Competition between luminescent and nonradiative decay channels of electronic excitations in wide-gap binary and complex metal oxides

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The main goals of our present studies are to investigate

- the processes of nonradiative decay of different electronic excitations forming under irradiation of wide-gap (E_g = 5–15 eV) inorganic materials.

radiation-induced electronic excitations

nonradiative decay → **heat release**, **formation of structural defects**

radiative decay → **luminescence**

- the influence of a crystal structure, peculiarities of intrinsic EEs as well as some impurity ions (in particular, heavy rare-earth and transition metal ions) on the defect creation efficiency at the irradiation of wide-gap metal oxides.

Mechanisms of radiation damage in inorganic WGMs

1. Knock-out (impact) mechanism –

elastic collisions of incident particles with the atoms. Formation energy of a Frenkel pair (E_{FD}) for this rapid (~10^{-15} s) impact mechanism is about 50–60 eV (in MgO E_{FD}~ 50 eV). It is the main mechanism in metals.

2. Excitation and ionization of an electron subsystem – decay of radiation-induced electronic excitations (adiabatic mechanisms, ~10^{-10} s). In MgO, E_{FD}^{adiab}~ 25 eV .

A. Materials with $\boldsymbol{E_{FD} < E_g}$ Frenkel pairs are efficiently formed at the decay of self-trapping excitons or the recombination of even totally relaxed *e*–*h* pairs.

Alkali halides with $r_c \approx r_a$ – formation of interstitials is facilitated.

$r_c < r_a$ high T is needed – anharmonic vibrations

I. Luminescent protection against creation of Frenkel defects

Creation of FDs in the materials with $E_{\mathrm{FD}} < E_{\mathrm{g}}$ can be suppressed by introducing isomorphic (with respect to size and valence) impurity ions, which provide recombination impurity luminescence with high QY.

So, the energy released at e–h recombination is partly transformed into impurity luminescence and is not used for defect creation. At high concentration of impurity ions, QY for impurity recombination luminescence can be very high, $\rightarrow 1$.

Mechanisms of radiation damage in inorganic WGMs

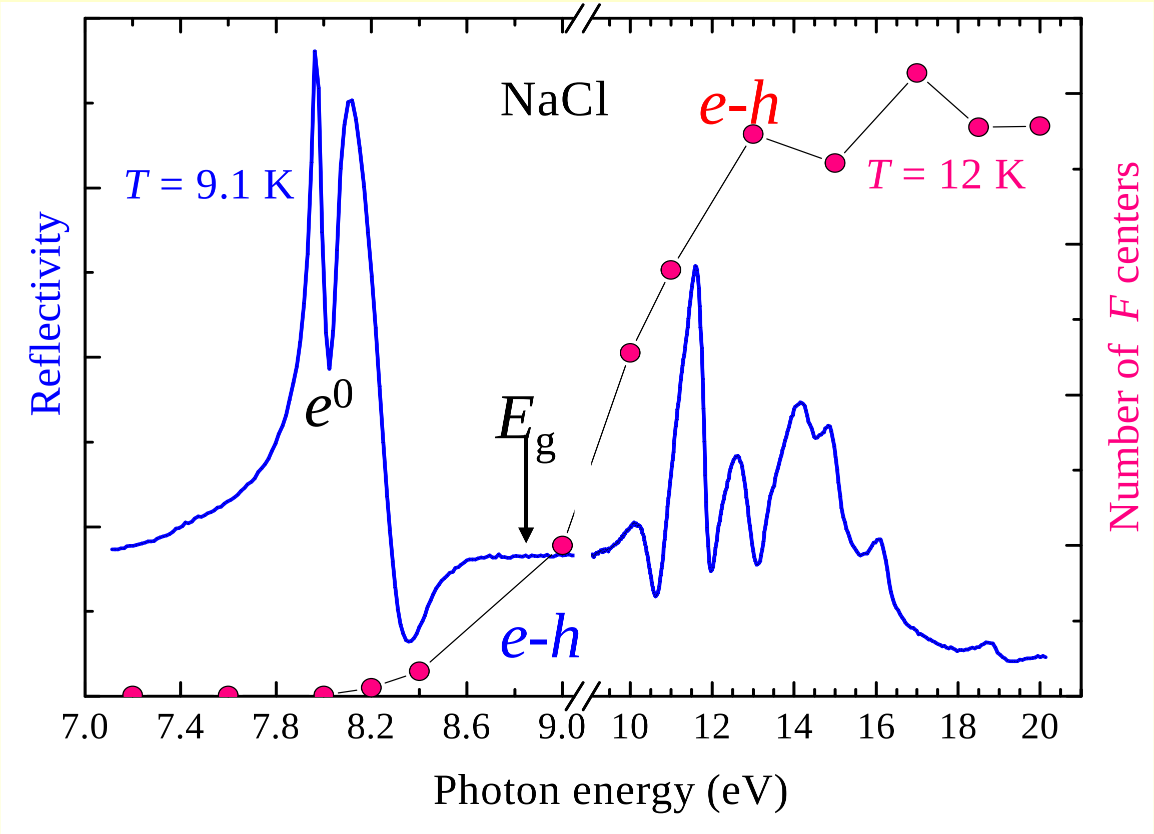
2. Excitation and ionisation of an electron subsystem – decay of radiation-induced electronic excitations (adiabatic mechanisms, ~10^{-10} s)

A. Materials with $E_{FD} < E_g$ Frenkel pairs are efficiently formed at the decay of self-trapping excitons or the recombination of even totally relaxed *e–h* pairs. Alkali halides

B. Materials with $\boldsymbol{E_{FD} > E_g}$ The excitonic and ordinary *e–h* mechanisms of defect creation are not realized. Decay of high-energy EEs (e.g., cation excitons) or **hot** *e–h* recombination should be considered.

Low-temperature creation of long-lived *F-H* pairs in NaCl

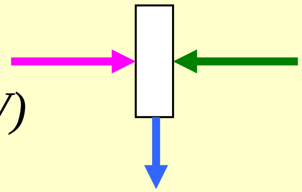
(T< 120 K, $E_{FD} > E_g$)



$N(F)$~ light sum of (3 – 4 eV)-flash stimulated in the maximum of F-absorption band (2.75 eV).

