Deep understanding of advanced optical and dielectric materials for fusion diagnostic application

Anatoli I. Popov, E Kotomin, V Kuzovkov, A Lushchik, Theo A Scherer



Anatoli Popov

popov@cfi.lu.lv
a.popov@cern.ch
popov@ill.fr
popov_a@enu.kz

Dr. Anatoli I. Popov

Leading research scientist, Institute of Solid State Physics, University of Latvia

H= 37, > 250 paper, > 4000 citations

1978 - 1984	**M.S.+B.S. degrees: Department of the Molecular and Chemical Physics (1978-1982), Department of General and Applied Physics (1982-1984), Moscow Institute of Physics and Technology, MIPT,**
1990	**Ph D in Physics, Institute of Physics, The Latvian Academy of Sciences**
1993	**Dr in Physics, Institute of Solid State Physics, University of Latvia**

RESEARCH INTERESTS

Radiation damage of insulators. Point defects. Optical properties of insulators. Luminescence. VUV, IR and FTIR spectroscopy. Synchrotron radiation spectroscopy (VUV, XD, XAS, EXAFS, FTIR). Neutron imaging and spectroscopy. **Scintillators.** Storage phosphors. Dosimetry and radiation imaging etc.

INTERNATIONAL ACTIVITIES

Long-term Collaboration with EUROfusion, CERN, ILL, ESS, MAX-IV, DESY.

Visiting professor Eurasian National University (Nur-Sultan, KZ) - 7PhD students (since 2020)

B**oard member of Fusion Science Department at EUROfusion**

Board member on Materials in **EUROfusion** enabling research programme.

Board member of Crystal Clear Collaboration at **CERN**

Distinctive features of diffusion-controlled defect recombination in irradiated functional ceramics for nuclear applications

The industrial progress of 21^{st} century could greatly benefit from development and exploitation **of fusion reactors producing environmentally clean friendly electrical energy**. One of a key problem here is need in new advanced materials able to operate under extreme conditions (high temperatures and intensive neutron/gamma radiation). **Search for such optical and dielectric materials is an essential part of EUROfusion-*Latvia* association activities.**

In this talk, I will give short overview of the most interesting results obtained in the framework two EUROfusion Enabling Research Project - "**Advanced experimental and theoretical analysis of defect evolution and structural disordering in optical and dielectric materials for fusion applications (AETA)**" (2019-2020) and "**Investigation of defects and disorder in nonirradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis** " (2021-2023).

In a series of joint works by ISSP UL (Latvia), UT (Estonia) and KIT (Germany), radiation damage of some promising functional materials from the priority list of the EUROfusion consortium was studied under neutron, proton, heavy ion and gamma irradiation.

The optical and dielectric, vibrational and magnetic properties of numerous crystalline and ceramic materials were carefully studied. Based on this study, we developed new theoretical methods able to evaluate and predict advanced materials functionality and radiation damage evolution under extreme reactor conditions.

OUR RECENT EUROfusion PROJECTS:

Eurofusion Enabling Research Project (2019-2020) 1.2 M €
Advanced experimental and theoretical analysis of defect evolution and structural disordering in optical and dielectric materials for fusion applications (AETA)
joint with Karlsruhe Institute of Technology (Prof. Theo Scherer)

EUROfusion Functional materials programme 560 k €
(WP-15-PPPT-MAT, **(2014-2020)**
“**Multiscale modelling of radiation effects in $MgAl_2O_4$ materials and general oxides**”

Enabling research (HORIZON 2020) **596 k€**
“**Investigation of defects and disorder in non-irradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis**”
Responsible person (ISSP): **A. Popov**
Partner Institutes : University of Tartu (Prof. A. Lushchik) and
Karlsruhe Institute of Technology (KIT) (Prof. T.A. Scherer)
Duration: 2021-2023

Functional materials (HORIZON 2020) **530 k€**
“**Multiscale modelling of radiation effects**”
Duration: 2021-2025

HORIZON 2020 RISE-RADON Project **"Irradiation driven nanofabrication: computational modelling versus experiment“ (PI -** MBN Research Center, Frankfurt-M, Germany) Duration: 2021-2025

Mobility

Eurofusion Projects: Research Tasks :

Multiscale theory and modelling of functional materials for diagnostics;

Kinetics of radiation defect creation and recombination;

First principles large scale modelling of radiation defects and processes;

Critical comparison of different types of irradiation (electrons, protons, neutrons, heavy swift ions);

Peculiarities of diffusion-controlled recombination kinetics at high radiation fluencies;

Comparison of radiation properties of single crystals and ceramics;

Combination of different experimental studies (optical, EPR, Raman etc) and multiscale computer modelling

Synchrotron and neutron measurements (VUV, neutron scattering)

What I will tell you today:

- **We have performed a detailed analysis of the kinetics of F-type center thermal annealing in the irradiated MgO, MgF_2 , Al_2O_3, $MgAl_2O_4$ etc**
- **F center annealing depends on the type of the irradiation as well as fluence**
- **Macroscopic disordering of the crystalline structure (cf. electron and neutron/ion irradiation results) Meyer–Neldel rule in MgO, MgF_2 , Al_2O_3 and $MgAl_2O_4$**
- **In strongly irradiated ionic solids radiation defect migration is not necessarily characterized by unique migration energy with constant pre-exponent!**
- **In some cases, the experimental data allows to obtain the activation energy for migration. This makes data analysis complicated**
- **Similar results are in progress for many other materials: $Y_3Al_5O_{12}$, CeO_2, BeO etc., We need more experimental data. We need more samples.**
- **Note that this is one of few first attempts to quantify the kinetics of the defect annealing in these materials which needs further detailed analysis.**
- **Short progress report on EUROfusion ENR project "Investigation of defects and disorder in non-irradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis“.**

Research Materials - EUROfusion projects

List of candidate ceramics for each component and materials irradiated in the course of T246 of ITER-EDA (Shikama et al, JNM,1999)

ITER-EDA =International Thermonuclear Experimental Reactor, Engineering Design Activities

