



# Determination of effective charge states for point radiation defects in fusion ceramic materials

A.I. Ryazanov <sup>a,\*</sup>, A.V. Klaptsov <sup>a</sup>, C. Kinoshita <sup>b</sup>, K. Yasuda <sup>b</sup>

<sup>a</sup> Russian Research Center 'Kurchatov Institute', Moscow, Russia

<sup>b</sup> Department of Applied Quantum Physics and Nuclear Engineering, Kyushu University, Fukuoka, Japan

## Abstract

Point defects in fusion ceramic materials under irradiation can have an effective charge due to ionization and covalent chemical bonding. The kinetics of charged point defects in these materials is determined by their effective charge and this kinetics is completely different from non-charged point defects in metals. The experimental investigation of point defect charge states in ceramic materials is rather difficult. In this paper, a new method is proposed for the investigation of charge states of point defects in irradiated ceramic materials. This method is based on a new theoretical model and experimental observations of defect cluster formation near permanent sinks, such as grain boundaries. Previous experimental investigations show that a denuded zone is formed in irradiated ceramic materials near free surfaces and grain boundaries. The effect of an applied electric field on the formation of interstitial-type point defect clusters (dislocation loops) near grain boundaries in irradiated ceramic materials is investigated. For this purpose a new theoretical model is suggested, which takes into account the effect of an applied electric field on the denuded zone formation. It is shown that the denuded zone size depends on point defect charge and direction of applied electric field. The obtained theoretical results are compared with experimental data.

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## 1. Introduction

Ceramic materials are expected to be used as structural materials for future fusion reactors due to their thermo-chemical stability, radiation resistance and low-induced radioactivity. The radiation resistance of ceramic materials under irradiation is determined by the kinetics of point defect accumulation and defect cluster (dislocation loops, voids, etc.) formation and growth in the matrix. The physical properties of ceramic materials differ from metals because they do not have free charge carriers, and point defects (vacancies and interstitial atoms) in ceramic materials can have an effective charge [1]. The effective charge state of point defects is determined by the kinetics of emission and absorption of

electrons and holes on these point defects. So for example the charge of vacancies in ceramics can change due to trapping of electrons (for example  $F^+$ ,  $F$  centers: vacancies with a single and two trapped electrons). Also the charged interstitial atoms and vacancies can change their effective charge during the diffusion process [2]. Due to the accumulation of charged point defects in the matrix, an effective internal electric field is formed, which affects the diffusion process of charged point defects. The kinetics of the nucleation and growth of point defect clusters (dislocation loops and voids) in such materials can have completely different behavior in comparison with metals [3–6]. Moreover, an internal electric field near charged clusters can change the physical mechanism of the nucleation and growth of such clusters [3,4]. So, the use of ceramic materials in fusion devices will require knowing how the macroscopic properties of such a material are modified by the internal and external electric field under irradiation. To understand this situation, the charge states of point defects

\* Corresponding author. Tel.: +7-095 196 91 77; fax: +7-095 421 45 98.

E-mail address: [ryazanoff@comail.ru](mailto:ryazanoff@comail.ru) (A.I. Ryazanov).

should be known. We propose here a theoretical model, which can be used for the experimental investigations of the charge states of point defects.

Grain boundaries are known as perfect sinks for point defects, so a denuded zone usually appears under irradiation in metals near the grain boundaries [7–9]. The denuded zone is a region where the number of the point defects and defect clusters is much less than that in the matrix. Denuded zone formation has also been observed in irradiated ceramic materials [10–12].

In our model, we will consider that only one sort of interstitial atom with negative charge ( $-q$ ) and only one sort of vacancy with positive charge ( $q$ ) are formed in an irradiated ceramic material. We will investigate how the denuded zone near grain boundaries can form in irradiated ceramics with an applied electric field and without it. The applied electric field is oriented in our model perpendicular to the surface of the irradiated specimen or grain boundary. The assumptions made in our model are used for simplicity but they allow to determine the dependence of denuded zone size as functions of strength and direction of an external electric field, and charge state of point defects.