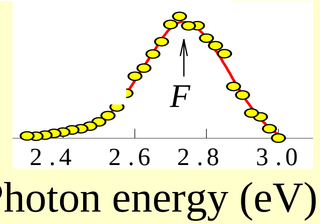
Synchrotron radiation - FINEST beamline with undulator, MAX-III, Lund

Synchrotron radiation (7-40 eV)



F-stimulation

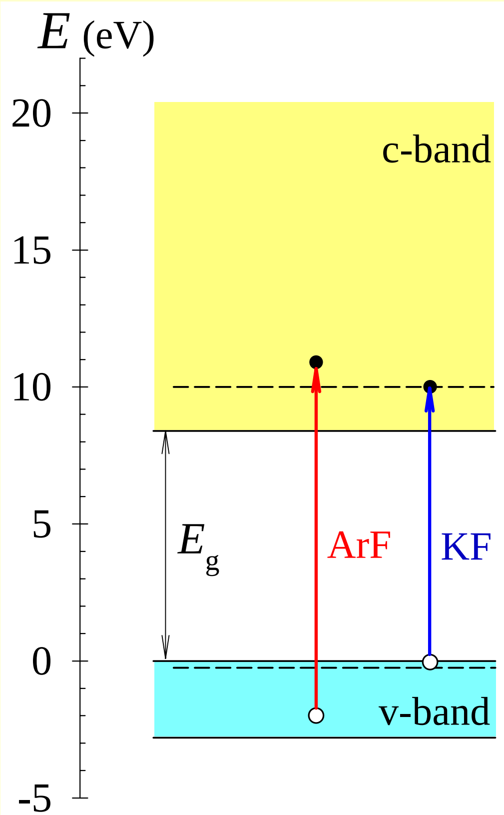
Luminescence, ~ N(F)

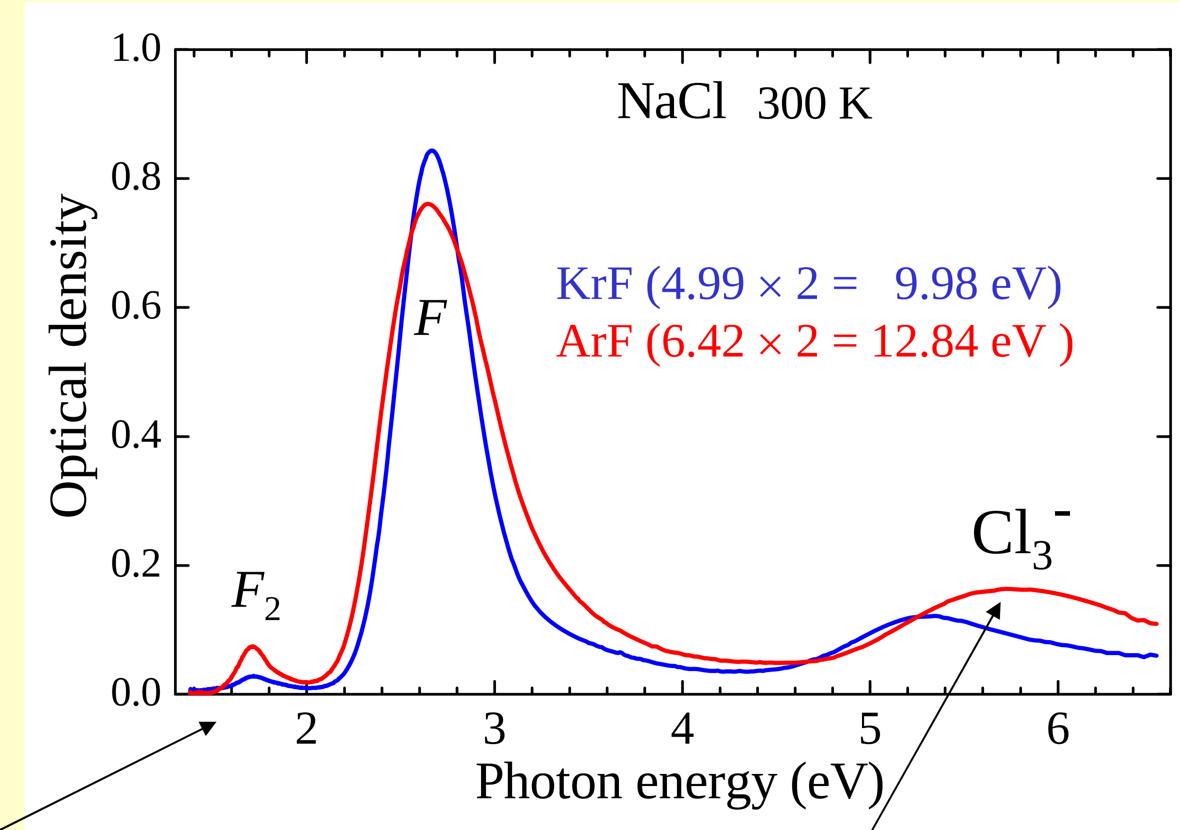


$$F \ldots .\ H \ +\ h\nu_F \rightarrow F^* \ldots .\ H \rightarrow h\nu_{Lum} + \ \alpha \ldots .\ I \rightarrow R$$

