Peculiarities of Long-Lived Defect Creation under Radiation of Metal Fluorides and Oxides by Photons, Electrons and Ions [1]

A. Lushchik, S. Dolgov, T. Kärner, Ch. Lushchik, K. Schwartz,* E. Vasil'chenko,

Institute of Physics, University of Tartu, 142 Riia Str., Tartu, 51014, Estonia,
Phone +372-7383026, Fax +372-7383033, E-mail: luch@fi.tartu.ee
** Gesellschafte fьr Schwerionforschung (GSI), Planckstr. 1, Darmstadt,D-64291, Germany*

Abstract – Peculiarities of the emission and absorption spectra and the processes of Frenkel defect creation have been investigated in LiF, SiO_2 and MgO crystals under irradiation by swift ^{238}U ions that form extremely high density of electronic excitations in the ion tracks. The manifestations of the nonimpact mechanisms, connected with the decay of anion and cation excitons in LiF or hot electron-hole recombination in SiO_2 with split valence band, have been analyzed. The energy released at the recombination of relaxed carriers is insufficient for the creation of Frenkel pairs in MgO, while the manifestations of oxygen interstitials O_i^0 have been detected in the samples irradiated by fast neutrons or ^{238}U ions. After the dissociation of H centres ($O_2^-v_c$) at 650–720 K a part of O_i^0 recombine with F^+ centres. The prospects of the suppression of hot electron-hole recombination by doping the materials with the luminescent impurities are considered.

1. Introduction

Insufficient radiation resistance of construction materials (metals, dielectrics, superconductors etc.) is the Achilles heel for thermonuclear energetics. In wide-gap dielectrics (E_g > 6 eV) Frenkel pairs (FPs) are created not only due to the knock-out (impact) mechanism but also at the decay of the electronic excitations (EEs) or at the recombination of electrons (e) and holes (h) formed during the irradiation [1,2]. It is commonly accepted that in MgO, SiO_2, Al_2O_3, $MgAl_2O_4$ etc. crystals the energy released at the recombination of totally relaxed (cold) carriers is lower that the formation energy of an FP, $E_{FP} > E_{eh} = E_g$. However, the situation is quite different in case of material irradiation by swift heavy ions (SHIs), when the density of the formed EEs is high because of high values of mean energy loss, dE/dx = 10–20 keV/nm [3]. For instance, the probability of hot e-h recombination with the energy release of $E > E_{FP}$ increases and other mechanisms of FP creation are possible [4]. The study of the peculiarities of the creation processes of long-lived (stable) defects has been carried out in the LiF [5], MgO [1,6,7] and SiO_2 crystals [1,8].

We have continued the investigation of these processes in LiF, MgO and SiO_2 crystals, pure and doped with various luminescent impurity ions, under irradiation by synchrotron radiation of 6–35 eV(MAX-lab in Lund and SUPERLUMI station at HASYLAB, Hamburg), x-rays (~50 keV), electrons (2–30 keV, ~300 keV) or SHIs (^{238}U). The radiation-induced defects were investigated by UV and VUV spectroscopy methods at 8 and 300 K and using the thermoactivation spectroscopy methods at 6–775 K.

We have compared the processes of FP creation in LiF crystals with self-trapping excitons and holes and $E_{FP} < E_g$ (see also [5]) and in MgO crystals, where excitons, electrons and holes are highly mobile and $E_{FP} > E_g$. In addition to thoroughly studied knock-out mechanisms of defect creation, the creation of FPs at the recombination of hot conduction electrons and valence holes takes place in MgO crystals [4].

One of our strategic goals is to elucidate the contribution of hot e-h recombination to the creation of radiation defects in LiF, MgO and SiO_2 wide-gap dielectrics widely used in technical applications. We also analyze the prospects of the suppression of hot e-h recombination and the increasing of the radiation resistance of dielectrics by the doping of these materials with various luminescent impurity ions. Before recombination hot electrons and holes transfer a part of their kinetic energy to the impurity centres causing the excitation of impurity luminescence [4,9].