- Diamond
- MgO
- Al_2O_3
- BeO
- $MgAl_2O_4$
- AlN
- SiO_2
- TiO_2
- ZnSe

Diagnostic components	Primary candidate materials	Irradiated materials
Ceramics for insulator	• Alumina (Al_2O_3) • High purity silica glass	Alumina, silica glass, BeO, AlN, Si_3N_4, $MgAl_2O_4$, MgO, pyrolitic BN
Windows-1 (300–1200 nm)	• High purity quartz and fused silica (SiO_2) • Single crystal alumina (sapphire)	Sapphire, quartz, fused silica glass KU quartz[a]
Windows-2 (2000–5000 nm)	• High purity quartz and fused silica (SiO_2), same as shorter wavelength	Single crystal alumina (sapphire), fused silica
Window-3 (10 mm)	• ZnSe	
Window-4 (100–10 mm)		Diamond, silica
Fiber optics UV to IR (300 nm to 5 mm)	• Low OH, pure silica core, F-doped cladding, aluminum jacket	Quartz, core(pure silica)/clad (F-doped silica) • Improved type, core (pure SiO_2)/clad(F-doped SiO_2), low OH-content (from 1 to 100 ppm), 2 samples, Al jacket or High OH-content (300 ppm) polymer or Al jacket,
	• Fluorine-doped core fiber • Hydrogen-treated fibers • Gamma hardened fiber	• F-doped SiO_2 core • Gamma hardened fibers • Single crystal fibers
Mirrors/reflectors-2 Secondary mirror (UV/visible/infrared)	Aluminum-coated spinel ($MgAl_2O_4$)	
Mirrors/reflectors-3 High-power laser mirror (laser mirror and collection systems) (UV/visible/infrared)	• HfO_2/fused silica • TiO_2/fused silica	High-power laser mirror (laser mirror and collection systems)
Mirrors/reflectors-4 (X-rays 1–500 Å)	• Various diffraction crystals • Layered synthetic microstructure (LSM)	LSM
Mineral-insulated cables	• MgO, stainless steel sheath, nickel or copper center with diameter from 0.3 to 2.3 mm OD • Other insulator	• Al_2O_3, MgO, MgO-insulation; Ni, NiCr, SS-wire; SS-shield • Ten different improved MI cables
Ceramic coated wire		• 70$MgAl_2O_4$ + 30Al_2O_3, plasma spraying insulation, Ni-wire

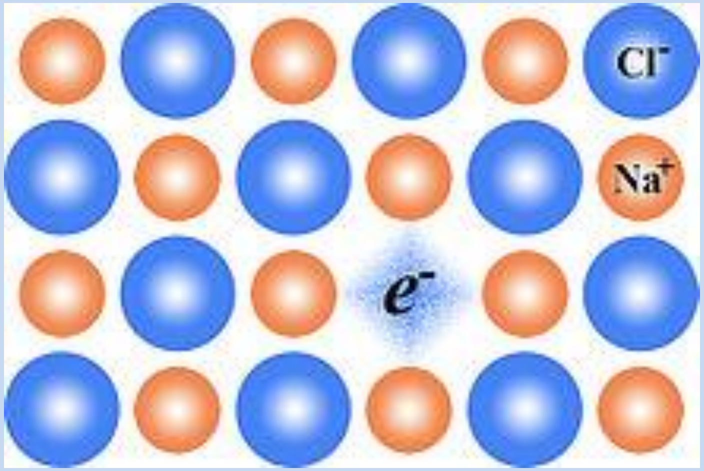
[a] KU1 (round-robin materials)

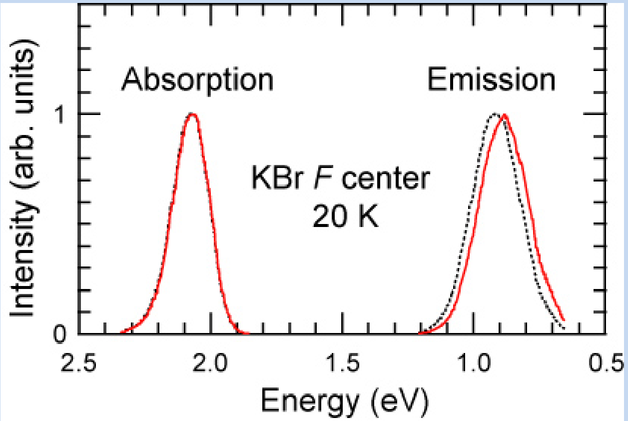
F center in alkali halides:

(from the original German Farbzentrum; Farbe means color, and zentrum center)

F- center **is a type of crystallographic defect in which an anion vacancy in a crystal is filled by one or more unpaired electrons (NaCl as an example)**

Different type of charged and neutral F_2=M; F_3 = R , F_4=N etc





F-type center:

scintillators (CsI, BaF_2 etc), TLD materials (LiF, Al_2O_3 etc), color center laser applications (LiF, NaCl etc), photostimulable storage phosphors (BaFBr, CsBr etc) and many others.

Resistant and sensitive materials

- **Resistant**:

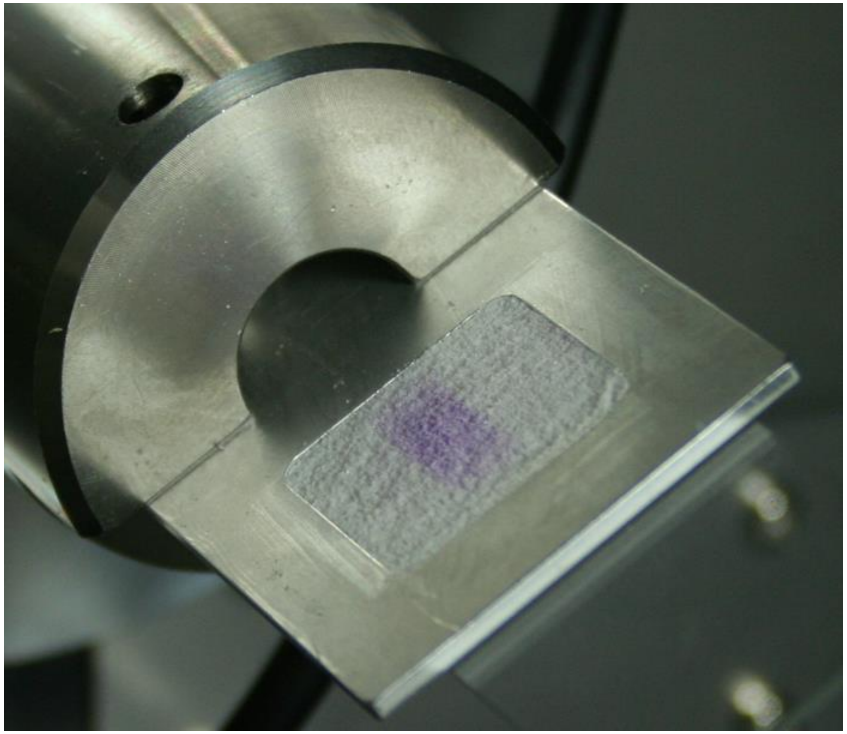
Metals, semi-conductors.
Crystalline Oxides: MgO, Al2O3, BeO, MgAl2O4
Nitrides: AlN, Si_3N_4
metastables (c-SiO2) **etc**

- **Sensitive:**

Alkali halides
Alkaline-earth halides CaF_2, MgF_2, SrF_2 :
$KMgF_3$, BaFBr, $LiYF_4$:
Silver halides AgCl; AgBr
Amorphous solids a-SiO_2 , a-As_2Se_3, a-As_2S_3, a-Se, a-As

Water and organic mater (bio matter)

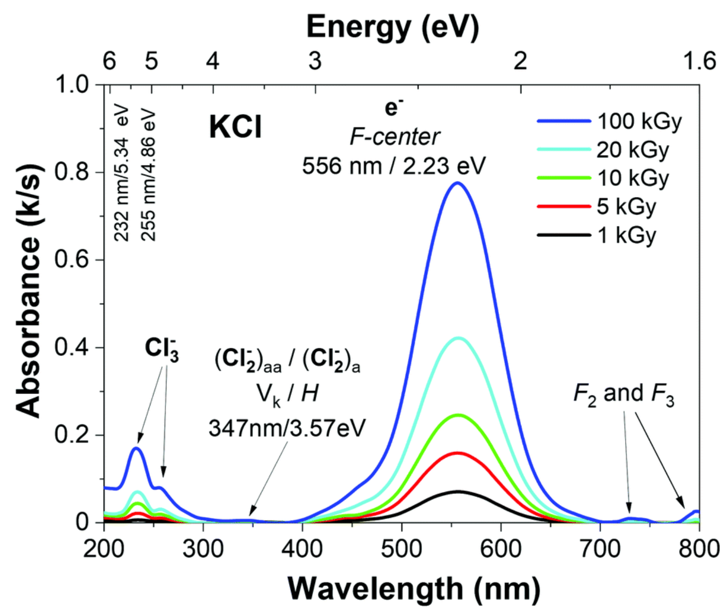
Short note on radiation damage:



Radiation damage is very important and needs to be studied in details.