$v_a e$ i_a^0 v_a i_a^-

Contribution of mobile hot holes into F_2 and Cl_3^- creation





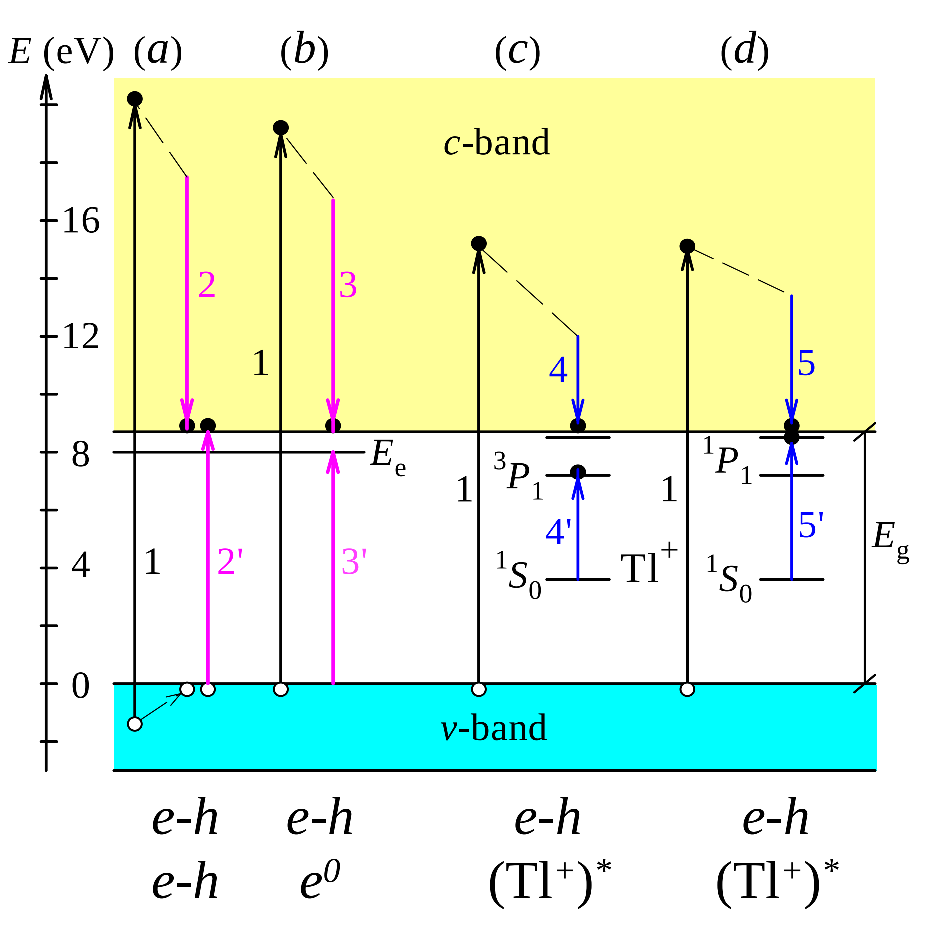
F_2 center creation:

Cl_2^- (H) + $h \rightarrow Cl_3^-$

- Fast ionization of F centers by hot holes (i.e. v_a creation)
- $F + v_a + e \rightarrow F_2\,(v_a e v_a e)$

II. Luminescent protection against creation of Frenkel defects

The main mechanisms of photon multiplication in NaCl:Tl$^+$



(a) $E_t \geq h\nu$ = 22 eV

(b) $h\nu$ = 18-20 eV

(c) $^1S_0 \rightarrow {}^3P_1$ (Tl$^+$)*

(d) $^1S_0 \rightarrow {}^1P_1$ (Tl$^+$)*

E_g = 8.75 eV

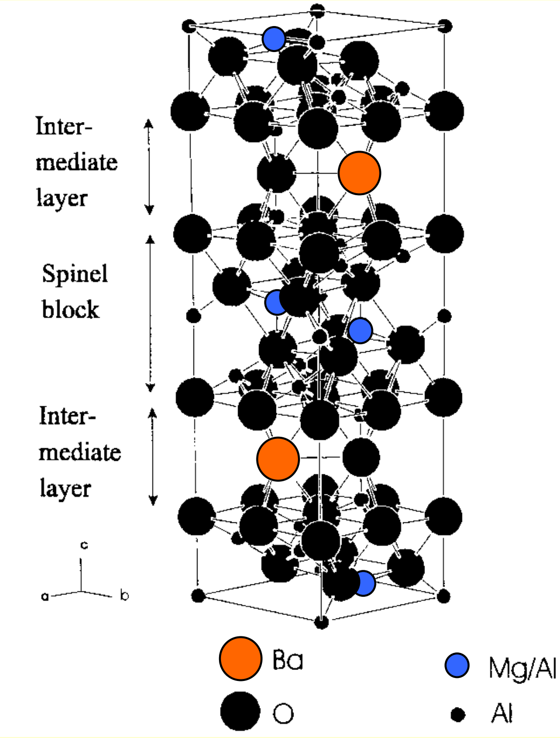
E_e = 8 eV

$E_v \approx$ 3 eV

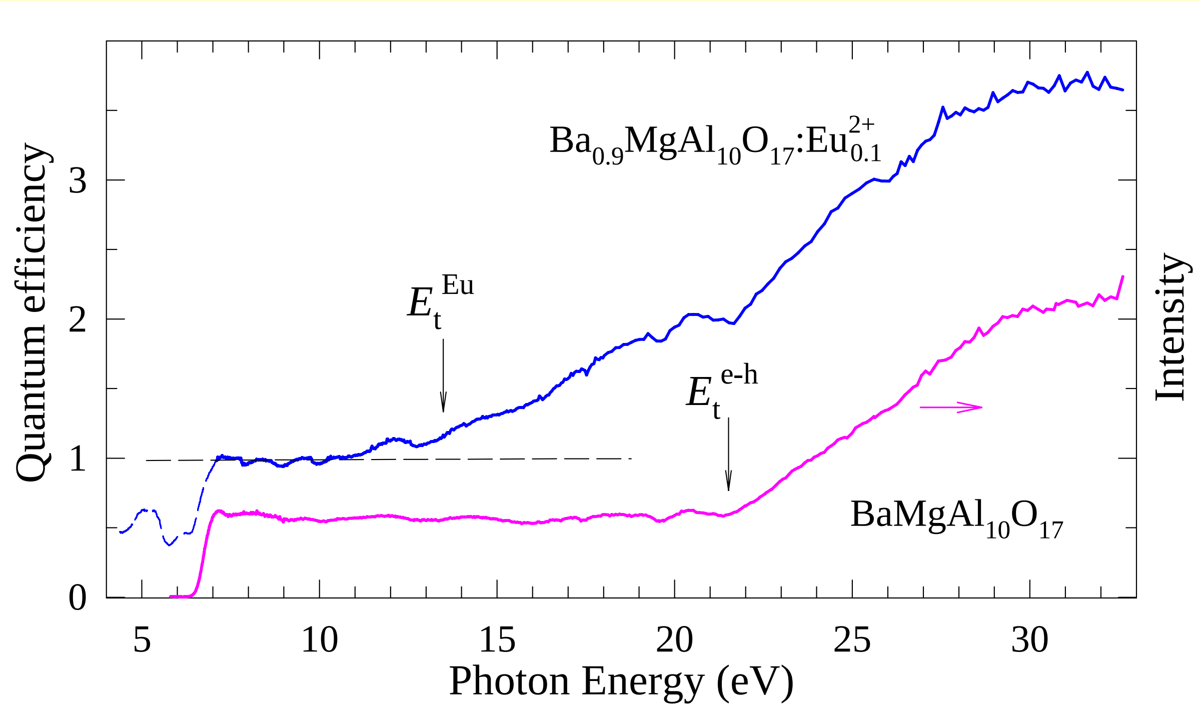
solid-state analogue of the Franck-Hertz effect

The energy excess of a hot conduction electron (cases *c* and *d*) is transformed into impurity luminescence, while cold *e–h* pairs in NaCl at LHeT are not able to cause FD creation.

