ANOMALOUS KINETICS OF DIFFUSION-CONTROLLED DEFECT RECOMBINATION IN IRRADIATED OXIDE CRYSTALS

Abstract: The annealing kinetics of the primary electronic F-type centers (oxygen vacancies with trapped electrons) is analysed for three ionic materials (α-Al₂O₃, MgO and MgF₂) exposed to intensive particle irradiation by electrons, neutrons, and heavy swift ions. Phenomenological theory of diffusion-controlled recombination of the F-type centers with much more mobile interstitial ions (complementary hole centers) allows us to extract the migration energy of interstitials and pre-exponential factor of diffusion. It is demonstrated that with the increase of radiation fluence the migration energy decreases, and pre-exponent factor exponentially decreases for all three materials, irrespective of the type of irradiation. These two parameters satisfy the Meyer-Neldel rule [1] observed earlier in many areas of materials science in physics, chemistry and biology [2], which indicates for peculiarities of defect migration in ionic materials locally disordered by radiation (e.g. along incident ion tracks). This study demonstrates that in the quantitative analysis of the radiation damage of materials, the dependence of the defect migration parameters on the radiation fluence plays an important role and cannot be neglected.

Keywords: kinetic, diffusion - controlled defect recombination, α-Al₂O₃, MgO and MgF₂, Meyer - Neldel rule

Introduction. α-Al₂O₃ (sapphire, corundum) is a promising material for fusion reactors, mainly for diagnostics as a general insulator or optical components. Another two important radiation-resistant ionic materials are MgO and MgF₂. It is very important to predict/simulate the kinetics of defect accumulation in sapphire under neutron irradiation as well as long-time defect structure evolution. As is well known, the F center mobility is much smaller than that of the complementary Frenkel defects - interstitial oxygen ions. Thus, at moderate radiation doses and temperatures, the kinetics of the F-type center annealing is controlled by their diffusion-controlled recombination with mobile oxygen interstitials.

Despite numerous experimental data on defect kinetics, very few theoretical efforts were devoted so far to the quantitative analysis of available data, in order to extract main kinetic parameters-interstitial migration energy $E_a$ and diffusion pre-exponent $D_0$, necessary for further prediction of the secondary defect kinetics and radiation stability of sapphire and related materials.

Recently, we developed simple phenomenological theory of diffusion-controlled defect recombination and applied it to irradiated insulators [3,4]. As it was shown therein, the kinetics of bimolecular recombination of the primary radiation defects - F type centers and interstitial ions is controlled by the two parameters: the activation energy $E_a$ for migration (diffusion) of more mobile component (interstitial) and the pre-exponential factor $X = N_0 \cdot R \cdot D_0 / \beta$, where $N_0$ is initial defect concentration, $R$ recombination radius, $D_0$ diffusion pre-exponent, and $\beta$ heating rate. Assuming standard parameters $N_0 = 10^{17} \text{cm}^{-3}$, $R = 10 / \mu\text{A}$, $D_0 = 10^{-3} \text{cm}^2 \text{s}^{-1}$, $\beta = 10 \text{K/min}$, one gets the estimate $X = \log_{10}^8 \text{K}^{-1}$ for normal diffusion. Our analysis has demonstrated that the diffusion energy of oxygen interstitials varied considerably from one experiment to another, very likely
due to difference radiation doses. This means in particular, that the diffusion energy is not unique parameter characterizing radiation defect kinetics.

**Results and discussion.**

The F-type center annealing analysis To ledgther to the problem, we analyse first the F-type center annealing kinetics for $\alpha$-$\text{Al}_2\text{O}_3$, MgO and MgF$_2$ irradiated by electrons, neutrons, and heavy ions with very different fluences, which are available from literature. All three materials have quite different crystalline structure and chemical bonding: MgO is cubic and ionic, MgF$_2$ has rutile structure and ionic, sapphire ($\alpha$-$\text{Al}_2\text{O}_3$) has hexagonal structure and partly covalent. As is known, three types of radiation create point defects with very different spatial distribution: almost homogeneous under electrons, strongly correlated along neutron trajectory and in heavy ion tracks. We will demonstrate that diffusion coefficients of point defects in all these materials and likely, in many other heavily irradiated ionic solids could no longer be described by a simple relation: $D=D_0 \exp(-E_a/kT)$, $D_0$ is constant, but under heavy irradiation it looks more as migration in liquids with high mobility and low migration barriers.