## 2. Physical model of denuded zone formation in irradiated ceramic materials with two types of charged point defects

In our model, we assume that the grain boundary can be considered as a plane at  $z = 0$  ( $z > 0$  is inside of material), which act as a perfect sink for point defects. This means that the concentrations of vacancies ( $C_V$ ) and interstitials ( $C_I$ ) near grain boundary are small for the defect cluster (dislocation loops, voids) formation, leading to the formation the denuded zone near grain boundary. We also include the mutual recombination of the vacancies and interstitial atoms for the formation of a denuded zone. In this case the contribution of other sinks such as voids, dislocations and dislocation loops is negligible compared to the grain boundary. If the temperature and diffusion coefficients are comparatively high, the concentrations of the point defects will reach steady-state values after a relatively short time.

For the calculations of the steady-state concentrations of  $C_I(z)$  and  $C_V(z)$  in the vicinity of the grain boundary, we have to solve the following one-dimensional diffusion equations:

$$G - \alpha C_I C_V - \frac{dj_I}{dz} = 0, \quad G - \alpha C_I C_V - \frac{dj_V}{dz} = 0. \quad (1)$$

Here  $G$  is the generation rate of point defects under irradiation,  $\alpha = \mu(D_I + D_V)$  is the point defect recombination coefficient ( $\mu = 3/a^2$ ,  $a$  is the lattice spacing),  $D_I$  and  $D_V$  are the diffusion coefficients of interstitial atoms and vacancies respectively. The second term on the left-

hand sides of Eq. (1) describes the mutual recombination of vacancies and interstitial atoms. The diffusion currents of the point defects, which take into account the influence of a driving force from an internal electric field on the diffusivity of charged point defects in one-dimensional case, are equal:

$$\begin{aligned} j_I &= -D_I \frac{dC_I}{dz} + \frac{qD_I C_I}{kT} \frac{d\varphi}{dz}, \\ j_V &= -D_V \frac{dC_V}{dz} - \frac{qD_V C_V}{kT} \frac{d\varphi}{dz}. \end{aligned} \quad (2)$$

Here  $T$  is the temperature,  $\varphi$  is the potential of internal electric field ( $E_{\text{int}} = -\nabla\varphi$ ), which is determined from the following Poisson equation:

$$\Delta\varphi = -\frac{4\pi}{\epsilon\omega} (qC_V - qC_I + eC_h - eC_e). \quad (3)$$

Here  $e$  is the electron charge;  $C_h$ ,  $C_e$  are the concentrations of holes and electrons,  $\omega$  is the atomic volume,  $\epsilon$  is the dielectric permeability of material.

We assume that the charge density  $\rho$  ( $\rho = eC_h - eC_e$ ) is constant in the whole specimen. One can see from Eq. (1) that a total electrical current from charged point defects is the constant ( $J_0$ ) in the whole specimen and is equal to

$$\begin{aligned} J &= -q(j_I - j_V) \\ &= q \left( D_I \frac{dC_I}{dz} - D_V \frac{dC_V}{dz} \right) + \frac{q^2}{kT} (D_I C_I + D_V C_V) E_{\text{int}} = J_0. \end{aligned} \quad (4)$$

For the concentrations of the vacancies and interstitial atoms we can write the following boundary conditions

$$\begin{aligned} C_I(z=0) &= 0, \quad C_I(z \rightarrow \infty) = C_I^0, \\ C_V(z=0) &= 0, \quad C_V(z \rightarrow \infty) = C_V^0, \\ J_0 &= \left( q \left( D_I \frac{dC_I}{dz} - D_V \frac{dC_V}{dz} \right) + \frac{q^2}{kT} (D_I C_I + D_V C_V) E_{\text{int}} \right) \Big|_{z=0} \\ &= \sigma\omega E. \end{aligned} \quad (5)$$

Here  $\sigma$  is the ionic conductivity of charged point defects,  $E$  is the applied external electric field,  $C_I^0$  and  $C_V^0$  are the steady-state concentrations of interstitial atoms and vacancies far from the grain boundary in the matrix. It is very difficult to obtain an analytical solution for Eqs. (1)–(3) with the boundary conditions (5). However, some values such as a denuded zone size can be obtained without solving the total system of Eqs. (1)–(3). Let us assume that the space dependent concentrations of the point defects near grain boundary  $C_I^1$ ,  $C_V^1$  are small

compared with the average concentrations of them in the matrix  $C_1^0$ ,  $C_V^0$ ,

$$\begin{aligned} C_1 &\approx C_1^0 + C_1^1 \quad (|C_1^1| \ll C_1^0), \\ C_V &\approx C_V^0 + C_V^1 \quad (|C_V^1| \ll C_V^0). \end{aligned} \quad (6)$$