$BaMgAl_{10}O_{17}$ (BAM)



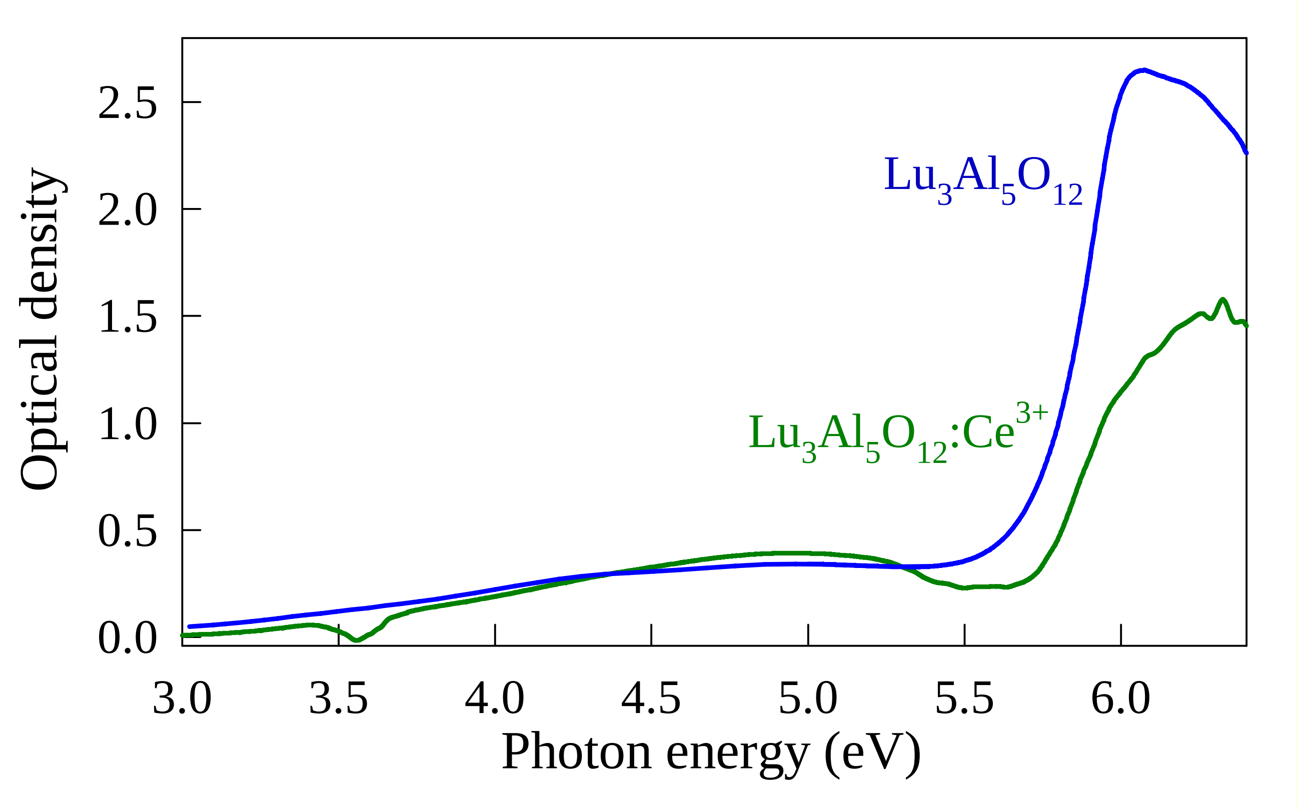
$Eu^{2+} \Rightarrow Ba^{2+}$
spatially separated from each other impurity ions



Excitation spectra for the emission of Eu^{2+} centers at 295 K and the 5.1 eV intrinsic emission at 8 K

$Ba_{0.9}Eu_{0.1}MgAl_{10}O_{17}$ phosphors (10% of Eu^{2+}) demonstrate a reasonably high resistance against irradiation by 5-30 keV electrons (current from 10 nA to 5 μA), while the Eu^{2+} emission efficiency decreases with time under electron-irradiation of BAM:Eu^{2+} (0.3%).

