Competition between luminescence and nonradiative processes in wide-gap scintillation materials

Institute of Physics
University of Tartu, Estonia

Aleksandr Lushchik
Ch. Lushchik, E. Shablonin, A. Shugai, E. Vasil'chenko

SCINT, Shanghai, April 2013

Wide-gap binary and complex metal oxides doped with rare earth or transition impurity ions (luminescence centers) – fast scintillators, spectral transformers.

The energy absorbed during irradiation is transformed into:

- ***luminescence***
- ***heat release*** (phonon package)
- ***creation of radiation defects***

(short-lived or stable interstitial-vacancy pairs of Frenkel defects)

The ratio between three transformation channels depends on:

→ *temperature,*

→ *concentration and spatial distribution* of *luminescence centers* (presence of pairs of heavy impurity ions!)

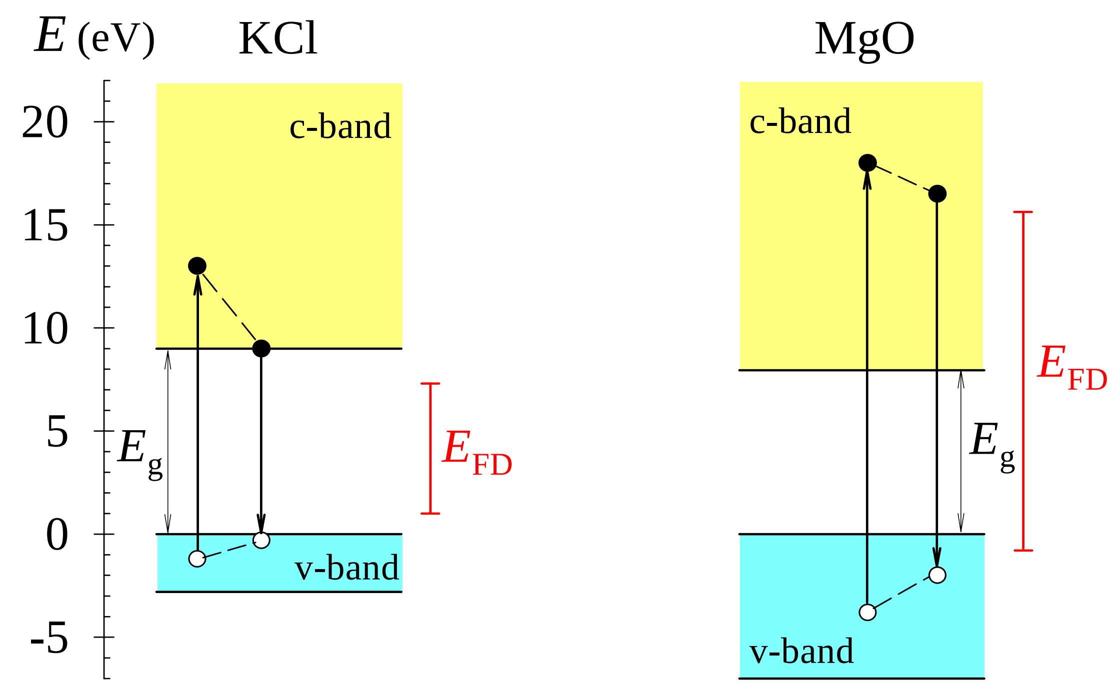
→ *density of radiation-induced electronic excitations.*

Scintillator energetic yield ≤ 1/3, CsI:Tl ~12%

Irradiation providing *low* (e.g., X-rays) *or* ***superhigh excitation density***

(~GeV Au^{197} or U^{238} ions: LET > 20 keV/nm, R~ 50–100 μm,
>99.9% → ionisation losses)

Materials with $\boldsymbol{E_{FD} < E_g}$, Materials with $\boldsymbol{E_{FD} > E_g}$



