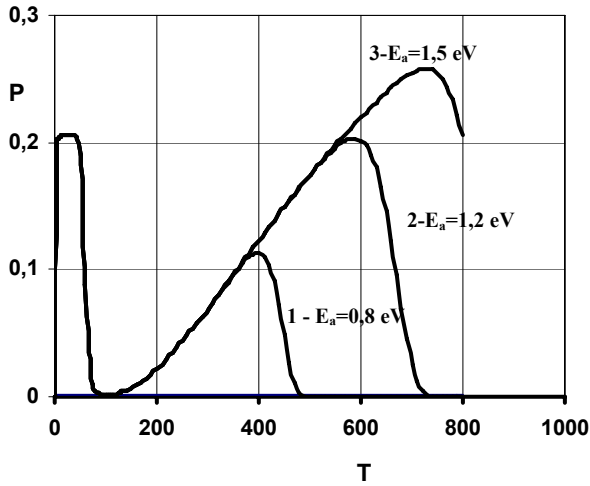
Fig. 3. Temperature dependence of the defect accumulation probability when the activation energy values of the created hole centre destruction process are equal to 0,8, 1,2 and 1,5 *eV*

The *primary pair* of radiation defects is a genetically connected Frenkel *F, H* –pair, its components can be identified experimentally in the totality of properties typical of the defect stable conditions.

The *pair accumulation* of stable radiation defects is the result of independent consecutive events:

● – *primary pair formation* of correlated defects;

● – *spatial separation* of pair components;

● – *pair component transformations* into steady defects under conditions of the experiment.

The probability P_s of the defect pair accumulation is

$$P_s = P_c P_p P_r , \qquad (2)$$

where P_c, P_p, P_r – conditional probabilities of the primary pair component formation, separation and transformation into a steady one.

The exciton and hole self-localization process is known to begin after barrier surmounting E_0 in some *meV*. Hence, the reaction output of the exciton disintegration into a pair of structural defects depends on the sample temperature in the range of very low temperatures. Then it is possible to write as follows:

$$P_c = D * \exp(-E_o /kT) \qquad (3)$$

where, N_0 – the number of low-energy excitations created by the radiation which is, apparently, proportional to the absorbed doze; N_m – the number of the predefective states formed of them, D – the factor.

The annihilation kinetics of radiation primary defect pairs connected genetically is approximately described as follows:

$$P_a = A' \cdot \exp(-a/n) \qquad (4)$$

where a – the constant depending on the lattice structure; n – the number of jumps during the experiment t:
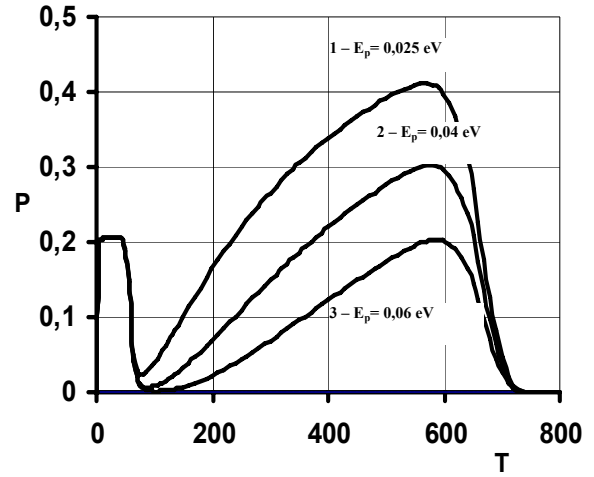

Fig. 4. Temperature dependence of the defect formation probability when the activation energy values of the primary defect spatial separation process are equal to 0,025, 0,04 and 0,06 *eV*

$$n = B \cdot t \cdot \exp(-E_H /kT) \qquad (5)$$

$$A' = A \cdot (1 - C \cdot \exp(-E_p /kT) \qquad (6)$$

A' – the factor defining the temperature dependence of annihilation probability and independent of the number of jumps; A, B, C – constant factors; E_H and E_p – activation energy of the migration process of a mobile defect and pair separation.