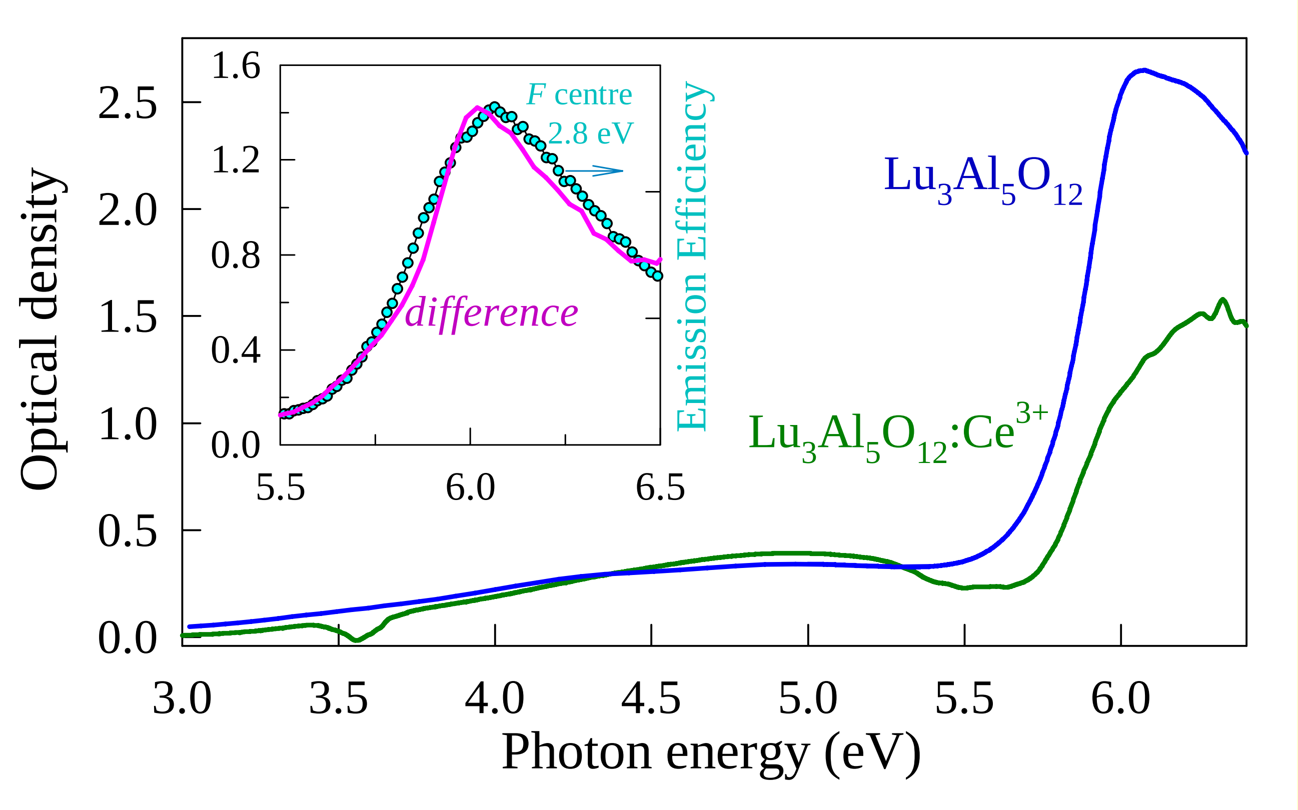
Luminescent protection against nonimpact mechanisms of radiation damage



Radiation-induced absorption of LuAG and LuAG:Ce^{3+} (~2000 ppm) at 295 K caused by isodose irradiation with 2.04 GeV Au^{198} ions at RT (10^{12} ions/cm^2).

Luminescent protection against nonimpact mechanisms of radiation damage

$E_{FD} > E_g$



Radiation-induced absorption of LuAG and LuAG:Ce^{3+} (~2000 ppm) at 295 K caused by isodose irradiation with 2.04 GeV Au^{198} ions at RT (10^{12} ions/cm^2).

Cubic *fcc* MgO single crystals $E_{FD} > 2E_g$

• bulk of a perfect crystal – very high resistance against X- and γ-rays

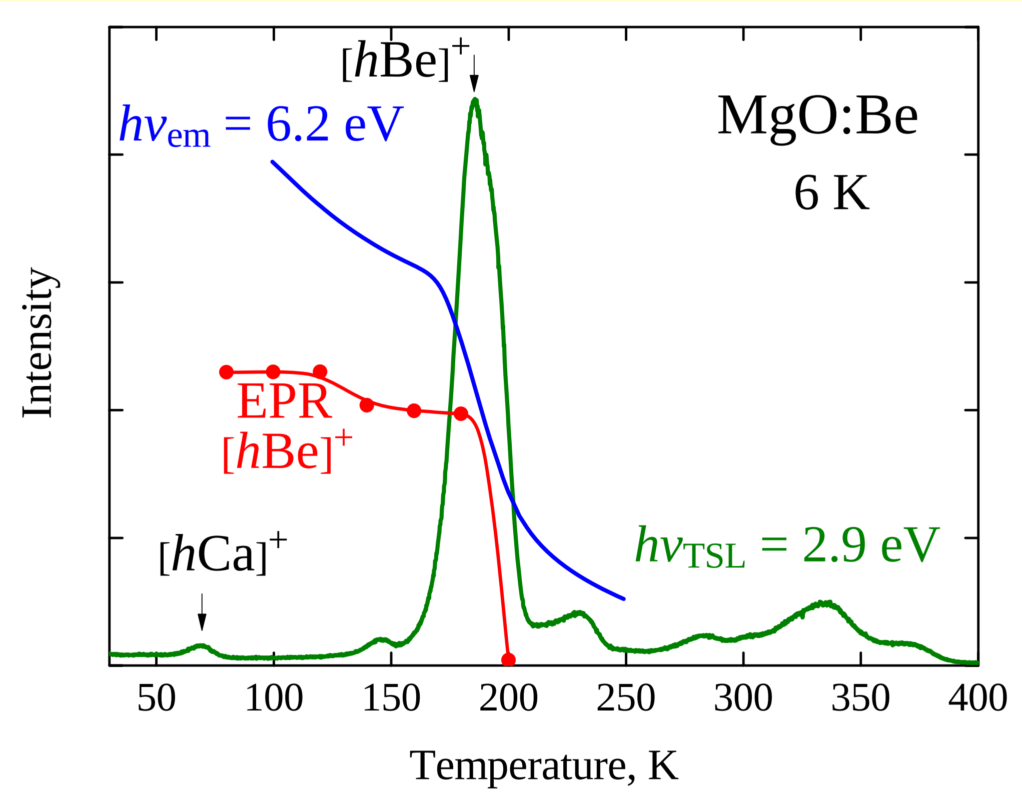
• E_{FD} ~ 50 eV for the knock-out mechanism (displacement of an oxygen) and at least a half of this for the EE-related creation mechanism

• in contrast to alkali halides, excitons and holes **do not undergo self-trapping** in regular regions of MgO

