Synchrotron radiation in solid state spectroscopy

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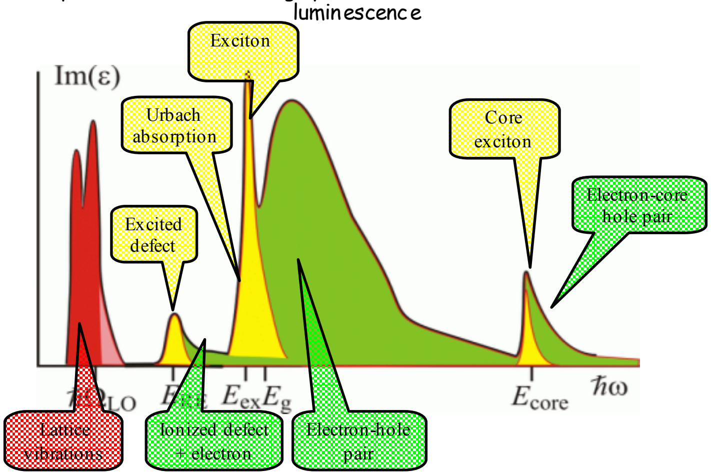
Unique spectral features and time structure of synchrotron radiation allows one to use this kind of excitation in investigation of electronic relaxation processes in insulators with wide band gap. The knowledge of these processes is important for understanding of scintillation efficiency in crystals. Luminescence excitation technique is convenient for study of energy transfer in these systems and for investigation of crystal energy structure.

In general, luminescence excitation spectra can be subdivided into several spectral regions:

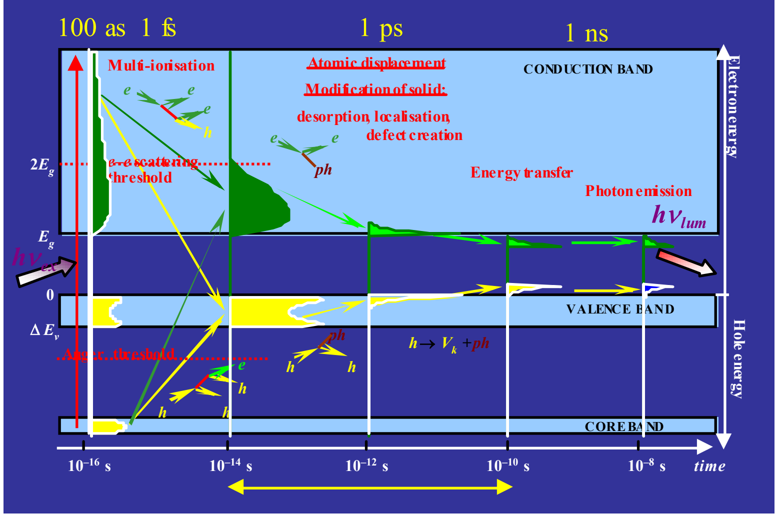
- Direct excitation of lowest defect excited state
- Ionization of defects by photons with energy below the matrix forbidden gap
- Excitation of matrix Urbach tail
- Excitation of excitons
- Production of separated low-energy electron-hole pairs
- Production of high-energy electron-hole pairs followed by impact excitation/ionization of defects

Each of these regions is characterized by different role of relaxation channels. Possible channels of energy transfer and relaxation are discussed in the presentation.