These requirements are not met on the surface of the specimen or grain boundary. However, these relations are correct at distances comparable with the size of denuded zone. Besides, the use of the relations (6) simplifies the analysis significantly. The linearization of Eqs. (1)–(3) will give the average concentrations  $C_1^0$ ,  $C_V^0$  ( $D_1 \gg D_V$ )

$$\begin{aligned} C_1^0 &= \sqrt{\left(\frac{\rho}{2q}\right)^2 + \frac{G}{\mu D_1}} + \frac{\rho}{2q}, \\ C_V^0 &= \sqrt{\left(\frac{\rho}{2q}\right)^2 + \frac{G}{\mu D_1}} - \frac{\rho}{2q}, \quad \rho = eC_h - eC_e. \end{aligned} \quad (7)$$

It is known that the electric field in the bulk is equal to  $E_{\text{int}}(z \rightarrow \infty) = E/\varepsilon$ . So from Eqs. (4) and (5) we obtain the famous relation  $\sigma_0 = q^2(D_1 C_1^0 + D_V C_V^0)/\varepsilon \omega k T$ . Assumption (6) results in the following system of linear differential equations:

$$\begin{aligned} \frac{d^2 C_1^1}{dz^2} + \frac{qE}{\varepsilon k T} \frac{dC_1^1}{dz} - \left[ \frac{\alpha C_V^0}{D_1} + \frac{4\pi q^2 C_1^0}{\varepsilon \omega k T} \right] C_1^1 \\ - \left[ \frac{\alpha C_1^0}{D_1} - \frac{4\pi q^2 C_V^0}{\varepsilon \omega k T} \right] C_V^1 = 0, \\ \frac{d^2 C_V^1}{dz^2} - \frac{qE}{\varepsilon k T} \frac{dC_V^1}{dz} - \left[ \frac{\alpha C_1^0}{D_V} + \frac{4\pi q^2 C_V^0}{\varepsilon \omega k T} \right] C_V^1 \\ - \left[ \frac{\alpha C_V^0}{D_V} - \frac{4\pi q^2 C_1^0}{\varepsilon \omega k T} \right] C_1^1 = 0. \end{aligned} \quad (8)$$

We can see from Eq. (8) that the solutions of these equations are  $C_1^1, C_V^1 \sim \exp(-\lambda_{\text{min}} z)$ , where  $\lambda_{\text{min}}$  is the minimum positive root of the following equation

$$\begin{aligned} \left( \lambda^2 - \frac{qE}{\varepsilon k T} \lambda - \frac{\alpha C_V^0}{D_1} - \frac{4\pi q^2 C_1^0}{\varepsilon \omega k T} \right) \\ \times \left( \lambda^2 + \frac{qE}{\varepsilon k T} \lambda - \frac{\alpha C_1^0}{D_V} - \frac{4\pi q^2 C_V^0}{\varepsilon \omega k T} \right) \\ = \left( \frac{\alpha C_1^0}{D_1} - \frac{4\pi q^2 C_V^0}{\varepsilon \omega k T} \right) \left( \frac{\alpha C_V^0}{D_V} - \frac{4\pi q^2 C_1^0}{\varepsilon \omega k T} \right). \end{aligned} \quad (9)$$

Finally, the size of the denuded zone is equal to  $L = 1/\lambda_{\text{min}}$ . For simplicity let us assume that the average concentrations of vacancies and interstitial atoms far from the grain boundary are equal ( $C_1^0 = C_V^0 = C_0 = \sqrt{G/\alpha}$ ), due to the electrical neutrality of matrix, i.e. the charge density of charged defects (voids, dislocations, dislocation loops), holes and electrons in the bulk  $\rho$  is

negligible. So in the case of the absence of external electric field ( $E = 0$ ), we have two different solutions of the Eq. (9) ( $D_1 \gg D_V$ )

$$L_q \approx \sqrt{\frac{\varepsilon \omega k T}{8\pi q^2}} \left( \frac{\mu D_1}{G} \right)^{1/4}, \quad L_T \approx \left( \frac{D_V^2}{\mu D_1 G} \right)^{1/4}, \quad (10)$$

where  $L_q$  depends on the charge of point defect and  $L_T$  is determined only by the temperature.

