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THE ORIGIN OF RADIATION RESISTANCE OF OXIDES WITH CATIONIC DISORDER

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Досліджені природа, кінетикі створення та розпаду центрів поглинання в кристалах магній алюмінієвої шпінелі. Кінетика накопичення смуг поглинання, наведених рентгенівським опроміненням, узгоджується з механізмом заповнення пасток вільними носіями зарядів через зону провідності та може бути описана моделлю, що враховує ефект кулонівського блокування на просторово корельованих дефектах. Двохстадійний розпад смуг поглинання після припинення рентгенівського опромінення пояснюється електронно-дірковою рекомбінацією між центрами, які знаходяться на різних відстанях та/або мають різну величину потенційних бар'єрів. УФ-опромінення підтверджує існування комплексних дефектів, які містять позитивні та негативні центри, та можуть слугувати центрами ефективної анігіляції радіаційно створених Френкелівських пар.

Исследовались природа, кинетики образования и распада центров поглощения в кристаллах магний алюминиевой шпинели. Кинетика накопления полос поглощения, наведенных рентгеновским облучением, согласуется с механизмом заполнения ловушек свободными носителями зарядов через зону проводимости и может быть описана моделью, которая включает эффект кулоновской блокировки на пространственно коррелированных дефектах. Двухстадийный распад полос поглощения после прекращения рентгеновского облучения объясняется электронно-дырочной рекомбинацией между центрами, находящимися на различных расстояниях и/или с различной величиной потенциальных барьеров. УФ-облучение подтверждает существование комплексных дефектов, которые включают положительные и отрицательные центры, и могут служить центрами эффективной аннигиляции радиационно созданных Френкелевских пар.

The nature, kinetics of formation and decay of absorption centers in magnesium aluminate spinel crystals were investigated. Kinetics of accumulation of the X-ray irradiation induced absorption bands consistent with mechanism of trap filling with free charge carriers through conduction band, and could be described by model that include Coulomb blocking effect on spatially correlated defects. Two-stage decay of absorption bands after termination of X-ray irradiation is explained by electron hole recombination between centers of two different distances and/or different value of potential barriers. UV-irradiation confirm existence of complex defects which include positive and negative centers and could serve as effective annihilation center for radiation created Frenkel pairs.

INTRODUCTION

Magnesium aluminate spinel $MgAl_2O_4$ ($MgO{\cdot}nAl_2O_3$) has been proposed as a potential optical and insulation material for use in nuclear fusion reactors, since it possesses excellent radiation resistance properties. The high tolerance of spinel can have several origins such as the high concentration of structural vacancies in spinel, difficulties in forming clusters of point defects, or high degrees of cationic disorder [1]. Therefore, the nature and initial state of defects in spinel crystals can play an important role in the behavior of this material under irradiation.

The unit cell of $MgAl_2O_4$ spinel consists of a face-centered cubic lattice of 32 oxygen ions and 64 tetrahedral and 32 octahedral interstices between these anions. In normal spinel crystals, Mg^{2+} ions occupy ⅛ of the tetrahedral interstices, while Al^{3+} ions occupy ½ of the octahedral positions. It is known that spinel crystals grown under laboratory conditions are partially inverse, i.e. up to 0.3 Al^{3+} ions per unit cell occupy tetrahedral sites and equal part of Mg^{2+} are placed in octahedral positions, producing so-called antisite defects $(Al^{3+}_{Mg})^{+}$ and $(Mg^{2+}_{Al})^{-}$ with excess of positive and negative charge, respectively. Non-stoichiometric spinel crystals of n>1.0 contain also additional cationic vacancies due to charge compensation of Al^{3+} in tetrahedral positions. Thermodynamically non-equilibrium process of crystal growth leads also to lattice defects in both cationic and anionic sub-lattices. Synthetic crystals also unavoidably contain impurity ions of different charges and sizes, such as Fe, Mn, Cr; these species replace constituent ions in different ways and lead to the formation of lattice defects.