It appears reasonable that the contribution of hot e-h recombination in the radiation damage increases under conditions of high density of EEs formed during irradiation by α particles and especially SHIs, with respect to the case of an irradiation by electrons or x-rays. In this connection a particular emphasis is given to the investigation of radiation effects in the tracks of SHIs. LiF and metal oxides were preliminarily irradiated by ^{238}U (2.25 GeV) ions at 300 K using linear accelerator UNILAC of the GSI, Darmstadt. The irradiation by α particles (5 MeV) or electrons was performed in Tartu. Integral (1.7–4.0 eV) thermally stimulated luminescence (TSL) at 300–775 K was measured at the heating of the samples with a constant rate of $\beta = 2.86\ K\ s^{-1}$, using a System 310 TLD reader.

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The EPR spectra were measured with an X-band ESR 231 spectrometer and a continuous-flow helium cryostat (Oxford Inst. ESR900).

2. Radiation effects in the ion tracks of LiF

Several radiation effects in the tracks of SHIs have been thoroughly studied by German physicists (see, e.g., [3,10] and references therein). Using highly sensitive luminescent methods and thermoactivation spectroscopy it was also shown that the efficiency of F centre creation by x-rays or 2–30 keV electrons decreases by several times if the radiation temperature of LiF falls down from 300 to 6 K. On the other hand, there is no such freezing of defect production in many alkali halides with close values of an anion and a cation radius [2]. In LiF, large-radius anions form a closely packed cubic lattice and the movement of anion crowdion-type configurations is impeded. However, the interdefect separation in close F-H Frenkel pairs, formed at the decay of anion excitons, and further defect stabilization via associations takes place at $T > 60$ K, when the hopping diffusion of H interstitials is started. A special feature of colour centre creation by SHIs in LiF lies in the fact that under conditions of high density of EEs in the ion tracks, the separation of F and H centres in FPs occurs even at 8 K because of fast local heating in the track regions during the irradiation. The process of local heating is studied in detail for NaCl crystals [10].

The decay of an optically formed cation exciton ($h\nu_{ex} = 62$ eV) in LiF leads to the formation of an anion exciton and three e-h pairs. Such group of EEs can be transformed into a triplet of spatially correlated defects [4]. The irradiation of LiF by SHIs at 300 K causes the efficient creation of F_2 centres and more complex associations of colour centres. The heating of the ion-irradiated crystals leads to the appearance of high-temperature TSL peaks at 600–700 K. These peaks are caused by ionic processes, formation of anion vacancies due to thermal fluctuations, resulting in extremely high values of frequency factors (10^{17}–10^{19} s^{-1}) [11]. The elaboration of selective dosimeters of fast neutrons based on LiF crystals is complicated by the coexistence of non-linear e-h and interstitial-vacancy processes.

3. Nonimpact creation mechanisms of radiation defects in metal oxides with $E_{FP} > E_g$

It is commonly accepted that in many wide-gap dielectrics (MgO, Al_2O_3, $MgAl_2O_4$, Y_2O_3, $Y_3Al_5O_{12}$ and even SiO_2) the impact (knock-out) mechanisms of radiation defect creation are dominant ones, because the energy released at the recombination of relaxed (cold) electrons and holes is insufficient for the creation of an FP, $E_{FP} > E_g$ (at least in the bulk of a crystal). Actually γ-irradiation provides low density of e-h pairs and, probably, the recombination of cold e-h pairs is the dominant process.

We have investigated the structure of the valence bands (v-bands) in a number of metal oxides and sulphates by measuring the spectra of subnanosecond intraband luminescence excited by electron pulses. According to our experimental data the complex v-band in some sulphates and SiO_2 is divided into several subbands separated by the energy gaps of 1–2 eV [4]. The presence of such gaps inside a split v-band allows the relaxation of hot holes from the lowest subband only up to the top of this subband. The energy released at the subsequent e-h recombination exceeds E_g by 1–2 eV and can be sufficient for the creation of an FP under the crystal irradiation by electrons, the energy of which is lower than the value needed for the impact mechanism. Right this process might be responsible for the defect creation detected in SiO_2 under electron-irradiation at 6 K [13].