In many cases it is due to the formation of structural crystal lattice vacancies and interstitials, changing many functional properties, including optical absorption (change of the colour) and luminescence .

One of the most simple examples:
KCl single crystal.
Violet color of the part of the sample that was in the beam of the X-rays.



Phys. Chem. Chem. Phys., 2021,**23**, 10384-10394

Properties of Materials that may be changed by irradiation

Dimensional swelling
Mechanical properties, e.g. yield stress, toughness
Stored energy
Electrical conductivity
Thermal conductivity
Dielectric behaviour
Optical properties
Magnetic properties
Chemical reactivity
Decomposition

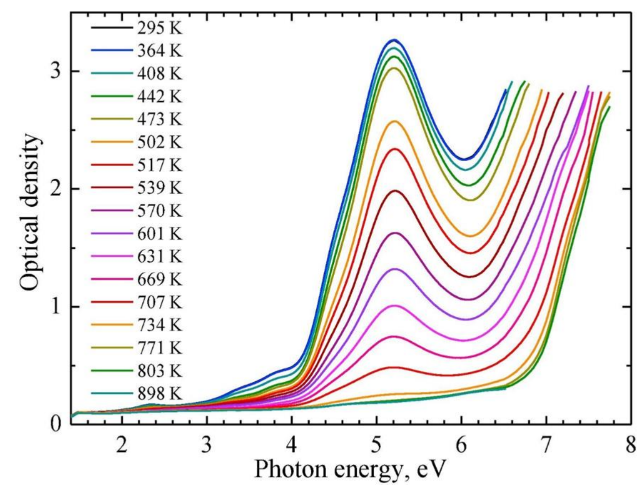
Neutron-irradiated $MgAl_2O_4$

Properties for examination:

a) permanent radiation damage (point defects etc) and corresponding photo& thermostimulated recovery.

b) transient optical absorption and Radioluminescence

c) saturation of radiation damage



Radiation Damage Processes

1. Electronic processes

2. Elastic collisions

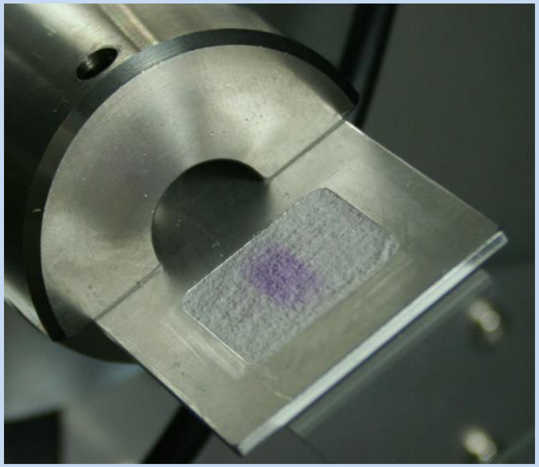
Five types of radiation may produce displaced atom or ions (1) γ- rays, (2) energetic electrons, (3) thermal neutrons, (4) fast neutrons, (5) energetic atoms or ions

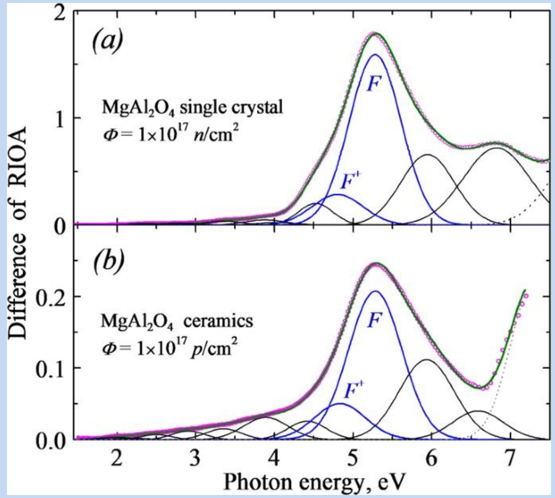
3. Radiolysis

(1) Electronic excitation $\rightarrow$creation of a polarized or charged electronic defects
(2) Conversion of this energy into kinetic energy of a lattice ion $\rightarrow$ ion moves
(3) The motion and stabilization of the ion.
Very often observed in photoexcitation

Properties of Materials that may be changed by irradiation

X-ray -irradiated KCl

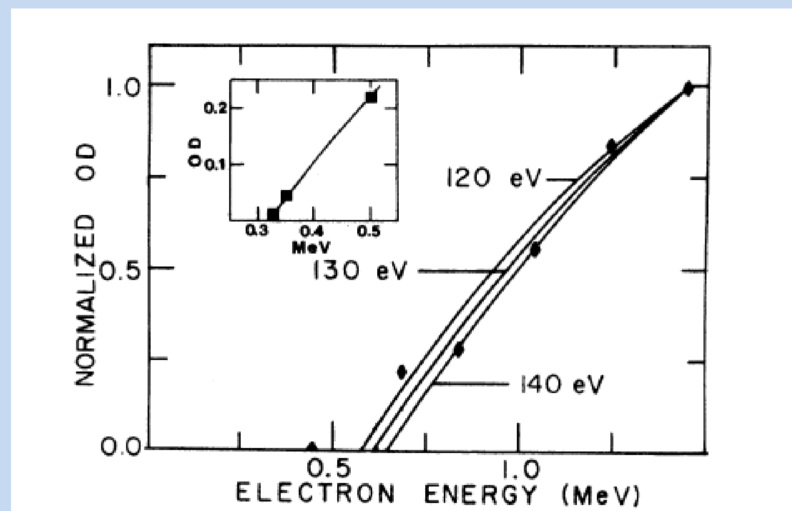




Neutron-irradiated $MgAl_2O_4$

MAIN DIFFERENCES:

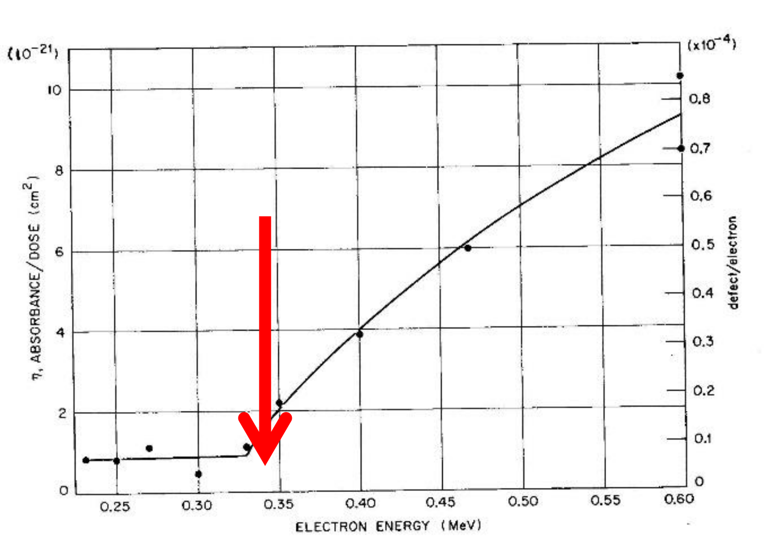
1. permanent radiation damage (new point defects) in **KCl** is produced by photons (E> Eg) **while in oxides (MgO, Al2O_3, $MgAl_2O_4$ etc), new vacancy and interstitial are produced only by energetic particles**
2. under neutrons there are some such effects that are never observed under normal conditions (activation, swelling etc)



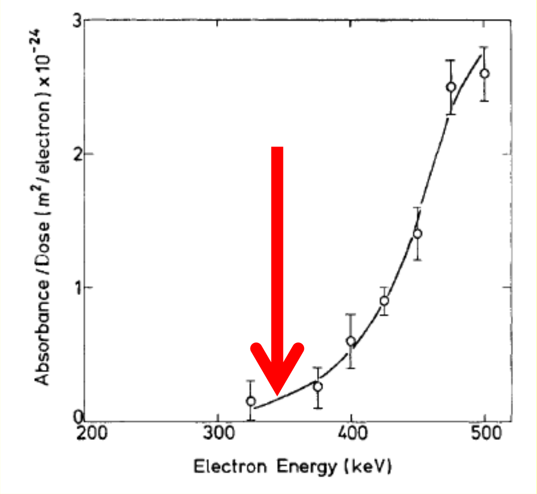
OD of F centers as function incident electron energy at RT.

Mechanism of elastic collisions (knock-out) - MgO

F –band growth as a function electron energy (Chen(1969); Pells (1982)



MgO
E_d



MgO, CaO, $MgAl_2O_4$, $SrTiO_3$ etc ($E_{FD} > E$g)

Rapid impact (knock-out) mechanism – elastic collisions of incident particles with the atoms. Threshold displacement energy (E_d) is about 50–60 eV.

$$E_d = 2E(E+m_0c^2)/Mc^2$$

E –energy of incident electrons (accelerating voltage),

m_o - the rest mass of an electron, M - mass of the displaced atom,

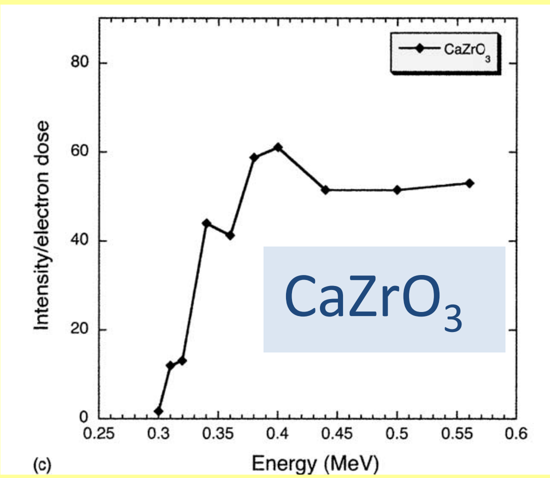
c - the velocity of light.

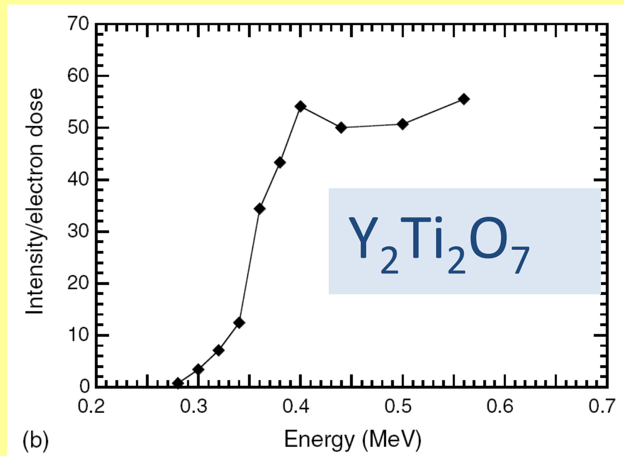
Threshold energy in oxygen compounds

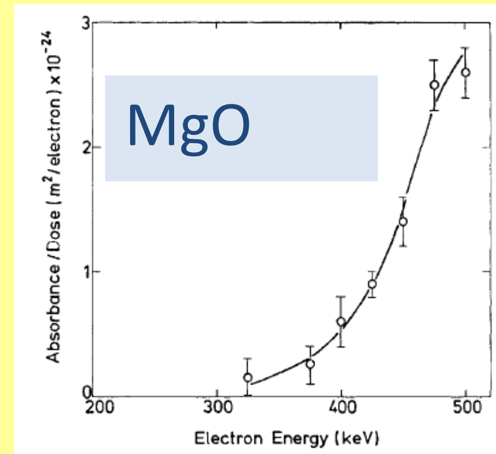
What is important to know:

E_d (oxygen) in all oxides lies between 39 and 58 eV

E_d (oxygen) does not correlate with either the coordination of the oxygen site or the average oxygen–anion bond length (Smith KL et al . (2003). *J. Nuclear materials*, ***321***,19).







The luminescence intensity per unit dose was measured as a function of electron beam energy over the range 0.2–0.6 MeV

If a threshold is observed to occur at an incident electron energy E, then T_m is equal to the displacement energy E_d of the atom or ion in the lattice whose displacement gives rise to the short-lived defect in excited state.

What we know about F-type centers in oxides

Material	F center		F⁺ center	
	Absorption	Luminescence	Absorption	Luminescence
MgO	5.0	2.3	4.9	3.1
CaO	3.1	2.1	3.7	3.3
SrO	2.49		3.0	2.42
BaO	2.3		2.0	
BeO	6.3, 6.6	4.9, 3.4	5.35	3.92
ZnO			2.95	2.38
Al_2O_3	6.0	3.0	6.3, 5.4, 4.8	3.8
Li_2O		3.65	4.00	3.26
$LiAlO_2$		4.43	5.25	3.26
$MgAl_2O_4$	5.3		4.8	
$Al_{23}O_{27}N_5$	5.46		5.00	
$YAlO_3$	5.84, 5.15	2.95	6.5, 5.63, 4.3	3.49
$Y_3Al_5O_{12}$	6.35, 5.16	2.7	5.27, 3.35	3.1

Popov, A. I., Kotomin, E. A., & Maier, J. (2010). Basic properties of the F-type centers in halides, oxides and perovskites. *Nuclear Instruments and Methods B 268*(19), 3084-3089.