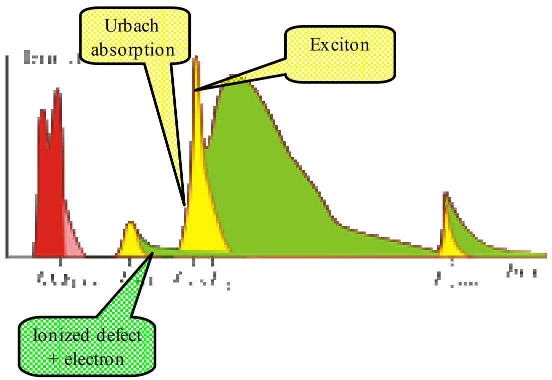
Absorption coefficient in wide photon energy range and different processes studied using synchrotron radiation excitation of luminescence



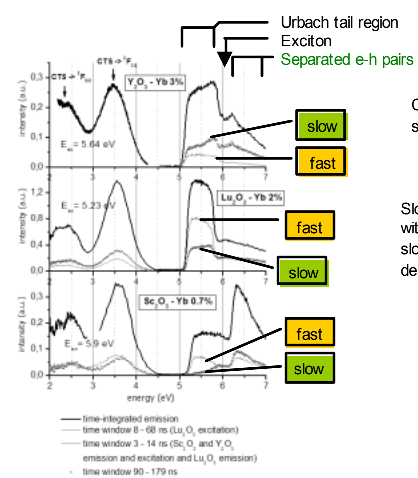
Dynamics of electronic relaxation in wide bandgap solids

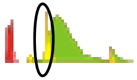


- Ionization of defects by photons with energy below the matrix forbidden gap
- Excitation of matrix Urbach tail



Yb^{3+} charge transfer luminescence (CTL) excitation (Guerassimova et al)

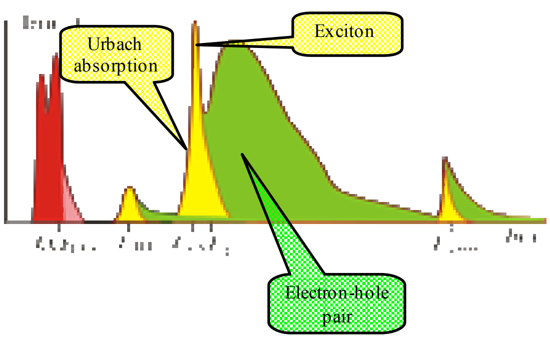




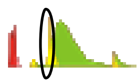
CTL spectra and excitation of CTL spectra of sesquioxides measured with different time windows, temperature 10 K.

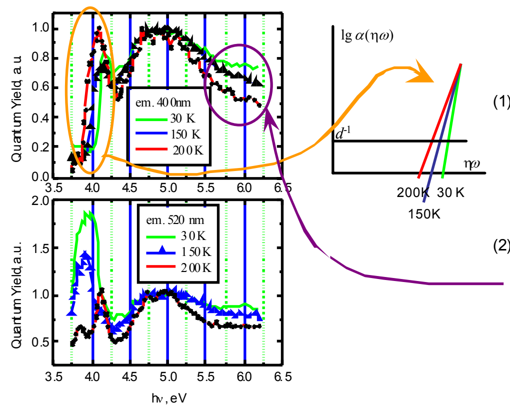
Slow/fast emission ratio increases with energy in Urbach tail region, i.e. slow component increases with delocalization.

- Excitation of matrix Urbach tail
- Excitation of excitons
- Production of separated low-energy electron-hole pairs



Urbach tail effect in PbWO$_4$ excitation spectra





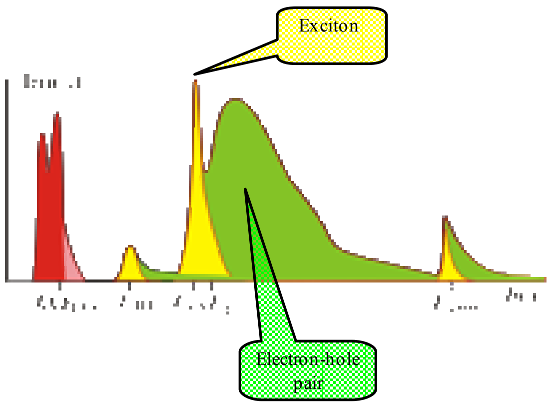
Temperature dependence of PWO excitation spectra shows two phenomena:

(1) dependence of excitation spectrum in Urbach absorption region due to change of the fraction of absorbed radiation in the sample and

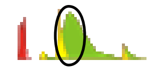
(2) increasing of the slope of quantum yield with T in the region of separated e-h pairs (see below)

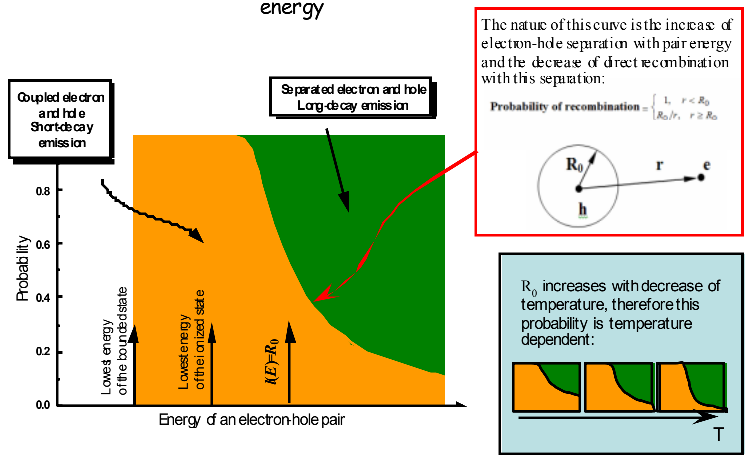
PWO excitation spectra for blue (top) and green (bottom) emission bands

- Production of separated low-energy electron-hole pairs

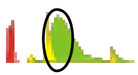


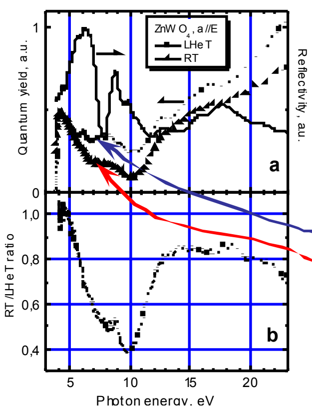
Probability of binding or separation of the components of an electron-hole pair vs their energy



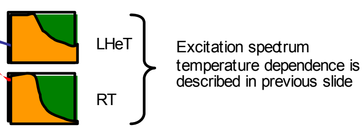


The effect of electron kinetic energy on the efficiency of energy transfer to the luminescence center as a function of temperature (Spassky et al)

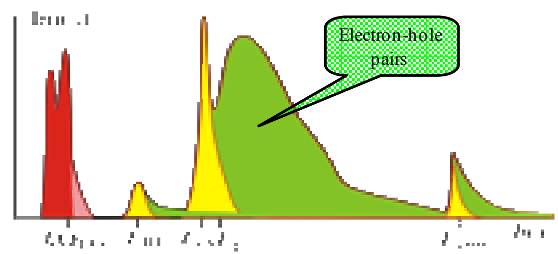




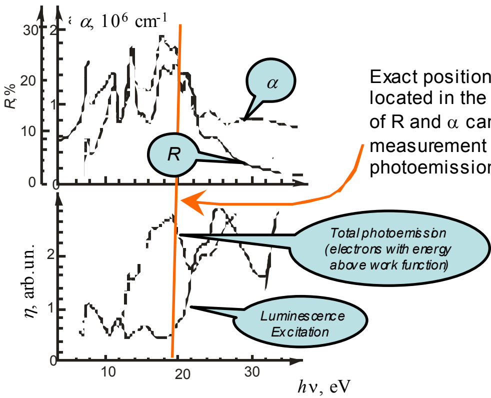
$ZnWO_4$:
(a) –quantum yield spectra at RT and LHeT and reflectivity (thin curve);
(b) – the ratio of the above quantum yield spectra.