![Figure 1](image.png)

**Figure 1** – The kinetics of the F or F$^+$ center annealing in $\alpha$-$\text{Al}_2\text{O}_3$ (neutron irradiation)

Table 1 The explanation of curves 1-5 in Fig.3 and the obtained migration energy of interstitial ions $E_a$ and pre-exponential factor $X$ under different types of radiation and different doses

<table>
<thead>
<tr>
<th>Nr.</th>
<th>Irradiation conditions</th>
<th>$E_a$ (eV)</th>
<th>$X$ (K$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>electron irradiation, dose 1x10$^{16}$ electrons/cm$^2$ [5]</td>
<td>1.60</td>
<td>1.0x10$^8$</td>
</tr>
<tr>
<td>2</td>
<td>electron irradiation dose 1x10$^{17}$ electrons/cm$^2$ [5]</td>
<td>0.80</td>
<td>8.4x10$^4$</td>
</tr>
<tr>
<td>3</td>
<td>electron irradiation dose 2x10$^{17}$ electrons/cm$^2$ [5]</td>
<td>0.35</td>
<td>3.5x10$^4$</td>
</tr>
<tr>
<td>4</td>
<td>neutronirradiation, 15 min [5]</td>
<td>1.24</td>
<td>9.8x10$^6$</td>
</tr>
<tr>
<td>5</td>
<td>neutronirradiation, 10 h [5]</td>
<td>0.56</td>
<td>1.8x10$^2$</td>
</tr>
</tbody>
</table>

**Correlation of the diffusion energy and pre-factor** The pre-exponent $X$ is much smaller than the estimate for a regular diffusion in crystalline solids (see Table). Moreover, we have observed a strong correlation between the activation energy $E_a$ and pre-exponent $X(E_a)$ which is no longer constant but fits very well to the exponential function of $E_a$.
Effect of Xenon Ion Irradiation on the Raman Spectra of BaFBr Crystals

Figure 2 – The kinetics of the F centers annealing in MgO for different types of radiation

Figure 3 – The kinetics of the F centers annealing in MgF₂ for different types of radiation (see Table for details)

In fact, as radiation dose increases, both the migration energy \( E_a \) and pre-exponent \( X \) decrease, as the result defect diffusion rate effectively grows. Moreover, we observed this correlation for several irradiated ionic materials - Al₂O₃, MgO and MgF₂ which indicates that this could be quite common phenomenon.

The presented results could be understood as a growing topological disordering of materials under irradiation with a continuous transition from a perfect crystalline structure to the amorphous-like one [6]. This could explain drastic reduction of the activation energy for diffusion. As is well observed [7,8], in liquids the main migration mechanism is not thermally activated overcome of the energy barrier between two lattice positions, but particle (molecule) penetration into nearest cavity due to density fluctuation when nearest molecules are collectively move apart opening the path for a random walk with a low activation energy. The characteristic feature of liquids and amorphous solids is a strong temperature dependence of the pre-exponential factor which is no longer a constant.
The Meyer-Neldel rule

The above observed correlation of the migration energy $E_a$ and pre-factor $X$ (Fig.4) fits quite well to the relation known as the Meyer-Neldel rule [1,2]:

$$\ln(X) = \ln(X_0) + \frac{E_a}{k_B T_0},$$

where $X_0$ is a constant and $T_0$ some characteristic temperature. Eq. (1) shows how reduction of the activation energy with growing disorder is compensated by orders of magnitude decrease of the pre-factor $X$. Fig. 4 demonstrates that this relation indeed is well satisfied for all three materials,
and the more so, for different types of irradiations (and initial defect spatial distributions). Note that all experimental points lie below the characteristic temperature $T_0$.

Eq. (1) could be also interpreted as the diffusion coefficient with exponentially dependent pre-exponent

$$D \sim \exp\left(\frac{E_a}{k_B T_0} - \frac{E_a}{k_B T}\right), \quad T < T_0,$$

(2)

Fig. 5 shows how the effective diffusion coefficient depends on the activation energy $E_a$: the smaller energy, the larger diffusion coefficient and defect mobility, which shifts the recombination region to lower temperature side (see Figs. 1-3).