Kotomin, E. A., & Popov, A. I. (1998). Radiation-induced point defects in simple oxides. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *141*(1-4), 1-15.

Experimental measurements of optical properties for dimer centers in oxides, energies are in eV

Material	F_2		F_2^+		F_2^{2+}	
	Absorption	Lumin	Absorption	Lumin	Absorption	Lumin
MgO	3.63 [48]	3.31 [48]		2.61 [49]	3.82 [49]	2.81 [49]
Al_2O_3	4.1 [50]	2.4 [50]	3.5 [50]	3.26 [50]	2.7 [50]	2.22 [50]
$MgAl_2O_4$	3.45 [13]	3.3 [13]				
$Al_{23}O_{27}N_5$	4.1 [25]		3.68 [25]	3.13 [25]		
Li_2O	3.31 [18]		2.16 [16]			

Samples - EUROfusion projects

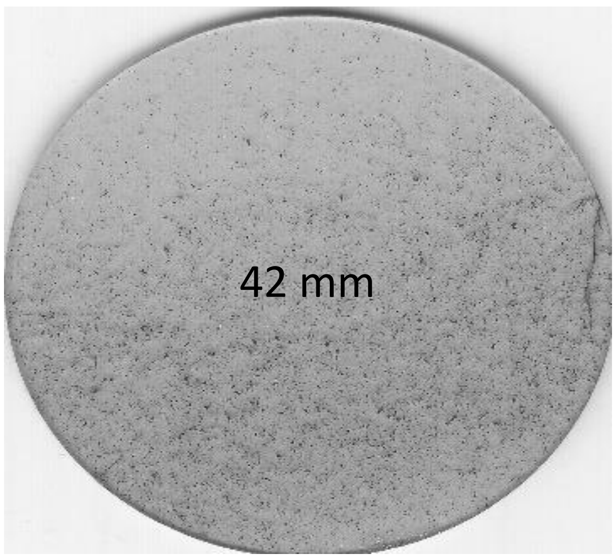
Neutron irradiated Al_2O_3 samples
in Petten 1998 -1999)

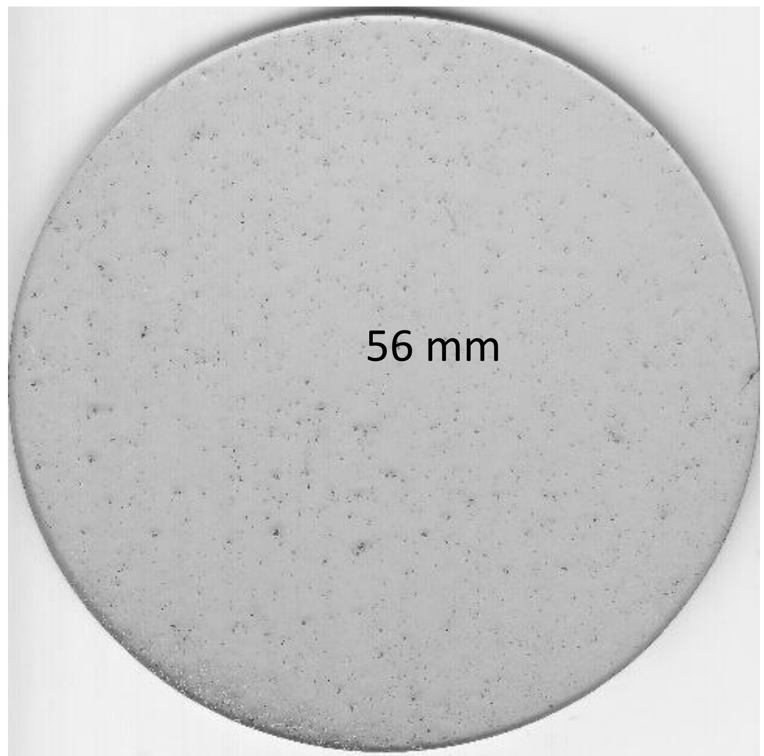
No.	Formula	Synthesis/ dopant	Neutron irradiation Dose
1	Al_2O_3	Sintered	10^{21} n/m^2
2	Al_2O_3	V	10^{21} n/m^2
3	Al_2O_3		10^{21} n/m^2
4	Al_2O_3		10^{22} n/m^2
5	Al_2O_3	Sintered	10^{23} n/m^2
6	Al_2O_3	V	10^{23} n/m^2
7	Al_2O_3	Sintered	10^{23} n/m^2
8	Al_2O_3	V	10^{22} n/m^2
9	Al_2O_3	Ni	10^{21} n/m^2
10	Al_2O_3	Ni	10^{22} n/m^2

Neutron irradiated CVD diamonds, silica and alumina
From KIT - 2017

Characterization of CVD diamond disks (work in progress)

Undoped polycrystalline diamond disks with a respectable size from several tens of millimeters up to 180 mm produced by <u>plasma assisted chemical vapor deposition</u> (PACVD) in a microwave reactor are state of the art in **functional optical and dielectric windows.** Diagnostics, heating and current drive systems need these components as filters for well-defined frequency bands in IR, VIS, UV-VUV, microwaves and sub-millimeter waves (THz-range) as well as window materials for transmission of low and high-power electromagnetic waves.





Insulators vs metalls – extra complications

Materials of interest: MgO, Al_2O_3, $MgAl_2O_4$, CeO_2, MgF_2, BeO etc

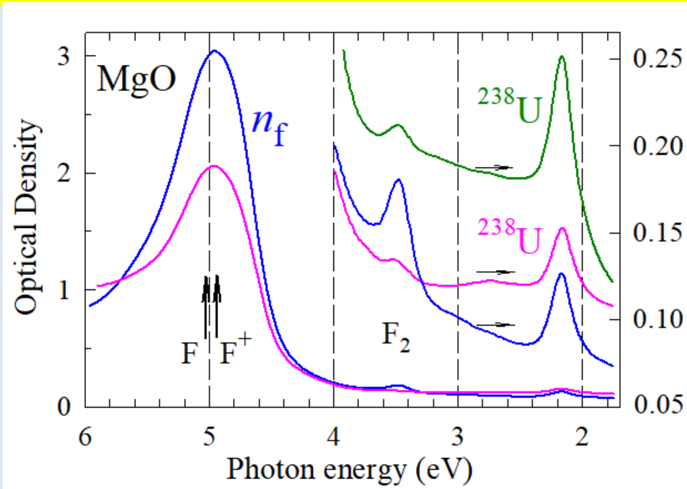
There are extra complications that give radiation effects in insulators a special place, both from the point of view of assessing and understanding their behaviour. These can be listed as follows.

1. There are generally two or more sublattices in the structure that do not readily tolerate mixing, unlike even ordered alloys.
2. There are therefore more types of defects, including different charge states.