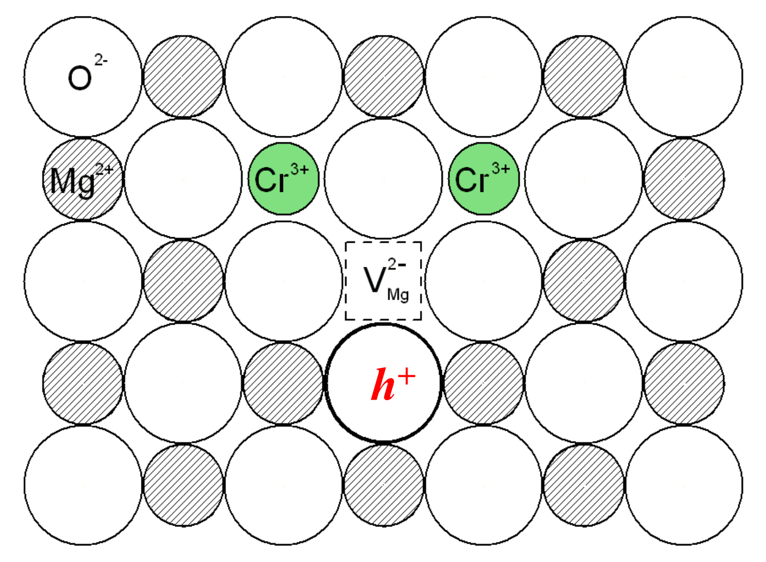
Electronic excitations via transitions from core bands!

E_{FD}- creation energy of an *i*-*v* pair of Frenkel defects

- Pure (< 1 ppm of impurities) and stoichiometric MgO single crystals exhibit extremely high resistance against irradiation

- MgO doped with ~10 ppm of light Be^{2+}, OH^{-} – sharp decrease of resistance

- MgO:Cr^{3+} (~1000 ppm, heavy ^{52}Cr-^{52}Cr)



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

Rhombic pair chromium center containing a cation vacancy

$$e + h[Cr^{3+}\text{-}v_c\text{-}Cr^{3+}]^0 \rightarrow \text{defects}$$

Rhombic center is a trap for a hole that becomes localized at oxygen. Coulomb center possesses a large cross-section for the recombination with electrons (hot conduction electrons or 100–300-eV electrons formed via transitions between inner shells).

Luminescence efficiency of $[Al^{3+}\text{-}v_c\text{-}Al^{3+}]$ is close to 1 at direct excitation (even after X-irradiation), Al^{3+} is two times lighter than Cr^{3+}

Theoretical predictions (A.J. Sievers, V. Hizhnyakov, et al.) – a new kind of discrete vibronic mode (discrete breathers or discrete solitons) with a large amplitude and frequency above the top of the acoustic phonon spectrum can be excited in a crystal lattice predisposed to anharmonic interactions.

A.J. Sievers and S. Takedo, PRL 61, 970 (1988).
M. Haas, V. Hizhnyakov, A. Shelkan, M. Klopov, A. J. Sievers, PRB 84, 144303 (2011).
H. Guo, M. Zhang, J. Han, H. Zhang, N. Song, Physica B 404, 2262 (2012).