It should be remarked that  $L_q$  depends on the charge of point defect  $q$  and  $L_T$  is determined only by temperature. Moreover, both of these relations are extremely different from the expression for the denuded zone size in metals [10], where the denuded zone size is proportional

$$L \propto \left[ \frac{D_V}{\mu G} \right]^{1/4}. \quad (11)$$

The denuded zone size in metals is determined by applying the following relation  $D_1 C_1^0 = D_V C_V^0$  far from the grain boundary. In ceramic materials, the condition of electrical neutrality  $qC_V^0 - qC_1^0 + \rho = 0$  was used instead and this relationship is not taken into account in metals. So the temperature dependence of denuded zone size in ceramic materials should be expressed by Eq. (10). The real size of the denuded zone is the largest value in Eq. (10). There is a critical temperature  $T^*$ , when the size of the denuded zone changes its behavior ( $L_q = L_T$ ). This temperature is equal to

$$kT^* = \frac{\Delta E_m}{\ln\left(\frac{8\pi q^2}{\mu \varepsilon \omega k T^*}\right)} \sim \frac{\Delta E_m}{\ln\left(\frac{8\pi q^2}{\mu \varepsilon \omega \Delta E_m}\right)}, \quad (12)$$

$$\Delta E_m = E_{mV} - E_{mI},$$

where  $E_{mI}$  and  $E_{mV}$  are the migration energies of interstitial atoms and vacancies, respectively. The migration energies of point defects in MgO and  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> are presented in [1,13]. So, the migration energies of Mg and O vacancies are located in the range of  $E_{mV} = 2.0$ – $2.3$  and  $2.0$ – $2.5$  eV, respectively. The migration energies of Mg, O interstitials are located in the range of  $E_{mI} = 0.5$ – $1.5$  eV [1]. The migration energies of point defects in Al<sub>2</sub>O<sub>3</sub> are equal to  $E_{mV} = 1.8$ – $2.1$  eV for Al and O vacancies and  $E_{mI} = 0.2$ – $0.8$  eV for Al, O interstitials [1]. The temperature dependences of  $L_q$  and  $L_T$  are given in Figs. 1 and 2 using typical values for the different migration energies and some material parameters (see Table 1). It is obvious that due to a presence of charged point defects in ceramics the size of denuded zone will depend on an external electrical field (see Fig. 3). Indeed, in the case of a small external electrical field  $E$  and assuming that  $C_1^0 = C_V^0 = C_0 = \sqrt{G/\alpha}$ , the solutions of Eq. (9) are equal to:

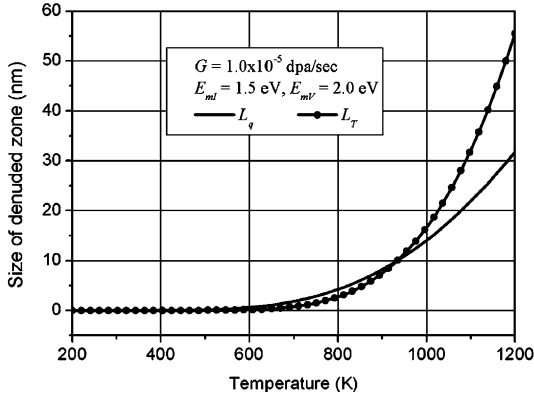


Fig. 1. The temperature dependence of denuded zone size without an applied electric field.

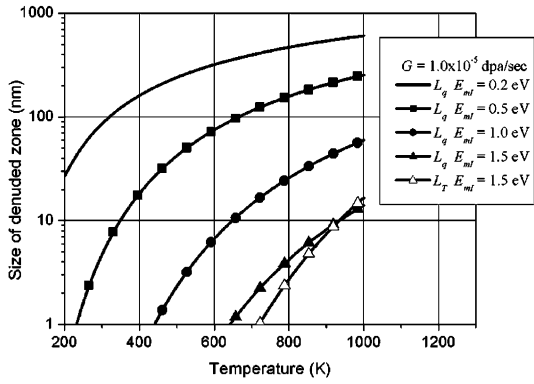


Fig. 2. The temperature dependence of denuded zone size on migration energy of interstitial atoms without an applied electric field. Migration energy of vacancies is assumed to be 2 eV.