Note that this effect [1] is well known in chemistry, biology, even semi-conductor physics [2,9]. The foundations of this empirical rule are still not fully understood. One of possible phenomenological models (Dyre1986) [10] claims that eq. (1) holds in disordered systems with exponential probability distribution of energy barriers of localized quasi-particles, and parameter $T_0$ could have the meaning of glass transition. The relation (1) was observed also in multicomponent systems (metallurgical slags [11]) containing tens of oxides, and in glasses under irradiation [9,12]. Recently, by applying high pressure or changing the Ce content in Y-doped BaMO$_3$, it has been shown that the proton conductivity in these materials follows the Meyer - Neldel rule well [13]. It has also recently been established in detail that the nature of the conduction spectra in oxide and chalcogenide systems is different, which should indicate different mechanisms of conduction through polaron hopping [14]. This has been well studied using the Meyer - Neldel rule, which provides microscopic information about the behavior of conduction in various systems [14]. In particular, using the example of New chalcogenide glassy system, $x$Ag$_2$S - (1 - $x$) (0.5Se - 0.5Ge), it was found that DC conductivity shows a thermally activated nature, while AC conductivity via the Meyer-Neldel demonstrates the correlated nature of hopping conduction across the barrier [15]. In [16], as a first step, the authors relate the so-called Meyer-Neldel behavior in ionic conductors to phonon occupations. On the other hand, in [17], the nested Bi$_2$S$_3$ nano-networks with different morphologies were synthesized using topotactic transformation and used using the Meyer-Neldel relation to reveal the nature of its trap distribution (type and width). The fact that the temperature dependence of ac conductivity obeys the Meyer - Neldel rule was shown using the example of borate glasses doped BaTiO$_3$ for energy storage devices [18]. Finally, it turns out that the entropy of a material is critical for ionic conductivity [19].
It was also noted that the search for anti-Meyer-Neldel rule materials with a highly distorted structure would have great potential [19]. Recently, much research has focused on the extraordinary characteristics of ionic conductors with the deepgoing comprehending about the reasons for Meyer-Neldel rule lacked [19]. This is important for the research and development of new materials for potential solid electrolytes.

**Conclusion.** It is demonstrated for the first time that in strongly irradiated ionic solids of different crystalline structure and chemical nature, the pre-exponential factor of diffusion is strongly related to the migration energy. In other words, the defect recombination kinetics is not characterized uniquely by the activation energy for diffusion with a constant pre-exponent but instead these parameters depend on the radiation fluence which considerably complicates analysis of the radiation-induced kinetic processes.

**Acknowledgements.** This work was performed under the grant project AP08855879 "First-principles design of effective magnetostriction materials for practical applications" for 2020-2022 by the Ministry of Education and Science of the Republic of Kazakhstan.

**References**

Effect of Xenon Ion Irradiation on the Raman Spectra of BaFBr Crystals

Abstract. F-type (carbonated electrons present vacancy defects) begins to be converted into a lattice with electrons, neutrons, and heavy fast ions, leading to the activation of self-organized systems [1, 2]. Meyer-Neldele rule is applied [1], but the activation of defects in the material is determined by the migration of defects, which are presented by the so-called ion diffusion. In this study, the migration of defects in the material under radiation is studied, where the parameters of the migration are determined by the fluence of radiation and the absence of migration that is determined by the migration behavior of defects. (Examples, carbonated ions of the another). This study under radiation the radiation of a material under radiation is determined by the migration of defects, which is determined by the migration behavior of defects. Information about the authors: Kotomin E.A. - Doctor of Physical and Mathematical Sciences, Academician of the National Academy of Sciences of Latvia, Leading Researcher Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia. Kuzovkov V.N. - Doctor of Physical and Mathematical Sciences, Head of the Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia. Popov A.I. - Corresponding author, Doctor of Physical and Mathematical Sciences, Leading Researcher Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia. Kotomin E.A. - Doctor of Physical and Mathematical Sciences, Academician of the National Academy of Sciences of Latvia, Leading Researcher Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia. Kuzovkov V.N. - Doctor of Physical and Mathematical Sciences, Head of the Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia. Popov A.I. - Corresponding author, Doctor of Physical and Mathematical Sciences, Leading Researcher Laboratory of Kinetics in Self-Organizing Systems of the Institute of Solid State Physics of the University of Latvia.