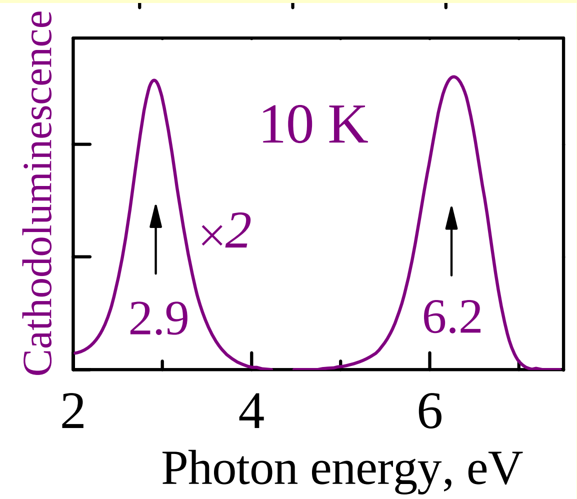
• for the efficient hot *e*–*h* recombination the holes should be initially localized at impurity or intrinsic structural defects
alkaline-earth Be^{2+} and Ca^{2+} ions $\rightarrow$ $[hBe]^+$ and $[hCa]^+$ Coulomb trapped-hole centers with large effective cross-section for the recombination with hot electrons

$[hBe]^+$ are stable up to 195 K, $[hCa]^+$ – up to 50 K

$[hBe]^+$ centers in MgO:Be (~150 ppm)

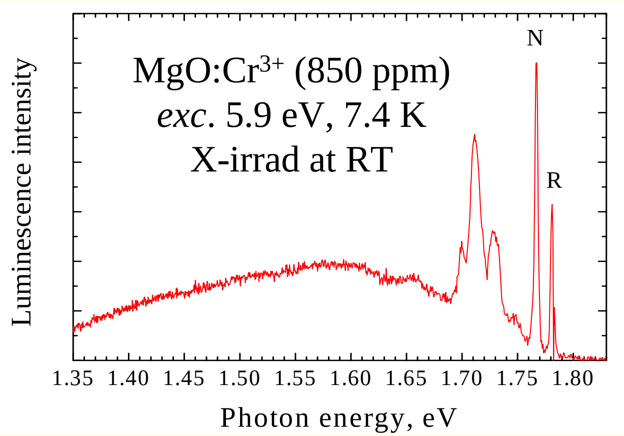


MgO samples were previously irradiated by 5-keV electrons (TSL) or X-rays (EPR) at 5-10 K



$$e + [hBe]^+ \rightarrow [Be]^0 \; + \; 6.2\,\text{eV emission}$$

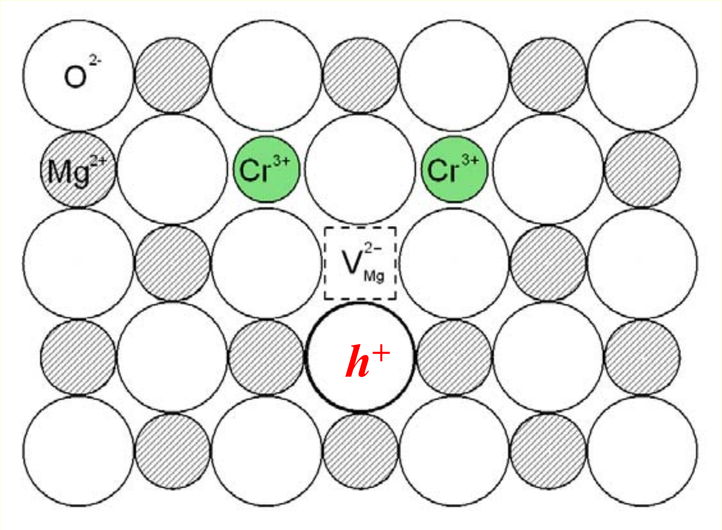
$$[hBe]^+ \rightarrow h, \quad h + e v_a v_c \; \rightarrow \; v_a v_c \; + \; 2.9\ \text{eV emission}$$



Rhombic pair chromium center containing a cation vacancy

MgO:Cr^{3+} (850 ppm)