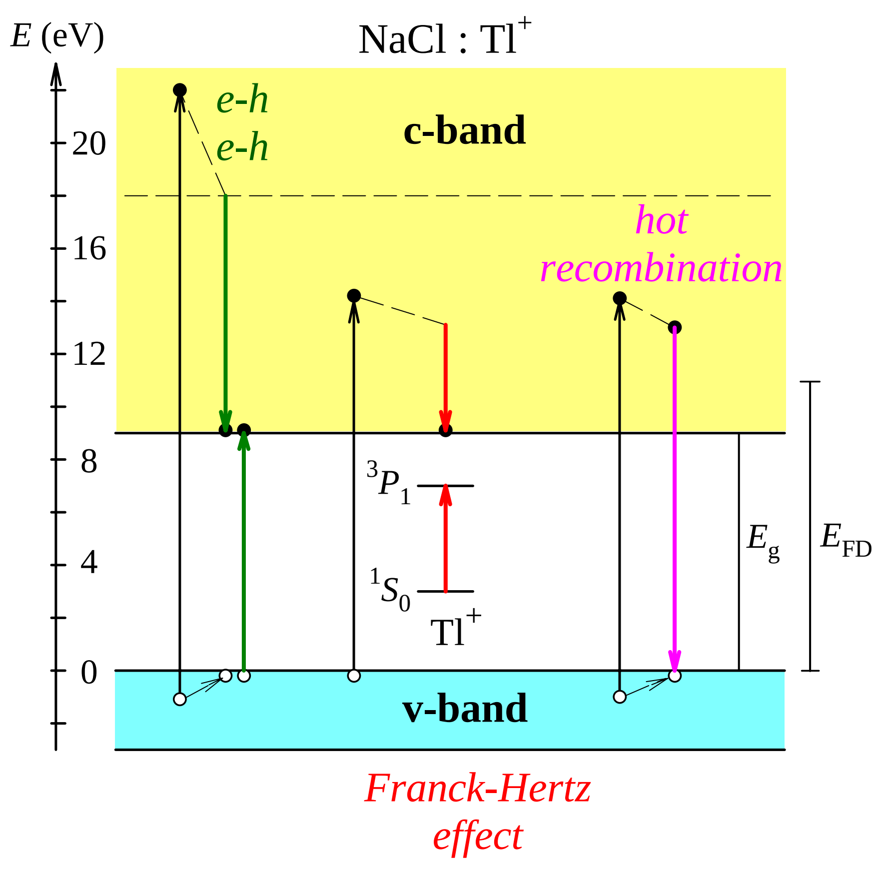
These unusual excitations are expected to be especially strong in wide-gap materials built up of ions with different masses

Under high-dense excitation (e.g., by swift heavy ions)

collapse of discrete soliton → **cooperative rearrangement of many host ions, creation of nanosize 3D defects**

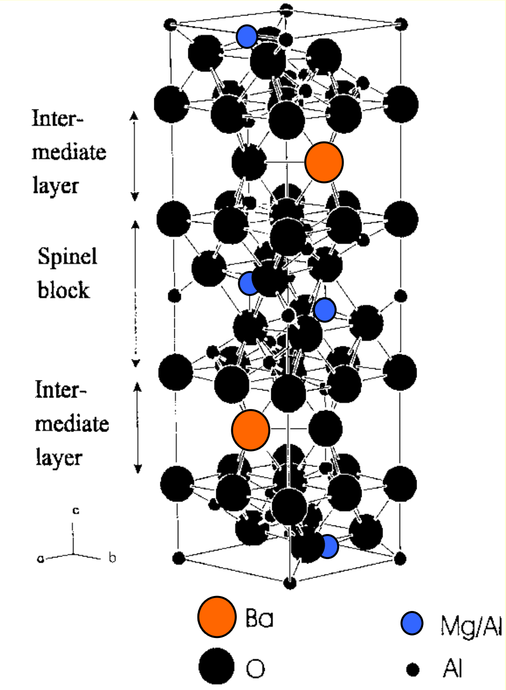
V.E. Zakharov and E.A. Kuznetsov, Phys. Usp. 55, 535 (2012) [UFN 55, 569 (2012)].

“Luminescent protection” against non-impact creation of Frenkel defect in wide-gap materials with $E_{FD} > E_g$.