- Production of high-energy electron-hole pairs followed by impact excitation/ionization of defects

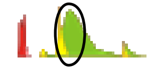


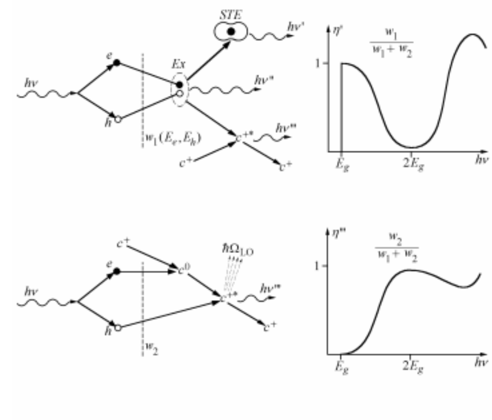
MgO:Al – threshold of multiplication of electronic excitations (Ch. Lushchik, Mikhailin et al)



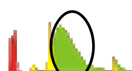
Exact position of e-e scattering threshold located in the region of abrupt decrease of R and α can be estimated using measurement of luminescence and total photoemission excitation spectra

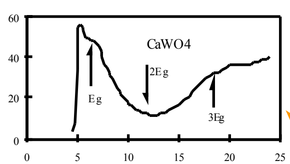
Two types of recombination channels: excitonic one (upper part) and recombination on a centre (lower part).
Figures on the right display typical energy dependence of the quantum yield of these channels





Experimentally observed two types of recombination channels





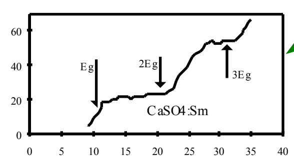
Luminescence excitation spectra of intrinsic luminescence of

$CaWO_4$ (upper panel) [S. I. Golovkova, A. M. Gurvich, A. I. Kravchenko, V. V. Mikhailin, A. N. Vasil'ev, Phys. Stat. Sol. (a), 77 (1983) 375]

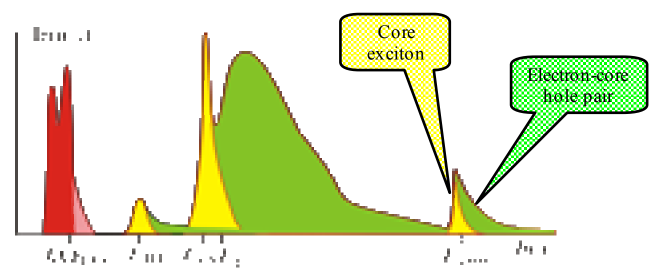
and

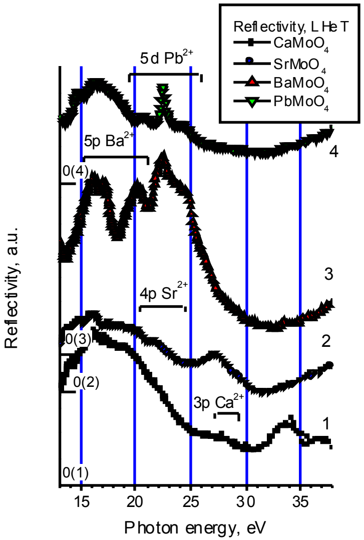
activator luminescence of

$CaSO_4$:Sm [I. A. Kamenskikh, V. V. Mikhailin, I. N. Shpinkov and A. N. Vasil'ev, Nucl. Instr. and Meth., A282 (1989) 599] (middle panel)



- Manifestation of core excitons in optical functions in VUV reguion



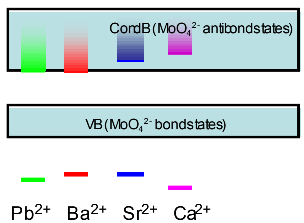


Manifestation of core excitons in in optical functions in VUV region

Intensity of core exciton peaks correlates with the nature of the bottom of the conduction band (Kolobanov, Spassky et al)

Cation core excitons are visible only if the lowest states of conduction band are formed from cation states (Pb and Ba molibdates).