MgO - 3 types of oxygen vacancies and interstitials
plus
3 types of Mg vacancies and interstitials

3. Atomic displacement rates and defect mobilities may be different on each
4. Defects on one sublattice may influence those on another.
5 Defects may in some cases be produced or influenced by purely electronic excitation as well as by atomic collisions.

F center thermal annealing in oxides: MgO

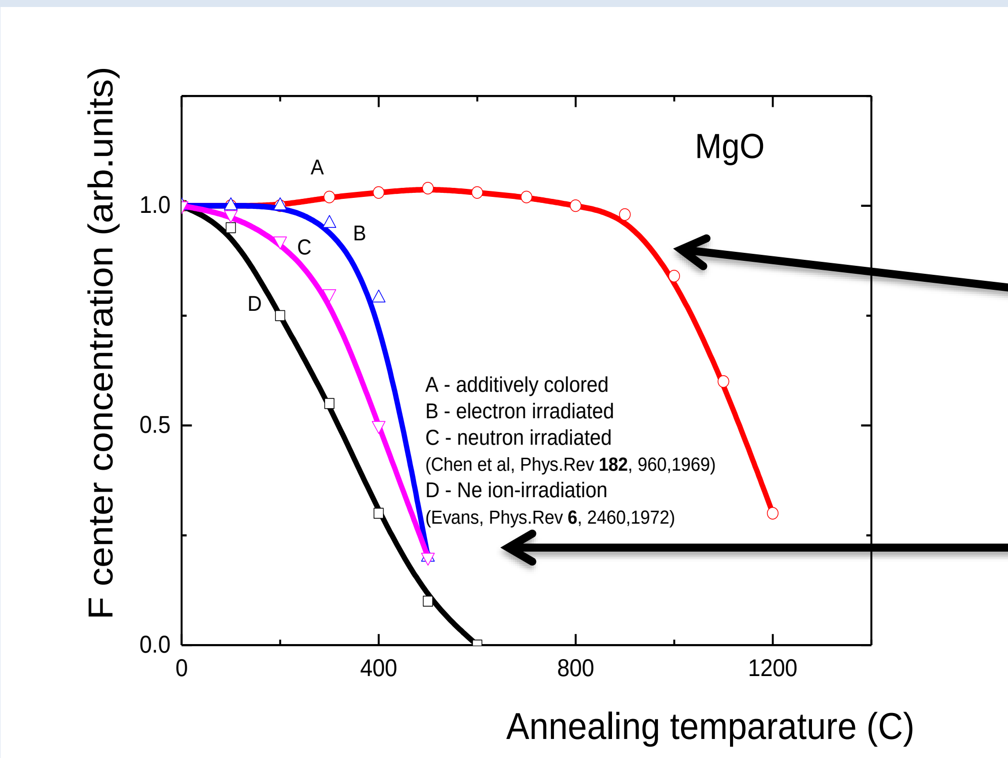


A – additively coloured or thermochemically reduced

B – electron irradiated Energy > 330 keV

C – neutron irradiated

D – ion irradiated

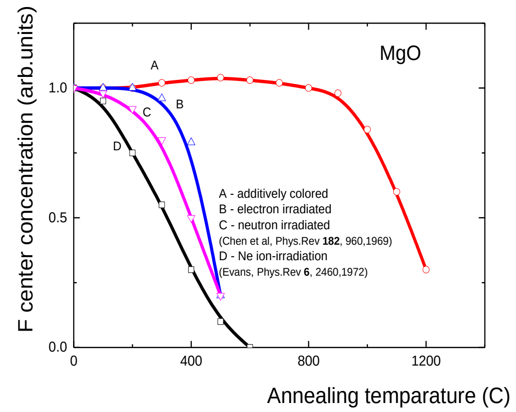


Intrinsic migration of F center

E_{act} for F-center diffusion ~3.4 eV

F center thermal destruction by oxygen interstitials

Theoretical model of
defect annealing &colloid formation



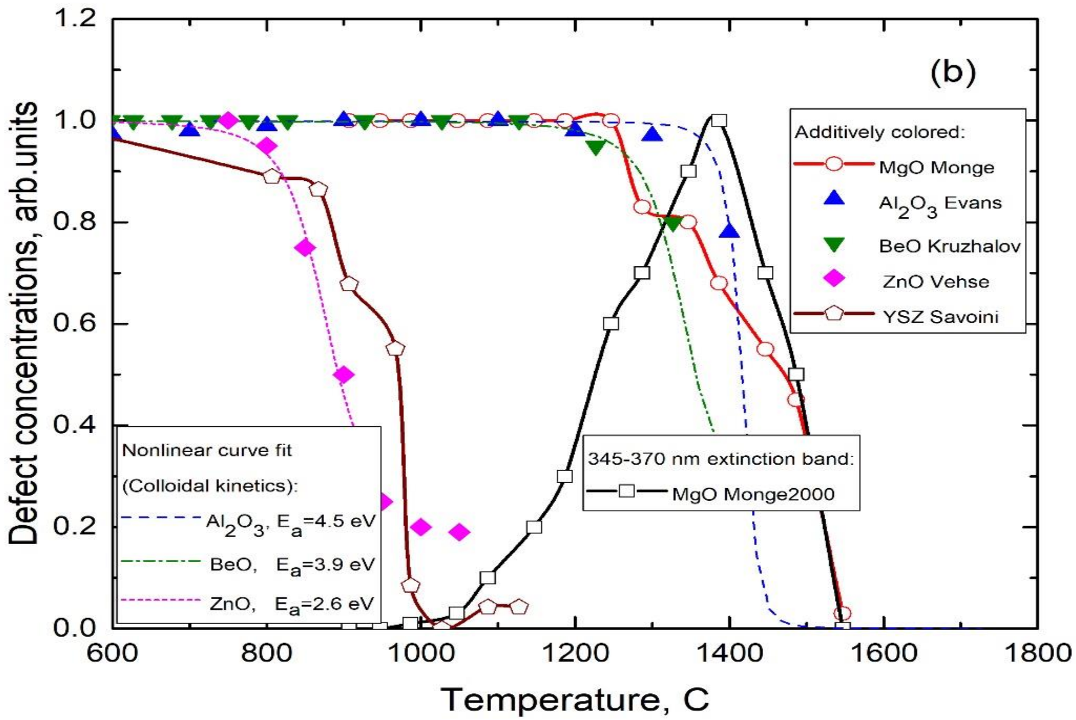
The atomistic model of radiation damage takes into account the following steps:

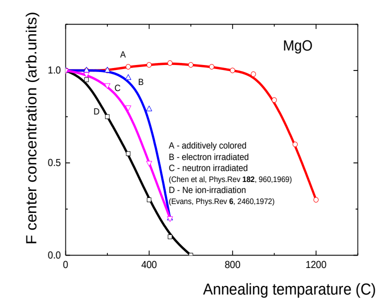
- Frenkel defect production (e.g. F, H pairs in alkali-halides, *F* center- O_{int} pair in oxides)
- Defect migration with the diffusion coefficient determined by the activation energy Ea and pre-exponent D_0,
- Similar (*F*-*F*) defect mutual attraction with the energy ε when they approach each other to nearest neighbor distance
- Dissimilar defect recombination upon mutual approach within the critical radius a_0
- Post-irradiation annealing with linear increase of temperature

The main calculated properties are

- Change with time (temperature) of concentrations of single-, dimer-, trimer- defect aggregates and metal nano-colloids
- The size of colloid and number of defects therein
- The effective diffusion coefficient of defects in aggregates
- A similar model was successfully used by us earlier for analysis of the LiF and CaF2 metallization under low energy electron irradiation .