It is known, that impurity ions of different valence to compare with substituting ions create charged defects, and because the potential of such defect is long-range Coulombic one, it may influence on the behavior of defects in the vicinity of this impurity ion. Also if impurity ion isovalent to substituting ions, but different size it also creates distortion in regular crystal lattice. On different estimation methods it is not short-range also. The range of elastic deformation, in the vicinity of impurity ions or lattice defects could be tenths of Angstroms. So, during growth process when temperature is high and mobility of different species also high, we can expect the coagulation of some defects forming complexes of spatially correlated point defects. Particularly, we can expect the formation of interacting pairs impurity ion – vacancy, or pairs of antisite defects. The interaction of defects situated on some distances each other (and also optical centers) will lead to peculiarities in processes of optical center

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formation under irradiation, and their stability in dependence on time after termination of irradiation and annealing temperature. In this work we describe the results of investigations of the nature of defects and their spatial distribution in spinel crystals from studies of time dependencies of optical absorption in stoichiometric (n=1.0) and nonstoichiometric (n=2.5) spinel crystals during and after prolonged X-ray or UV-irradiation, that allow us to reveal the existence of spatially correlated defect pairs, which could serve as centers of annihilation of radiation created Frenkel pairs.

EXPERIMENTAL DETAILS

Single crystals of stoichiometric magnesium aluminate spinel ($MgO{\cdot}nAl_2O_3$) of stoichiometric (n=1.0) and nonstoichiometric (n=2.5) compositions were grown by the Verneuil method using the same starting materials. Samples with dimensions of 12x10 mm^2 and 0.7 mm thickness were cut from single crystals and polished on both sides to an optical finish. Optical absorption was measured in the range of 1.2-6.4 eV using either a single or dual beam spectrophotometer. Irradiations were performed using a Cu X-ray tube operating at 40 kV and 10 mA. For ultraviolet (UV) irradiation there were used either mercury 600 W lamp or deuterium 400 W lamp, both with quartz tubes. During irradiation sample were cooled with powerful fan to keep its temperature below 30ºC. Accumulation experiment was provided with the same samples annealed after each irradiation at 650ºC during 0.5 hour.

NATURE OF DEFECTS AND OPTICAL CENTER

In as grown spinel crystals there exists a variety of defects, which can create the optical centers capturing charge carriers created by ionizing irradiation. Anionic vacancies capture free electrons leading to formation of F^+- (one electron) and F-center (two electrons). Both tetrahedral and octahedral cationic vacancies could capture one or several holes creating V-type centers. The spectra of radiation induced optical absorption of stoichiometric spinel are shown in Fig.1. From previous investigations it is known [2,3], that transitions in V-type centers lead to formation of wide absorption band with maximum at photon energy of 3.1 eV. Absorption bands of F-type centers are at 4.75 and 5.3 eV for F^+- and F-center, respectively. Decomposition of experimental spectra with Gaussian curves taking into consideration of position of well defined bands gives additional bands at the 3.87 and 4.15 eV [4]. These bands were tentatively identified with optical centers on antisite defects. Al^{3+} in tetrahedral site creates excess of positive charge and can capture free electron forming optically active center $[Al^{3+}_{tet}]^+ + e^- \rightarrow [Al^{3+}_{tet}]^0$, which has absorption band at 4.15 eV, Mg^{2+} in octahedral site creates defect with uncompensated negative charge and could capture hole, also forming optically active center $[Mg^{2+}_{oct}]^- + h^+ \rightarrow [Mg^{2+}_{oct}]^0$, which has absorption band at 3.78 eV. Because of low affinity of electron in $[Al^{3+}_{tet}]^0$–center

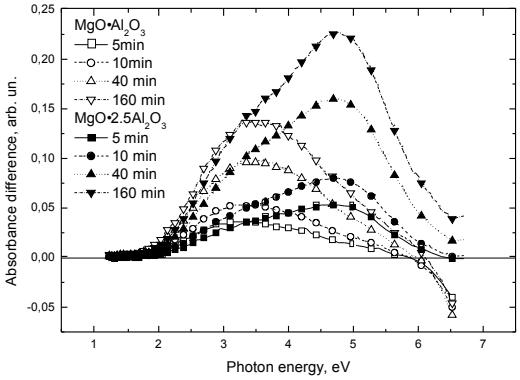

Fig.1 Radiation induced optical absorption in magnesium aluminate spinel.