The expression (4) can be rewritten as follows (7):

$$P_a = A * (1 - C * exp(-\frac{E_p}{kT})) * (exp(-\frac{a}{Bt} exp(\frac{E_H}{kT}))) \qquad (7)$$

Then the separation probability of $F – H –$ pair components is defined by the ratio:

$$P_p = (1 - P_a) = (1 - A(1 - C * \exp(-E_p /kT)) * (\exp(-\frac{a}{Bt} \exp(\frac{E_H}{kT}))) \qquad (8)$$

In the place of defect formation the heating of the local crystal occurs. The local crystal heating falls down quickly within the time $\tau < 10^{-11}$s. The short-term local crystal heating in the place of the pair's origin can lead to the thermoactivated movement of a mobile component. During 10^{-11}s lattice heating the mobile component can make on the average one or several single jumps n_o. Then the full number of jumps of a mobile defect within time t makes:

$$n = Bt * \exp(-\frac{E_H}{kT}) - Z * \exp(-\frac{E_H}{kT_l}) \qquad (9)$$

The second member of the sum defines n_0 at T_l – the temperature of local heating. Then the expression (8) will be as follows: (10)

$$P_p = (1 - A(1 - C * \exp(-E_p /kT)) * (\exp(-\frac{a}{Bt \exp(-\frac{E_H}{kT}) - Z * \exp(-\frac{E_H}{kT_l})}))$$

And, finally, *at high temperatures* (for alkali halides $T > 300$ K) the accumulated radiation defects are unstable and destruct in pairs at thermal activation. The activation energy of the color center destruction process E_a in alkali halides at high temperatures has

the value *1 eV*. Then at rather high temperature the number of the defects which have survived, depending on the character of the destruction process should be defined as follows:

$$dn_F/dt = \sigma_1 \cdot n_F, dn_F/dt = \sigma_2 \cdot n_F \qquad (11)$$

For the first case the probability of the pair survival, already having been spatially separated and fixed, by the moment of time *t* at temperature *T* is equal to:

$$p_r = \exp[-Q \cdot t \cdot \exp(-E_a/kT)] \qquad (12)$$

where Q – the constant factor.
While combining (3, 10, 12), we can obtain the analytical expression for the description of the accumulation temperature dependence of radiation defects: (13)

$$P_s = P_c P_p P = D * \exp(-E_o/kT) (1-A(1-C*\exp(-E_p/kT)) *$$

$$*(\exp(-\frac{a}{Bt\exp(-\frac{E_H}{kT})- Z * \exp(-\frac{E_H}{kT_\pi})}))\exp[-Q\cdot t\cdot\exp(-E_a/kT)$$

3. Results of studies

We have done the investigation researches of survival probability dependence of defect pairs in the course of time after their formation. We have chosen the totality of the parameter values to calculate by the following reasons. The values of the process activation energy have been taken close to the experimentally measured ones, known for alkali halides (E_0=0,001 *eV*, E_p=0,025…0,06 *eV*, E_H=0,07*eV*, E_a=0,8…1,5 *eV*). The values of factors were selected so that the calculated values of formation and accumulation process probabilities corresponded to the measured alkali halides in (T_l=200…300 K, A=D=1, C=0,7, B=2*10^{10}s^{-1}, Z=1*10^3s^{-1}, Q=10^{12}s^{-1}). The examples of the calculated temperature dependence are presented in Fig. 1–4. You can see the temperature dependences of the created defects survival probability in the course of time in Fig. 1. The first curve corresponds to the measured probability immediately after an instant irradiation pulse. In the course of time there is a gap in the region above the temperature of *H*-center delocalization. The gap value grows in the course of time. The number of survived centers is reduced in all the range of temperatures especially in the range of high temperatures. The described mechanisms qualitatively correspond to the experimentally measured ones.

When the local temperature increases the probability of primary pair formation decreases (Fig. 2). It can be explained by the fact that several jumps are enough for interecting pairs to annihilate. One or several single jumps can be made within the local lattice heating. At low temperatures the annihilation probability is higher.
The values of the activation process energy of the primary pair, its components being spatially separated, and the stability of the accumulated centers influence the kind of temperature. The steadier the accumulated centre is, the more complete the destruction of the created defects at higher temperatures occurs (Fig. 3). With the activation energy increase of spatial separation the temperature dependence of color centre accumulation becomes of the low grade when the temperature grows (Fig. 4).

In conclusion, we should note that the described model does not consider the probability of tunnel annihilation influence of primary pair components. The probability of the tunnel annihilation depends on the mutual distance between the pair components. The probability of the tunnel annihilation should be high at low temperature when the defects created in primary disintegration act are immobile. The presence of the tunnel annihilation should become apparent in defect destruction in the course of time at low temperatures.

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