F center annealing in TCR oxides

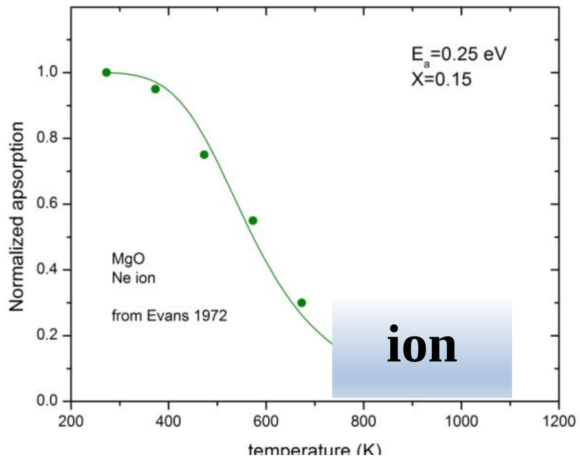


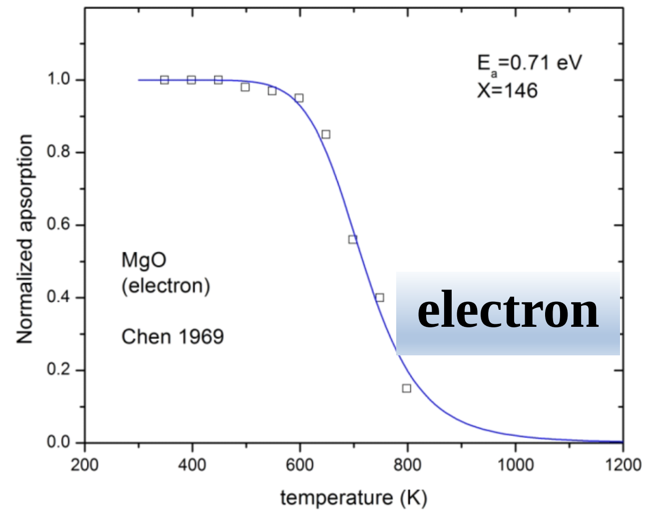


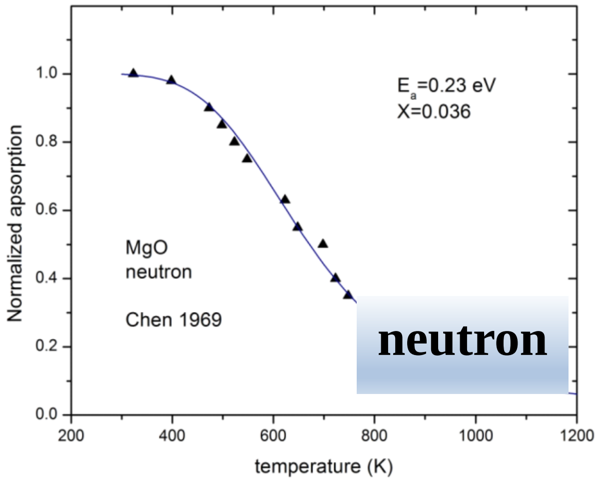
1. **F center are stable up to 800-1200 C**
2. **Only in MgO, the MgO colloid band was found, when $N_F > 5x10^{18}$ cm^{-3}**

Monge, Popov et al . Phys.Rev.B. 62 (2000) 9299

MgO: comparison F center annealing for different irradiation conditions - electron, neutron and ion irradiations







Electron irradiation: uniform (statistical) defect distrubution. E~ 0.65 -0.71 eV The greater the concentration of defects, the lower the activation energy !!!
Neutron and ion irradiations: non-uniform defect distribution E~ 0.23 -0.25 eV

Note that fast electron irradiation predominantly creates F centers
while neutron and ion irradiations mostly create F^+ centers (Ehrhart, 1993; Evans, 1974, Roberts and Crawford, 1974)

Electron irradiation produce the most uniform defect distribution and show largest energies for F center annealing by oxygen interstitials !!!

INVITED REVIEW J. Mater. Res., Vol. 30, No. 9, May 14, 2015

Challenges to the use of ion irradiation for emulating reactor irradiation

Gary S. Was, University of Michigan, Ann Arbor, Michigan 48109, USA

- Development of new materials for current and advanced reactor concepts is hampered by long lead times and high cost of reactor irradiations coupled with the paucity of test reactors. Ion irradiation offers many advantages for emulating the microstructures and properties of materials irradiated in reactors but also poses many challenges. Nevertheless, there is a growing body of evidence, primarily for light ion (proton) irradiation showing that many, if not all of the features of the irradiated microstructure and properties, can be successfully emulated by careful selection of irradiation parameters based on differences in the damage processes between ion and neutron irradiation. While much less has been done to benchmark heavy- or self-ion irradiation, recent work shows that under certain conditions, the complete suite of features of the irradiated microstructure can be emulated.
- This study summarizes the contributions of ion irradiation to our understanding of irradiation effects, the options for emulating radiation effects in reactors, and experience with both proton irradiation and heavy ion irradiation.

•Pressurised water reactor (PWR) ...
•Boiling water reactor (BWR) ...
•Advanced gas-cooled reactor (AGR) ...
•Light water graphite-moderated reactor (LWGR)
•Fast neutron reactor (FNR)
• Traveling wave reactor (TWR)

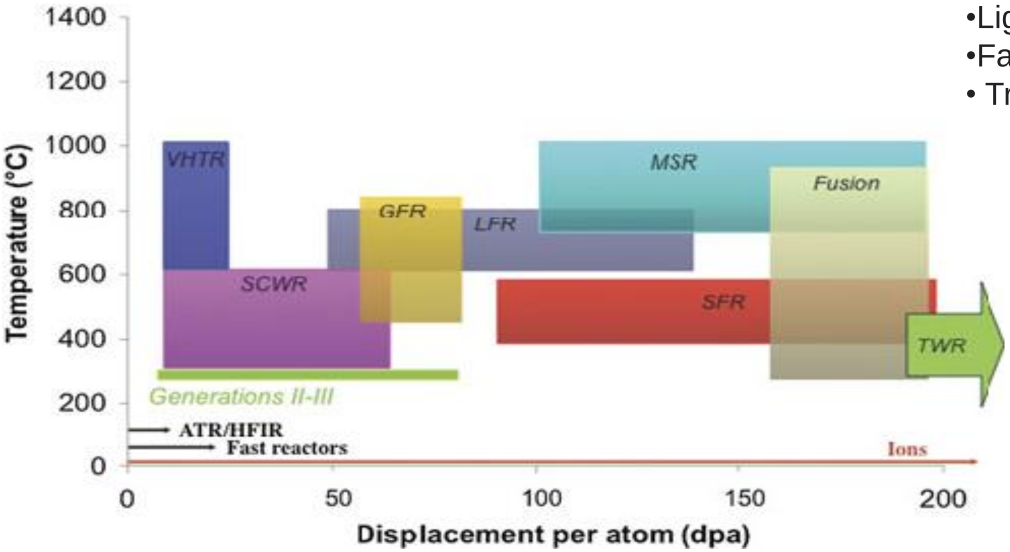


FIG. 1. Schematic of the temperature–dpa requirements for various reactor concepts and the achievable annual damage rates in different test reactors and with ion irradiation.