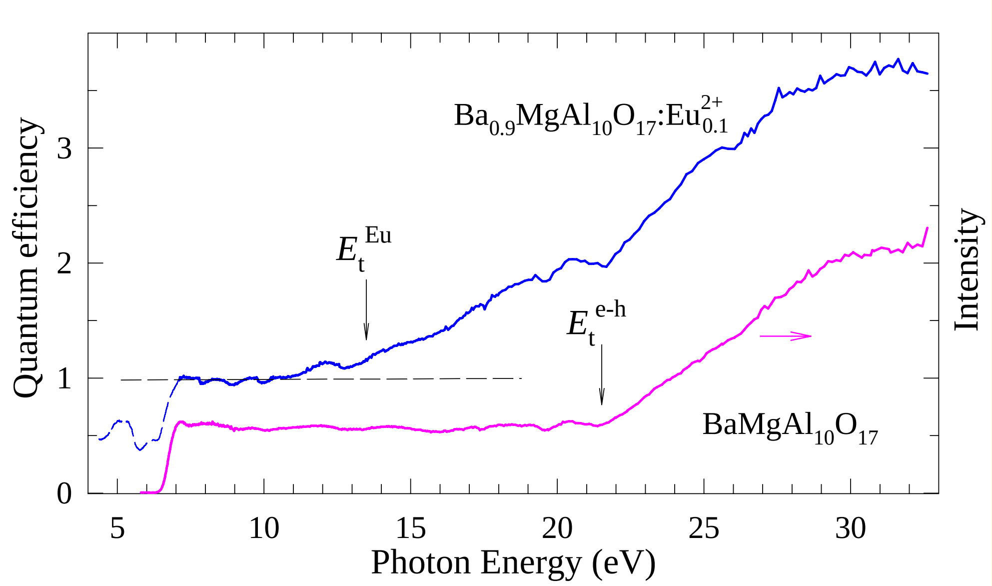
A solid-state analogue of the Franck-Hertz effect – a hot conduction electron can spent its energy excess for the direct excitation of an impurity center, while a subsequent recombination of the cooled *e* with a valence *h* does not create a Frenkel pair.

$BaMgAl_{10}O_{17}$



$Eu^{2+} \Rightarrow Ba^{2+}$

spatially separated 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 demonstrate high QY and reasonably high resistance against electron or VUV irradiation.

In $BaAl_{11}O_{16}N$:Eu – MgO is replaced by AlN and Eu^{2+} is located near 3 aluminum vacancies. As a result, both QY and radiation resistance are lower (similarity with MgO:Cr).

$E_{FD} > E_g$

F^+ centers

Antisite defects

host *impurity*

$Lu^{3+}\big|_{Al^{3+}}$ *or* $Ce^{3+}\big|_{Al^{3+}}$

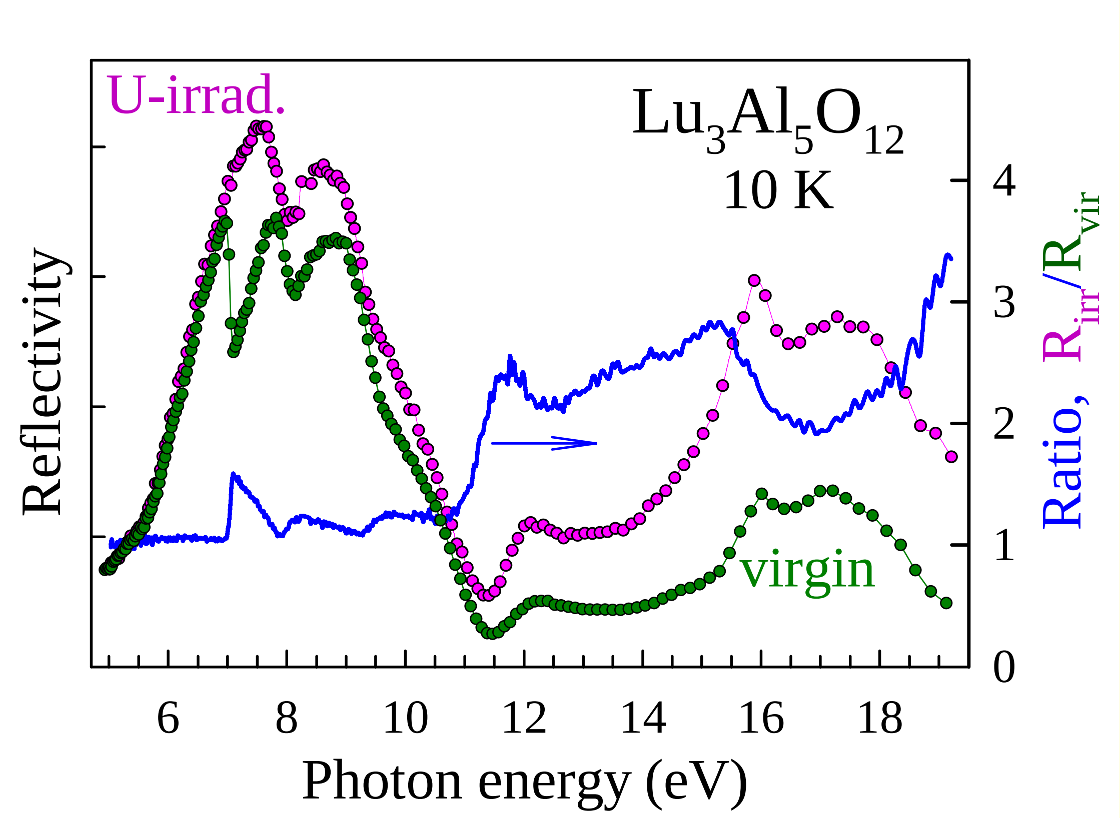
Impurity pairs:

$Ce^{3+}\big|_{Lu^{3+}} - Ce^{3+}\big|_{Al^{3+}}$

↑

place for the collapse of discrete breathers

creation of temperature-stable 3D defects



Reflection spectra of LuAG single crystal before and after irradiation with ^{238}U ions (2.14 GeV, 10^{12} ions cm^{-2}, RT) at 10 K. The ratio R_{irr}/R_{vir}.

Concluding Remarks

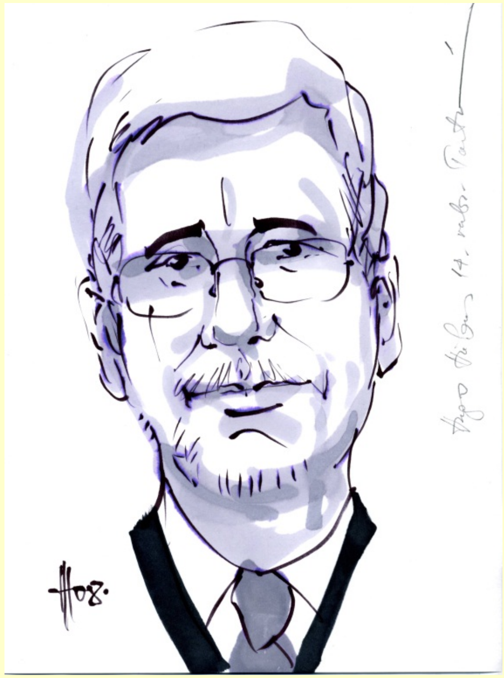
High light yield and acceptable radiation resistance can be simultaneously reached only in doped wide-gap materials where not only *valence* and *ion radius* but also an **atom mass** are close for all elements of a solid solution. CsI:Tl^{+}, $LaBr_3$:Ce^{3+} and $SrBr_2$:Eu^{2+} fulfill all these requirements.

In LiI:Eu^{2+}, $LaCl_3$:Ce^{3+}, CaSO:Tb^{3+},F^{-} both LY and radiation resistance are low even at low impurity concentration.

Especially harmful is the presence of the pairs of spatially close heavy rare-earth impurity ions in cation sites.

Mass disbalance results in the appearance of *discrete breathers*, the collapse of which under high and superhigh excitation density takes place at pair-impurity centers and leads to the creation of complex defects. 3D defects serve as stoppers for dislocations and cause a cracking of single crystals.

It seems that if a pair consists of heavy but different impurity ions (for instance, Ce^{3+} and Tb^{3+}), the formation of a unified complex molecule is unlikely and a material is more resistant against radiation as compared to the presence of pairs of identical RE ions.



THANK YOU