According to theoretical calculations and the existing experimental data, there are no energy gaps inside wide and structured valence bands in some binary metal oxides. For example, the width of the v-band with continuous structure in MgO is $E_v = 6.7$ eV [12]. The experimental data confirm that the radiation resistance of MgO single crystals against x-rays is significantly higher than of SiO_2 single crystals. The ratio is also valid for the crystal irradiation by ^{238}U ions with kinetic energy of 2.25 GeV at fluence of 10^{12} U/cm^2. Such ion irradiation causes drastic changes in the spectrum of optical absorption of MgO but does not lead to the breakdown of the sample. The layering on the irradiated side of SiO_2 takes place already at the fluence of 2×10^{11} U/cm^2.

It is widely believed that the irradiation of MgO by fast neutrons mainly causes the creation of F^+ centres (absorption band peaked at 4.95 eV and the emission band at 3.15 eV), while F centres (emission at 2.4 eV, absorption at 5.02 eV [1,14]) dominate in MgO crystals additively coloured at high temperatures. Figure 1 shows the spectra of the induced optical absorption of MgO irradiated at 300 K by 2.25 GeV uranium ions at two different fluences. The penetration depth of ^{238}U ions is about 80 μm. In addition to the intense absorption of F^+ and F centres (~5 eV) there are relatively narrow and weak bands with the maxima at 3.48 eV (F_2 centres) and 2.17 eV. The emission of F_2 centres is peaked at 3.3 eV. According to Fig. 1, the absorption peak intensity for F^+ and F centres (~4.95 eV) is ~ 100 times as high as that for F_2 centres in MgO irradiated by ^{238}U ions (2×10^{11} ion/cm^2). The same ratio equals ~50 for a MgO crystal irradiated by fast neutrons (10^{17} n/cm^2). By comparison, the ratio equals 3 in a LiF crystal irradiated by ^{238}U ions (fluence of 2×10^{11} ion/cm^2). In MgO with extremely high melting temperature $T_{melt} \approx 3040$ K, anion vacancies v_a are undoubtedly immobile at 300 K, while v_a are highly mobile thus facilitating the formation of F_2 centres in LiF crystals (see [11]). The origin of the centres responsible for the absorption peaked at 2.17 eV is still to be explained. The number of these centres increases

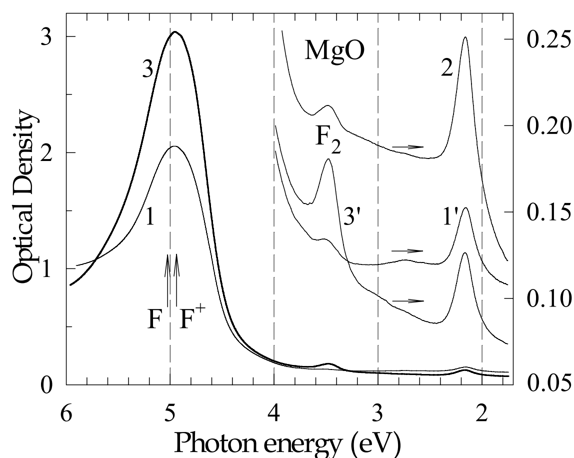

Fig. 1. The absorption spectra measured at 295 K for MgO crystals irradiated by ^{238}U ions (2×10^{11} ion/cm^2 – curves 1, 1' and 10^{12} ion/cm^2 – curve 2) at 300 K or by fast neutrons (> 0.2 MeV, 10^{17} n/cm^2, crystal thickness of 0.74 mm – 3, 3') at 320 K.

In the stressed samples, in particular, after high-dose ion irradiation (fluence of 10^{12} U/cm^2).

The excitation spectrum for the 2.4 eV emission of F centres has been measured using synchrotron radiation of 6–30 eV at 10 K. The emission is excited in the whole region of band-to-band transitions (7.9–30 eV). A sharp increase of the efficiency of F centre emission at 26–30 eV is connected with the creation of secondary e-h pairs by hot conduction electrons. This process of e-h pair multiplication takes place if the energy of a hot electron exceeds E_g, thus causing the drastic decrease of the efficiency of hot e-h recombination with the possible creation of FPs.