$$L_1 \approx L_q \left[ 1 + \frac{\lambda_T^2 \gamma}{2\lambda_q (\lambda_q^2 - \lambda_T^2)} - \frac{\gamma^2}{2(\lambda_q^2 - \lambda_T^2)} + \frac{\lambda_T^4 (5\lambda_q^2 - \lambda_T^2) \gamma^2}{8\lambda_q^2 (\lambda_q^2 - \lambda_T^2)^3} \right], \quad (13a)$$

$$L_2 \approx L_T \left[ 1 + \frac{\lambda_T \gamma}{2(\lambda_T^2 - \lambda_q^2)} - \frac{\gamma^2}{2(\lambda_T^2 - \lambda_q^2)} + \frac{\lambda_T^2 (5\lambda_T^2 - \lambda_q^2) \gamma^2}{8(\lambda_T^2 - \lambda_q^2)^3} \right], \quad (13b)$$

$$L = \max \{L_1, L_2\}, \quad (13c)$$

Table 1

Main parameter values used for numerical calculations of size of denuded zone [1]

$G$	Point defect generation rate	$1.0 \times 10^{-5}$ dpa/s
$a$	Lattice parameter	$3.0 \times 10^{-8}$ cm
$\epsilon$	Dielectric permeability	1.0
$e$	Charge of electron	$4.8 \times 10^{-10}$ esu
$E_{mi}$	Migration energy of interstitial atoms	0.2–1.5 eV
$E_{mv}$	Migration energy of vacancies	2.0 eV

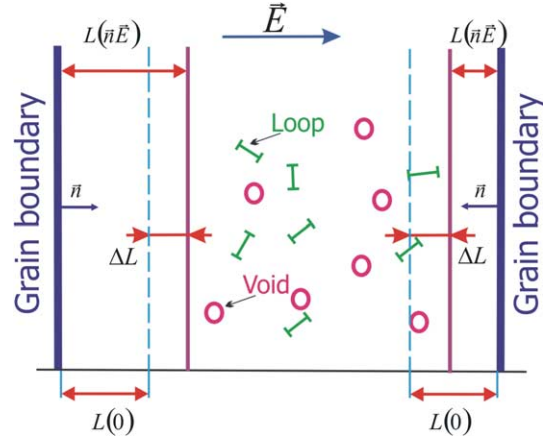


Fig. 3. A schematic showing of the effect of an applied electric field on the formation of denuded zone in irradiated ceramic materials. The electric field is applied perpendicular to the grain boundary plane.  $(L(\vec{n}\vec{E}) = L(0) + (\vec{n}\vec{e})\Delta L$ , where  $\vec{E} = \vec{e}E$ ,  $\vec{e}$  is the unit vector applied perpendicular to the grain boundary plane).

where  $\lambda_{q,T} = 1/L_{q,T}$  and  $\gamma = qE/\epsilon kT$ ,  $L$  is the size of the denuded zone. In the case of extremely different values of  $L_q$  and  $L_T$  in Eq. (10), the sizes of the denuded zones are equal to

$$L \approx L_q \left( 1 - \alpha E + \frac{1}{2} \alpha^2 E^2 \right), \quad L_q \gg L_T, \quad (14a)$$

$$L \approx L_T \left( 1 - \beta E + 2\alpha^2 E^2 \right), \quad L_T \gg L_q, \quad (14b)$$

$$\alpha = \frac{qL_q}{2\epsilon kT}, \quad \beta = \alpha \frac{L_q}{L_T}. \quad (14c)$$

The typical dependencies of the denuded zone on an external electrical field are shown in Fig. 4. Thus, in the case of a small-applied electric field the difference between denuded zone sizes with applied electric field  $L(E)$  and without it  $L(E = 0)$  has the following dependence on  $E$  and effective charge of point defect ( $q$ ) (see Figs. 5 and 6).

$$\Delta L(E) = -\frac{\omega}{16\pi q} \left( \frac{\mu D_1}{G} \right)^{1/2} E, \quad (15)$$

where  $\Delta L(E) = L(E) - L(E = 0)$ .

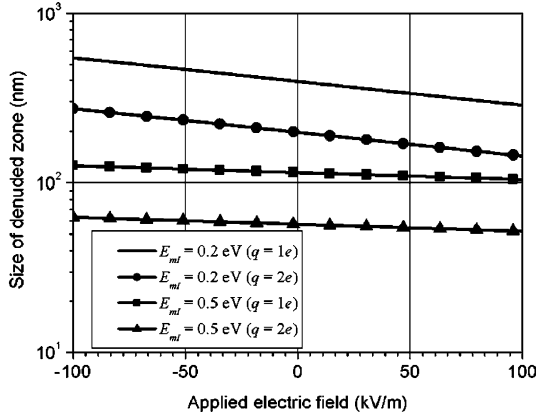


Fig. 4. The dependence of denuded zone size on the applied electric field for different point defect charge state and migration energies of interstitials. The vacancy migration energy and irradiation temperature are assumed to be 2 eV and 700 K respectively.