it is unstable even at room temperature, causing slow decay of absorbance in time. Annealing of neutron irradiated crystals first of all leads to destruction of band at 3.87 and 4.25 eV. It should be noticed that neutron irradiation was provided at 80°C, thus hole centers with absorption band at 3.1 eV were annealed during irradiation [5]. Comparison of absorption annealed at different temperatures for stoichiometric and non-stoichiometric spinel crystals allow us to find optical absorption bands related to corresponding centers in $MgO{\cdot}2.5Al_2O_3$ spinel crystals. The main absorption bands are at 5.02 eV (F^+-center), 5.7 eV (F-center), 3.66 eV ($[Mg^{2+}_{oct}]^0$-center) and 4.5 eV ($[Al^{3+}_{tet}]^0$-center). According to Mollvo-Ivey relation such shift of electron band to higher energy is caused by decrease of lattice constant in spinel from 8.084 Å to 7.989 Å for stoichiometric and non-stoichiometric spinel.

ACCUMULATION OF OPTICAL ABSORPTION CENTERS

The accumulation of optical absorption centers was studied by consequently measurements of additively irradiated to different time. Growth curves of different absorption bands in spinel crystals during the prolonged irradiation with X-rays is shown in Fig. 2.

Evidently dependencies of different bands on the irradiation time with X-ray are different. To understand the type of kinetics leading to growth of absorption centers we replotted this graphs in semilog scale and found these dependences close to straight lines (Fig. 3).

Let us consider processes that take place in insulators under X-ray irradiation. High energy of X-ray photons leads to generation of free electrons in conduction band, which could be trapped by defects as an independent random process. The trapping rate could be described by a simple first – order reaction rate:

$$\frac{dn}{dt} = (n_0 - n)\,\sigma\, Q \qquad (1)$$

where n_0 - is the initial concentration of traps, n- the number of filled traps, σ- is the capture cross-section of traps, Q- is the flux density of generated electrons.

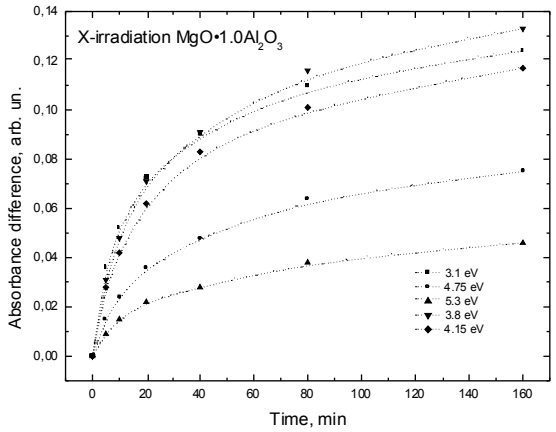

Fig. 2 Optical absorption difference curves in stoichiometric spinel crystals for various absorption bands (indicated by photon energy) as a function of X-ray irradiation time

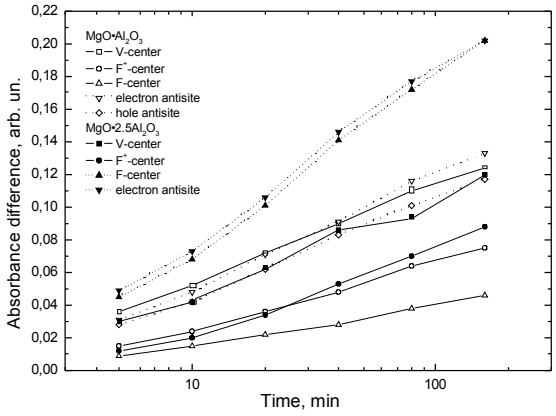

Fig.3 Accumulation of optical absorption bands under X-ray irradiation in spinel crystals

Because of rate of generation of free electrons does not depend on time, the total fluence of charge carriers after time t through unit area will be equal Qt.