The annealing processes of radiation-induced structural defects have been investigated by measuring the spectra of optical absorption (see Fig. 1) and the TSL curves for previously irradiated samples. Figure 2 presents the TSL curve measured after a MgO crystal irradiation by uranium ions (10^{12} U/cm^2) at 300 K and two-week storage in darkness at room temperature. TSL peaks detected in this sample can be approximated by first-order kinetics (shown by dashed lines) with the activation energy E_a and the frequency factor p_0: 410 K (E_a = 1.20 eV and p_0 = 10^{14} s^{-1}), 430 K (1.24 eV, 10^{14} s^{-1}), 455 K (1.32 eV, 10^{14} s^{-1}), 500 K (1.45 eV, 10^{14} s^{-1}), 520 K (1.51 eV, 10^{14} s^{-1}), 550 K (1.5 eV, 10^{13} s^{-1}), 615 K (1.40 eV, 4×10^{10} s^{-1}) and 690 K (1.63 eV, 10^{11} s^{-1}).

Figure 2 also shows the pulse annealing of the EPR signal of several paramagnetic centres in irradi ated MgO crystals. Two TSL peaks at 430 and 455 K accompany the annealing of the EPR signal of V^- centres (a hole localized at an oxygen ion in the field of a cation vacancy – O^-v_c). The 410 K TSL peak correlates with the annealing of the EPR signal of V_{Al} centres ($Al^{3+}v_cO^-$). The annealing of the absorption of F centres (5 eV) occurs at 600–800 K [15]. According to

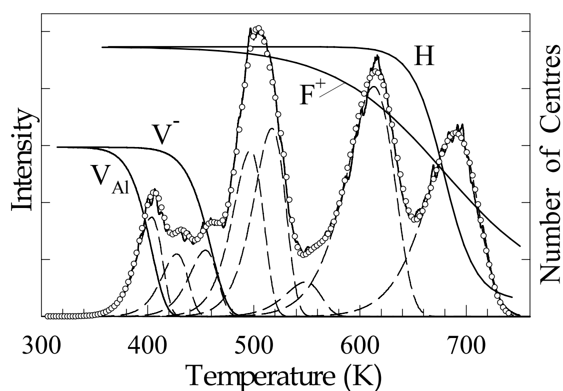

Fig. 2. TSL curve measured for a MgO crystal with β = 2.86 K s^{-1} after irradiation by ^{238}U ions (10^{12} ion/cm^2) at 300 K and two-week storage in darkness (solid line). Components of decomposition described by the first order kinetics (dashed lines) and their sum (oo). The pulse annealing of the EPR signal of V_{Al}, V^-, F^+ and H centres in irradiated MgO crystals. The pulse regime is approximately equivalent to the linear heating with β = 2.86 K s^{-1}.

our data the pulse annealing of the EPR signal of F^+ centres in a MgO crystal irradiated by fast neutrons (> 0.2 MeV) takes place at 600–750 K (see Fig. 2 and Ref. 16 for details). The annealing of the EPR signal of H centres occurs at 650–750 K [16] (see Fig. 2) and can be approximated by first-order kinetics – E_a = 1.7 eV, p_0 = 10^{12}–10^{11} s^{-1}. The H centre is created at the irradiation of MgO by fast neutrons or SHIs due to the localization of O_i^0 near a V^- centre resulting in the formation of an $O_2^-v_c$ association. The thermal dissociation of H centres leads to the appearance of mobile holes, that recombine with the electrons localized at F centres and impurities, and slowly moving O_i^0, which recombine with a part of F^+ centres (v_ae): $v_ae + O_i^0 \rightarrow O^{2-} + h$. According to theoretical estimations O_i^0 interstitials have the dumb-bell configuration oriented along <110> and the activation energy for the hopping diffusion of ~1.5 eV [17]. The hopping diffusion of O_i^0 causes a sharp decrease of the value of p_0 = 10^{14} s^{-1} for purely the hole TSL peaks at 430 and 455 K down to 10^{12}–10^{11} s^{-1}, which is typical of the recombination between O_i^0 and F^+ centres. Highly mobile holes, formed due to this recombination, are responsible for the appearance of impurity emissions. Unusual behaviour of MgO (as compared with LiF) results from the extremely high value of $T_{melt} \approx 3040$ K. The ionic processes connected with the diffusion of vacancies and efficient mass transport (except protons) begin near the Tammann temperature ($\approx 0.5T_{melt}$).