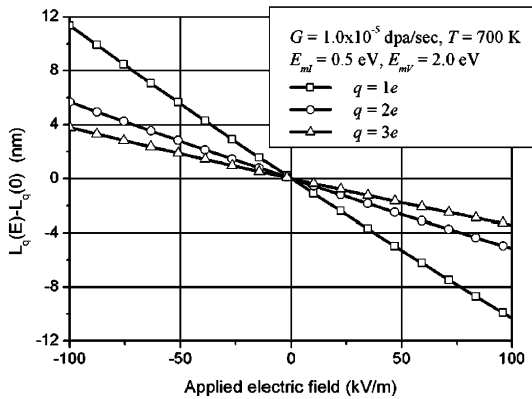


Fig. 5. The dependence of  $\Delta L_q(E)$  on the applied electric field for different point defect charge states.

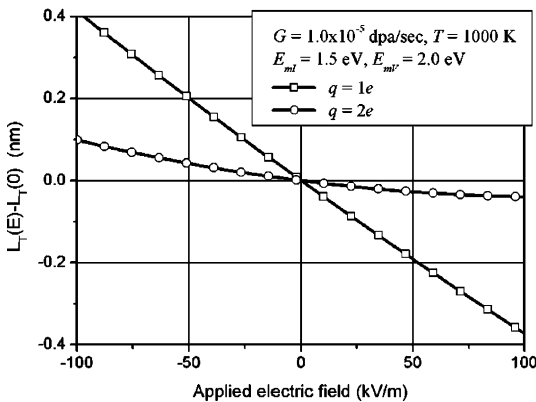


Fig. 6. The dependence of  $\Delta L_T(E)$  on the applied electric field for different point defect charge states.

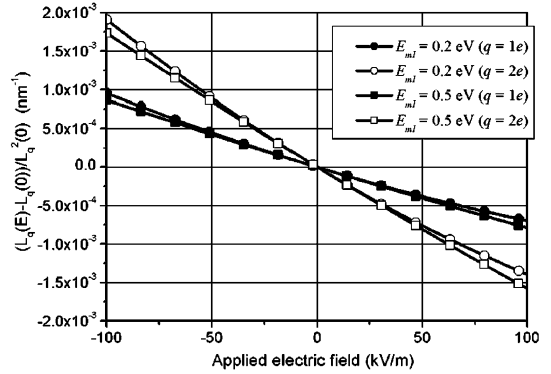


Fig. 7. The dependence of  $\Delta L_q(E)/L_q^2(E)$  on an applied electric field for the different point defect charge states and migration energies of interstitials. The vacancy migration energy and irradiation temperature are assumed to be 2 eV and 700 K, respectively.

Note that relation (15) is valid in both regimes  $L_q \gg L_T$  and  $L_q \ll L_T$ . We can see from Figs. 5 and 6 that depending on the direction of the electric field; the denuded zone size from one side of a grain boundary can increase or decrease. So, by applying an external electric field and measuring the difference  $\Delta L(E)$  of the denuded zone size from two sides of grain boundary at different temperatures as a function of electric field, we can experimentally obtain the value of point defect charge states and to find migration energy of interstitial atoms. Note also that the expression  $\Delta L(E)/L_q^2 \approx -qE/2\epsilon kT$  weakly depends on the migration energies of point defects, but it explicitly depends on the charge of point defects (see Fig. 7). So using this expression we can experimentally obtain a point defect charge state even in the case when the exact values of point defect migration energies are unknown.

### 3. Conclusions

- (1) A new theoretical model for the explanation of denuded zone formation in irradiated ceramic materials under the effect of an external and internal electric fields, taking into account the charged states for point defects has been suggested.
- (2) It was shown that the size of the denuded zone under an applied external electric field is determined by the effective charge of point defects, the direction and strength of the external electric field and the point defect diffusivity. The direction of applied electric field can increase or decrease the denuded zone size depending on the sign of point defect charge.
- (3) Theoretical results obtained for denuded zone formation under an applied electric field at different temperatures and generation rates for point defects can be used for the experimental investigation of

point defect charge and migration energy of charged point defects in irradiated ceramic materials.

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