Reflectivity shows no structure in core exciton region if the lowest states are formed from complex anion states (Sr and Ca molibdates).



The reasons of light yield instability induced by radiation

•Creation of the reversible damage:

a) transient defects - close *F*-*H* pairs

b) Change of electronic state of deep defect levels in the forbidden energy gap

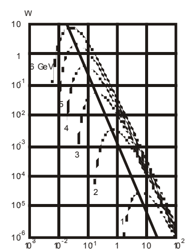
•Creation of the irreversible damage:

a) stable *F*-*H* pairs

b) defect conglomerates

Benefits of VUV and X-ray SR in radiation damage study

- VUV (especially XUV) and X-ray photons produce the same spectrum of elementary electronic excitations (electron-hole pairs, excitons, core level excitations, initial defect formation stages) as high-energy ionizing particle
- Absorption coefficient in XUV and X-ray region is extremely high (10^4 to 10^6 cm^{-1}), therefore accumulated dose in the thin absorption layer becomes huge
- Unique spectral features and time structure, and high intensity of synchrotron radiation allow one to use this kind of excitation in investigation of defects and their creation in insulators with wide band gap.



SR spectral distribution for various electron energy (R=32 m)

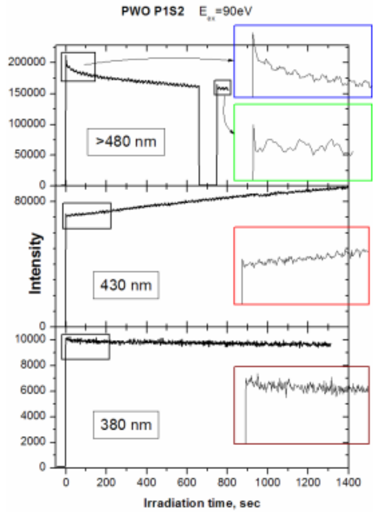
How to study radiation effects using luminescence spectroscopy

- Changes of luminescence emission spectra (additional emission bands)
- Changes of decay kinetics (radiation defects can result in sharpening of initial stages of decay and increasing of slow component)
- Changes of energy transfer (radiation defects can change ratio of several relaxation channels)

Usage of SR in X-ray region in the study of PWO radiation hardness

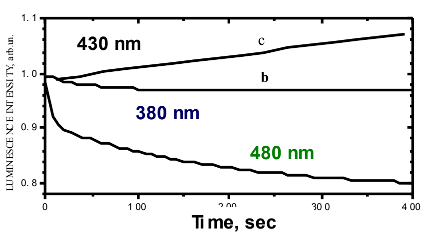
- •VEPP-3 (Budker INP): Flux of 10^{16} ph/s with energy from 2 to 100 KeV (“white” X-rays)
- •DCI (Lure, Orsay): Flux of 10^{12} ph/s of monochromatized 15 KeV X-ray photons

Radiation damage in PWO



- Dose rate is about 1 kGy/sec (in thin absorption layer, d~ 10^{-5} cm)
- Degradation / enhancing of emission under irradiation depends on the emission spectral region
- Fast and slow recovering of radiation defects (upper panel)

Dose dependence for different regions of PWO emission spectrum excited by X-ray SR



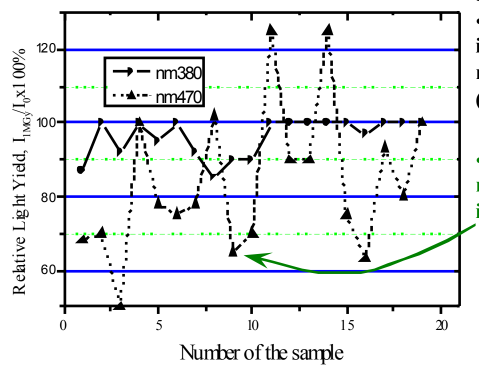
(a) Green emission (480 nm) – fast degradation at first 10 sec followed by much slower degradation