Solving Eq. (1) yields the well known first order relaxation expression:

$$n = n_0\left[1 - \exp\left(-\sigma\, Qt\right)\right] \tag{2}$$

If we suppose the existence of spatially correlated defects, the trapping of charge carriers is less probable on locations close to filled traps because of Coulombic repulsion. The capture probability decreases when the space –charge density increases. A simple derivation of this decreasing capture probability can be given when it is assumed, that every filled trap inactivates a fixed volume h of dielectric for further trapping [6]. The volume in which trapping can occur is then V-h, where V is the total volume of dielectric. When n charges are trapped the probability will decrease by a factor $\left(1-\frac{h}{V}\right)^n$. Because of $h/V << 1$ approximation is given $\left(1-\frac{h}{V}\right)^n \approx \exp\left(-n\frac{h}{V}\right)$. The trapping rate could be written by

$$\frac{dn}{dt} = \left(n - n_0\right) Q\sigma\, \exp\left(-n\frac{h}{V}\right) \tag{3}$$

In real situation a large fraction of available traps n_0 is inactivated by a relative small number n, hence $n << n_0$. Solving equation in this approximation we have:

$$n = \frac{V}{h}\ln\left[n_0\left(\frac{h}{V}\right)Q\sigma\, t + 1\right] \tag{4}$$

By using new denotes $k=V/h$, and $p=n_0Q\sigma$, we obtain

$$n = k\ln\left(\frac{p}{k}t + 1\right). \tag{5}$$

This leads to logarithmic dependence of optical center accumulation on irradiation time in accordance with experimental data (Fig. 3).

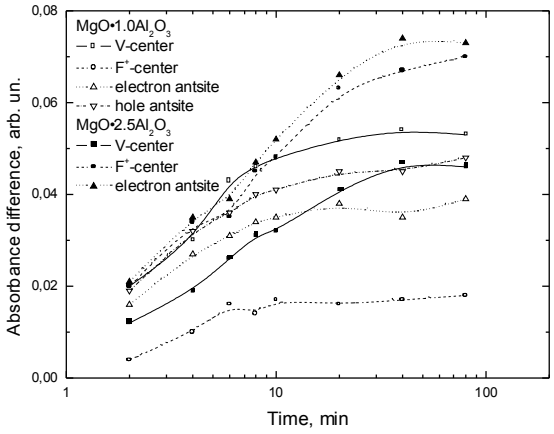

Fig.4. Optical absorption difference curves in spinel crystals for various centers as a function of UV irradiation time

Accumulation of absorption centers under UV-irradiation presented in the same scale is very different of that under X-ray irradiation (Fig. 4).

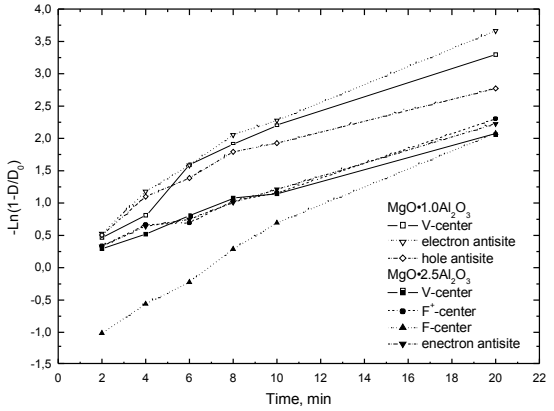

Fig. 5. –Ln(1-D/D0) as a function of UV irradiation time curves in spinel crystals for various centers

Because the UV-photon energy is less than gap in spinel crystals ($h\nu$=6.8 eV to compare with E_g=8.8 eV),

the generation of free charge carriers and formation of optical absorption centers through conduction bands is Very unlikely. According to results of X-ray irradiation experiments there exist spatially correlated nearby situated defects, so charge exchange under UV-

irradiation could take place directly from one defect to another, or from impurity ions to defect and vise versa. Such process could be described by the first-order reaction (1). Indeed, replotting of time dependences of absorption center accumulation under UV-irradiation in appropriate related to Eq. 1 coordinates $-\ln(1-D/D_0)$ show one-stage process, that support existence of close localized complementary defects (Fig. 5).