4. Luminescent protection againts defect creation due to the hot e-h recombination

Recently we have proposed the basic possibility (see also [4]) of the suppression of the recombination of hot (non-relaxed) electrons and holes, that cause the

creation of structural defects and thus the degradation of the irradiated materials even under conditions of low density of EEs, in the materials with $E_{FP} > E_g$. Fig. 3 shows a simplified energy-band diagram of a wide-gap dielectric (e.g., a $BaMgAl_{10}O_{17}:Eu^{2+}$ phosphor, BAM:Eu) with complicated conduction and valence bands (c-band and v-band). The absorption of a photon (an arrow line 1) of $h\nu_{ex} >> 2E_g$ leads to the formation of a hot conduction electron with the energy excess (with respect to the bottom of the c-band) sufficient to create a secondary e-h pair due to the nonradiative Auger transition (case *a*, arrow lines 2 and 2′). Conduction photoelectrons with lower energy cannot create secondary e-h pairs, but they are able to excite Eu^{2+} impurity centers (case *b*, a nonradiative Auger transition 3→3′). The case (*c*) demonstrates one more possibility to excite an impurity center due to 4→4′ Auger transition with the participation of a hot hole. Earlier the process of the energy transfer to an impurity center by a hot conduction electron was revealed in KCl:Tl, RbCl:Tl and RbCl:Ag crystals [9].

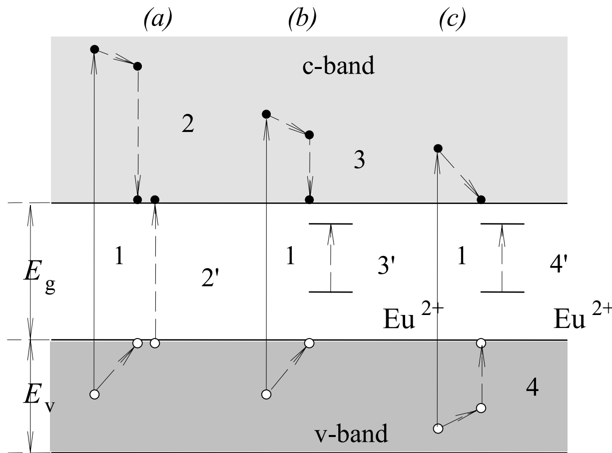

Fig. 3. A simplified energy-band diagram of a BAM:Eu phosphor. The creation of a secondary e-h pair by a hot conduction electron (case *a*) or the excitation of an Eu^{2+} impurity center by a hot electron (case *b*) or a hot valence hole (case *c*) due to nonradiative Auger transitions.

There is more favorable condition for the energy transfer to Eu^{2+} centers by hot holes in BAM:Eu with the wide v-band. According to our data, the cathodoluminescence intensity of a BAM phosphor with low concentration of europium ions (about 0.1% of Ba^{2+} ions are substituted by Eu^{2+}) significantly decreases under prolonged irradiation by 5 keV electrons, while the cathodoluminescence intensity in BAM:Eu (10%) remains practically constant under the same irradiation conditions. In BAM:Eu (10%) phosphors, used in plasma display panels (PDP), the value of luminescence quantum yield doubles (0.95 → 1.9) with the rise of the energy of exciting photon from $h\nu_{ex}$ = 14e V to $h\nu_{ex}$ = 20 eV due to the excitation of Eu^{2+} by hot photoholes [18].

The main investigations of the suppression processes of hot e-h recombination in radiation-resistant wide-gap materials ($E_{FP} > E_g$) doped with various luminescence impurities still lay ahead.

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