(b) Blue emission (380 nm) is more stable under irradiation

(c) Few cases of increase of emission in intermediate range (430 nm) under irradiation – the evidence of new emission center production

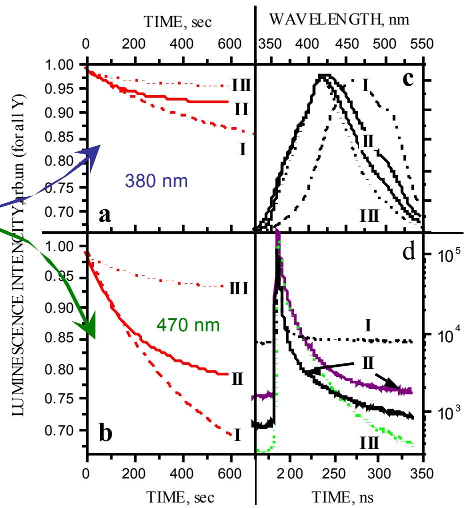
Lead Tungstate scintillators

- •20 $PbWO_4$ crystals of first generation
- •1 MGy dose accumulated in thin surface layer in 10 min, 15 KeV excitation (DCI, Orsay)

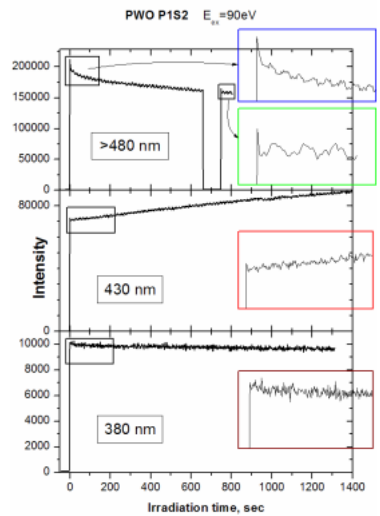


•green emission is much more sensitive to irradiation

Correlation between the radiation induced variation of light yield and the profile of emission spectrum, decay kinetics and the shape of optical transmission (I, II and III - different samples)



Excitation by 90 eV photons (SuperACO)

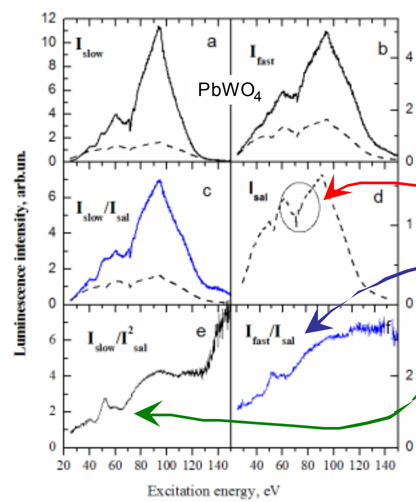


- Dose rate is about 1 kGy/sec (in thin absorption layer, d~10^{-5} cm)
- Degradation / enhancing of emission under irradiation depends on the emission spectral region
- Fast and slow recovering of radiation defects (upper panel)

PWO emission spectrum explanation

- Fast (blue) component – excitonic (Pb) emission, (should be linear with excitation intensity)
- Slow (green) component – defect recombination emission, (should be non-linear (quadratic?) with excitation intensity)

How to measure nonlinear excitation efficiency?



Modulation of SR spectrum by the grating spectral efficiency with sharp peculiarities allows one to estimate the order of the process

Sharp structure due to Pt covering of the grating dissapiars in

1st order fast PWO emission

and

2nd order slow PWO emission

Conclusions

Fundamental mechanisms of electronic relaxation in large bandgap solids and energy transfer can be studied by analysis of luminescence excitation spectra and kinetics excited by VUV-X synchrotron radiation photons, especially using Time-Resolved Luminescence VUV Spectroscopy.

High flux of SR enables to simulate and investigate radiation damage effects.