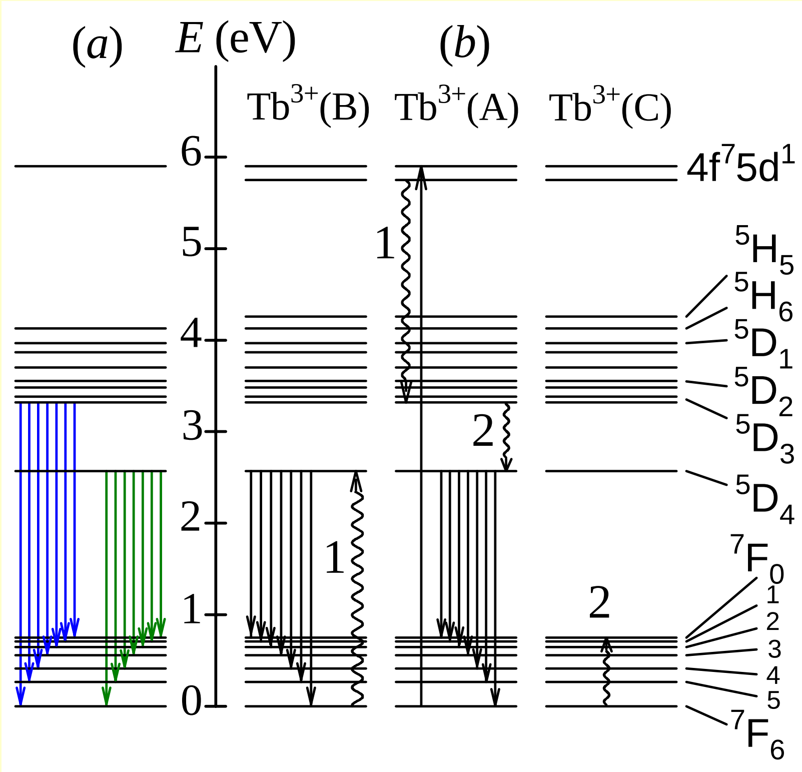
$[Cr^{3+}\text{-}v_c\text{-}Cr^{3+}]^0$



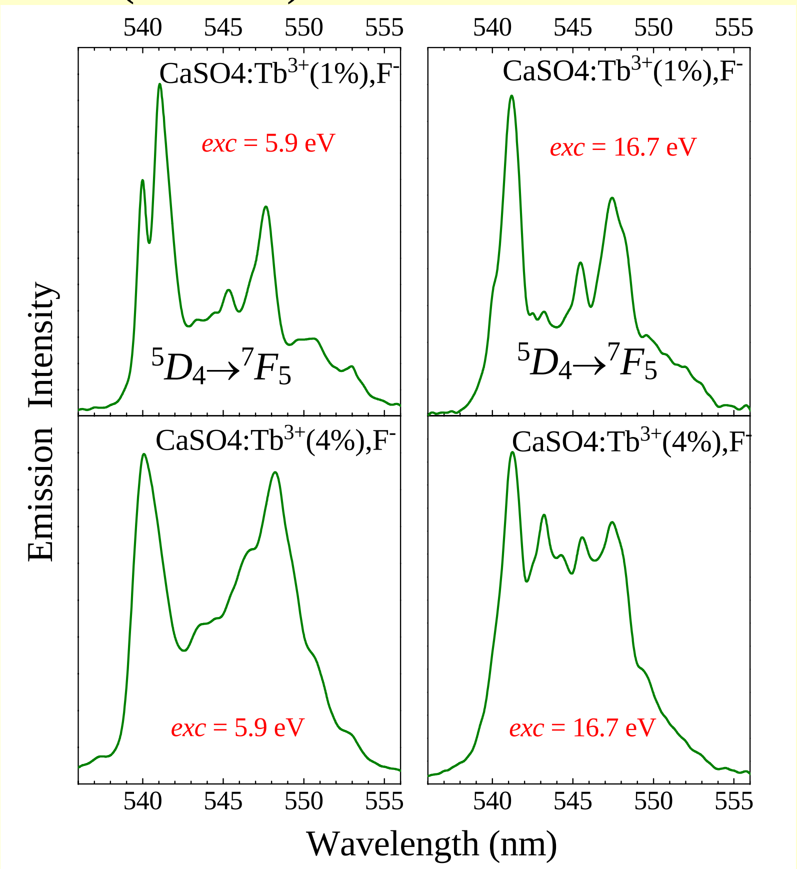
e + *h* $[\dots]^0 \rightarrow$ defects

Rhombic pair center is a trap for a hole that becomes localized at oxygen. Positively charged Coulomb center possesses a large cross-section for the recombination with electrons. It can be hot conduction electrons, but the released energy is ~20 eV – insufficient for FD creation. Under X-ray or electron irradiation there arise also Auger electrons of 100–200 eV (via transitions between inner shells), which recombine with trapped-hole centers causing rearrangement of many host ions – that is formation of 3D defects.

single	double/triple



Fine structure of the $^5D_4 \rightarrow {}^7F_5$ transition for Tb^{3+} centres at the photoexcitatioin of $CaSO_4$ in the region of $f \rightarrow d$ (5.9 eV) and band-to-band transitions (16.7 eV) at 9 K.



Phosphors with single RE^{3+} are stable against low-density irradiation.

Electron irradiation results in the destruction of pair centers, containing calcium vacancies (atomic mass of a pair center – 308).

$$[Tb^{3+}|_{Ca} V|_{\mathbf{Ca}} Tb^{3+}|_{Ca}]^0$$

$$[Tb^{3+}|_{Ca} F_i^- Tb^{3+}|_{Ca} F_i^-]^0$$

(flux) × (duration of irradiation)

The way how the same radiation dose is reached is important

low excitation density by photons and electrons (e.g., LET<100 eV/nm for γ-rays)

superhigh excitation density providing by powerful electron pulses or swift heavy ions

(300 keV) ns-electron pulses or
tracks of heavy ions (^{198}Au, ^{238}U) with energy about 2 GeV,
a range from 50 to 100 μm, LET = 20–30 keV/nm

Mechanisms of radiation damage in inorganic WGMs

3. Mechanisms at high and super-high density of EEs

high-current electron accelerators	swift heavy ions
GIN, Febetrons	~GeV
ns-, sub-*ns* pulses	range 50–100 μm
10^2–10^4 A/cm^2	*LET* > 30 keV/nm

David Vaisburd (Tomsk, Russia) – cracking and brittle destruction of single crystals at the electron current above 10^2–10^3 A/cm^2 as a result of the generation of shock acoustic waves causing a local phase transition (the third mechanism of radiation damage).

At slightly lower current – coherent migration of hot carriers ("high energy conductivity") and the appearance of intraband luminescence.

The processes considered as the third complex creation mechanism of radiation damage, even more evidently manifest themselves at the irradiation of WGMs with SHIs.

Theoretical predictions (Sievers, V.Hizhnyakov, V.Zakharov et al.) – a new kind of intrinsic vibronic mode (discrete breathers or discrete solitons) with large amplitude and frequency above the top of acoustic phonon spectrum may exist under dense excitation of a crystal lattice predisposed to anharmonic interactions.

LiI: $M(^{127}I)/M(^{7}Li)=18$ or $M(^{127}I)/M(^{6}Li)=21$, NaI:Tl *etc*.