Decay of absorption centers as a function of time

Decay of optical absorption bands after termination of X-ray irradiation follows the power low show two stages process with different characteristic times: short stage- (6—10) min) and long one- (50—80 min) (Fig. 6).

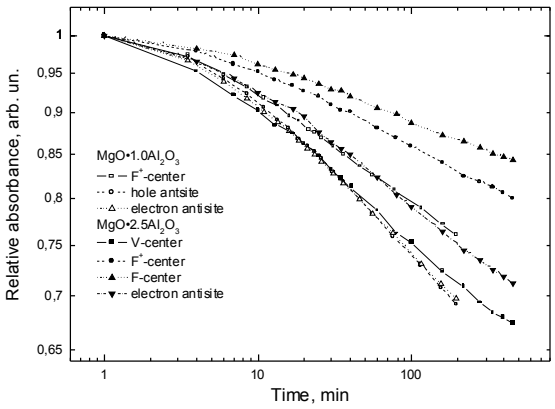

Fig.6. Decay of optical absorption centers after X-ray irradiation in spinels of different composition at room temperature

X-ray irradiation primary creates free charge carriers that could be captured by different traps to form optically active centers. Some of them, the opposite sign of charge carriers, interacting with each other have possibility to annihilate with different probabilities in dependence on separate distance. Two definite characteristic times indicate the existence of two kinds

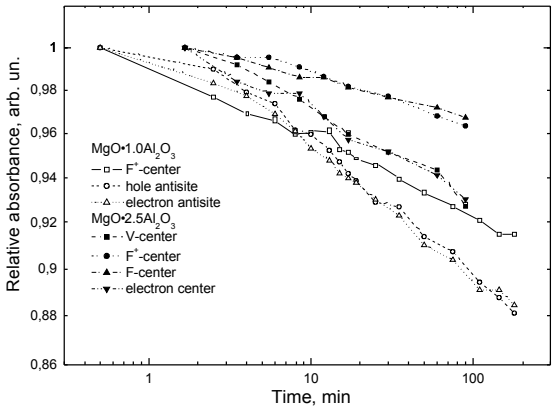

Fig.7. Decay of optical absorption centers after UV-irradiation in spinels of different composition at room temperature

of spatially correlated defects. Because of the possible process under UV-irradiation is charge exchange between defects only through intra-band transitions, which could happen for the nearby-situated defects, the reverse process (recombination) between the nearest centers goes through only one stage (Fig. 7).

The high concentration of antisite defects (about 0.2 per unit cell) could be one of the reasons for formation of complex defects. Because of lattice defects and impurity ions are centers of local distortion of crystal field with long-range elastic deformation, the interaction between defects and impurity ions, or between defects themselves, will lead to heterogeneous distribution and formation of complexes. Such complex defects are bipolar in nature [7] and could serve as centers of attraction of both counterparts of Frankel pairs leading to annihilation of radiation created defects. The existence of additional to displacive also ionizing irradiation [8] leads to formation of dipoles of optical centers, because of charge compensation of dipoles of defects, and consequently to retardation of radiation defect creation.

CONCLUSION

During these investigations it was shown that in as grown crystals there are high concentration of complex defects, which include both as point defect with positive charge excess also negative charge excess. One of the most important such complexes could be the spatially correlated antisite defects, concentration of which reaches as much as 0,2 per unit cell. Such complex defect creates the local lattice distortion (perturbation) in crystal lattice, which serve as a center of attraction of defects created by irradiation. Because the complex defects are bipolar in nature both interstitials and vacancies will be attracted by the same complex leading to annihilation of Frenkel pairs that prevents the formation of stable point defects including clusters for loop formation. So, the main reason of radiation resistance of spinel is the existence of spatially correlated defects of opposite charge at the background of high concentration of the intrinsic defects, which assist the high mobility of radiation induced defects to centers of annihilation.

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