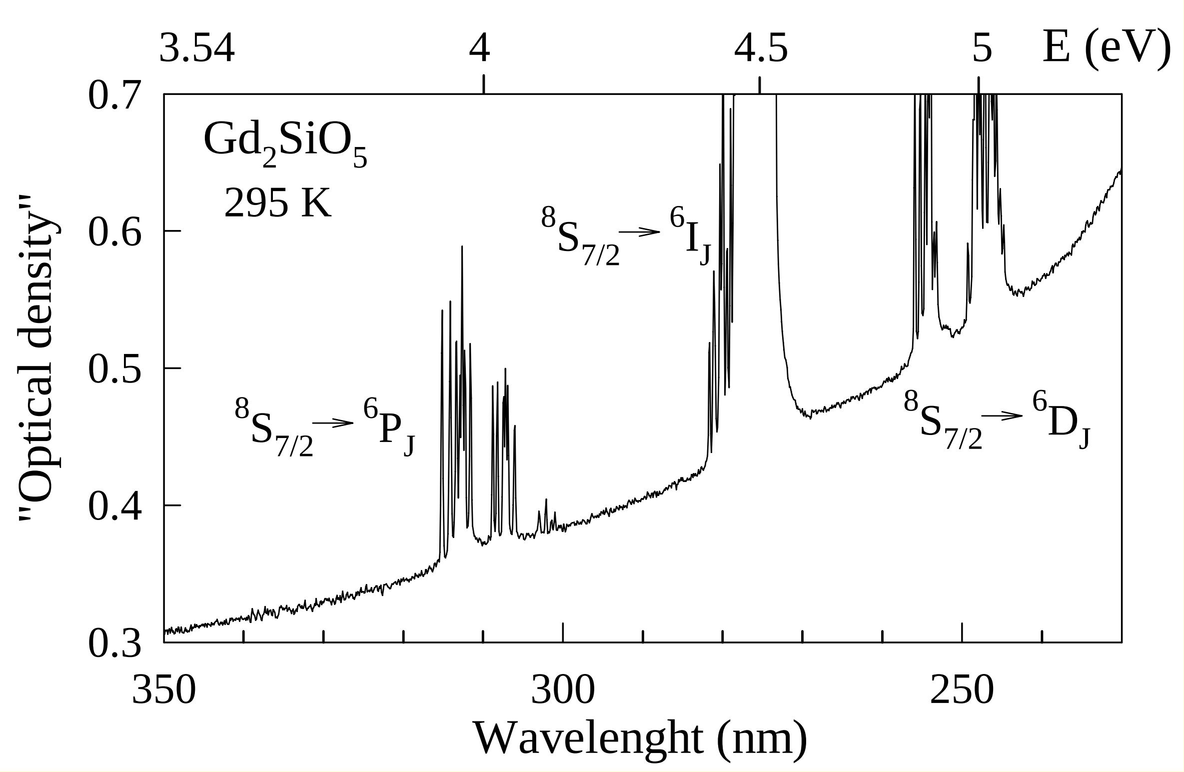
discrete soliton → cooperative rearrangement of many ions

MgO (4), α-Al_2O_3 (10), $Y_3Al_5O_{12}$ (160), **$Lu_3Al_5O_{12}$** (160)
$MgAl_2O_4$, α-SiO_2, Y_2SiO_5 (64), **Gd_2SiO_5** (32)

MgO	Gd_2SiO_5	$Lu_3Al_5O_{12}$
$M(Mg)/M(O) = 1.5$	$M(Gd)/M(O) = 10$	$M(Lu)/M(O) = 11$
	$M(Gd)/M(Si) = 5.6$	$M(Lu)/M(Al) = 6.5$

These unusual excitations are expected to be especially strong in WGMs built up of ions with different masses – the frequency of discrete breathers can fall in a gap between acoustic and optical vibration branches.

The spectrum of “absorption+scattering” for Gd_2SiO_5 irradiated with 2.04 GeV Au^{198} ions at RT (10^{12} ions/cm^2, GSI, Darmstadt).



In heavily irradiated crystals, the presence of complex radiation-induced defects causes large light scattering.

These 3D defect possess very high thermal stability.

High-absorbance spectrofotomeeter Jasco V-660 with double monochromator.

Single crystals of Gd_2SiO_5 were grown by the Czochralski method at ISMA, Kharkov, Ukraine. Nominally pure GSO contains some amount of Ce^{3+}.

• ***Third mechanism of radiation damage under superhigh excitation density***

1. Along a track 99% of ~GeV-ion energy is spent on EEs formation, while close to the end slowed down SHIs create FDs via the knock-out mechanism.

2. The damaged lattice part in the end of ion path serves as a wall for a supersonic discrete soliton formed in the track with the frequency above acoustic phonon branch.

3. After back reflection from the wall there occurs interference between breathers moving in opposite directions, and we have a set of lattice regions (points) with increased vibration amplitude and anharmonicity.

4. Theorists predict a collapse of solitons in these regions resulting in a rearrangement of many host ions – formation of temperature-stable 3D intrinsic defects, which serve as stoppers for dislocations and facilitate cracking and brittle destruction of irradiated materials.

In the literature there are some manifestations of this phenomenon obtained by different methods, e.g., enhanced radiation damage under applied uniaxial pressure. Our results also confirm the existence of this mechanism:

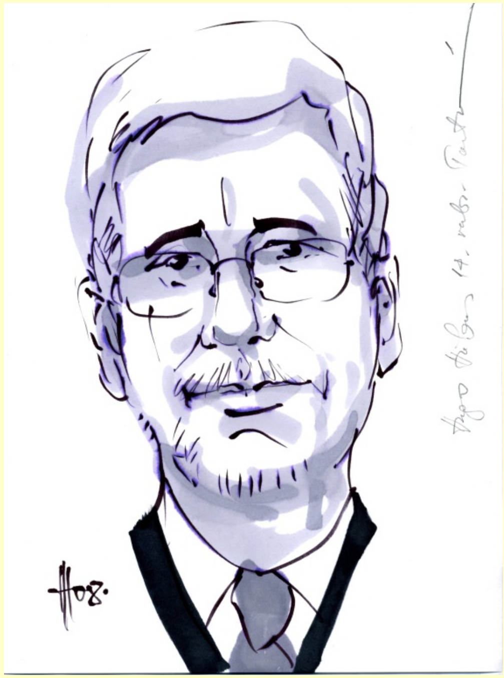
(i) sharply increased scattering and absorption in UV-VUV region of the spectra for ion-irradiated GSO; *(ii*) formation of microcracks, *(iii)* drastic changes in low-temperature thermoluminescence that can be detected after weak excitation of an ion-irradiated crystal by 10-keV electrons at 6 K.

Concluding Remarks

More and more complex luminescent solid solutions are used for technical application. Some isomorphic luminescent impurity ions intercept a large part of the absorbed energy thus increasing the radiation-resistance of WGMs.

Many metal oxides are doped with RE or other heavy ions – their atomic mass significantly exceeds that of oxygen, the main component of matrixes. However, vibronic spectra of complex solid solutions as well as peculiarities of electron-phonon interaction, which explain the enhancement of anharmonicity resulting in formation of supersonic shock waves, should be taken into account.

Especially dangerous is an impurity center containing two close RE^{3+} ions and a cation vacancy as a charge compensator. The recombination of high-energy electrons with the holes trapped at oxygen near such centers causes the rearrangement of many host ions – formation of 3D defects, which facilitate cracking and brittle destruction of materials, especially under irradiation with *LET* > 20 keV/nm. The latter situation is especially important for the elaboration of fusion reactors – the resistance of construction and functional materials should be increased.



THANK YOU