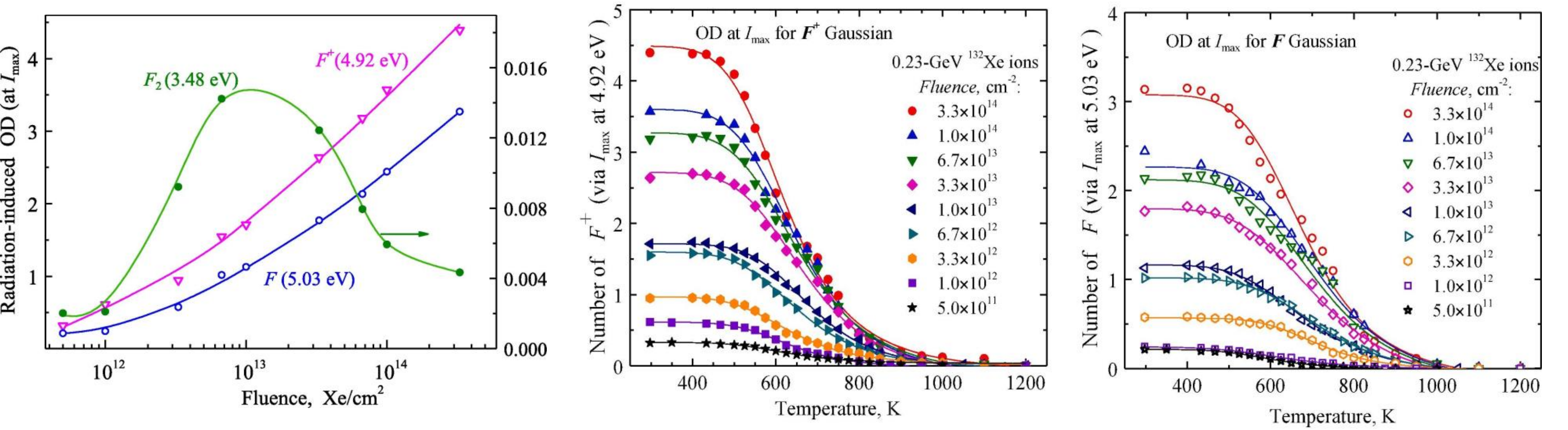
Where were the Irradiation Campaigns ?

Irradiation by swift heavy ions

(1) ~2 GeV, U^{238} , Au^{197} or Bi^{209}) at UNILAC linear accelerator, GSI, Darmstadt. Fluences 3×10^{11}, 10^{12}, 2×10^{12} ions/cm^2, R ~90 μ

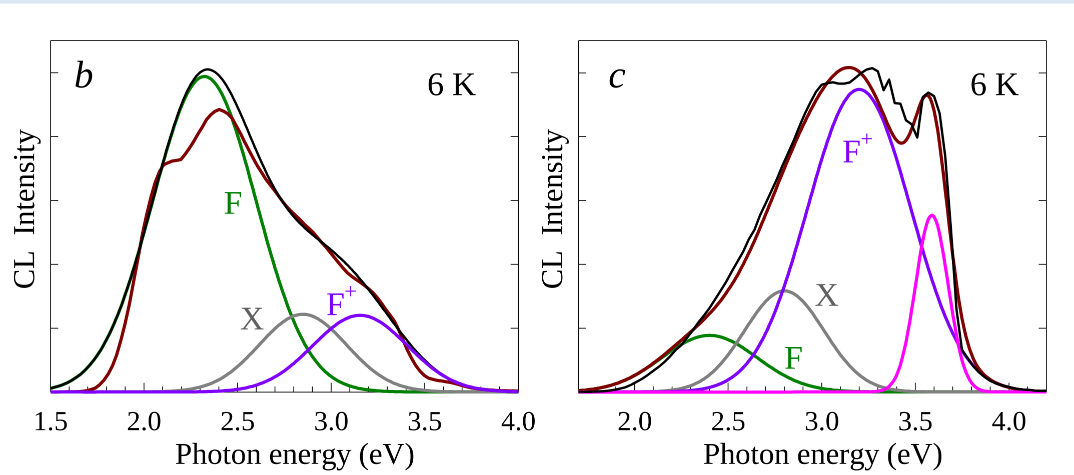
(2) Eurasian National University, Astana, cyclotron DC-60, ^{132}Xe, 1.75 MeV/nuclon, 10^{12}–10^{14} ions/cm^2, R ~20 μm)

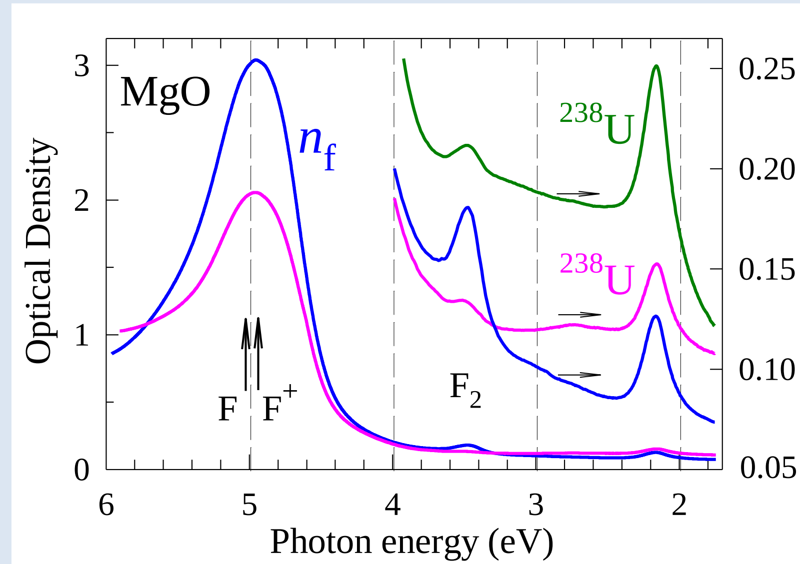
Irradiation by protons H^1, 100 keV, KIIA 500 kV implanter at Ion Beam Lab, Helsinki University,



Baubekova, G., et al. (2020). Accumulation of radiation defects and modification of micromechanical properties under MgO crystal irradiation with swift 132Xe ions. *Nuclear Instruments and Methods in Physics Research Section B: Beam Interactions with Materials and Atoms*, *463*, 50-54.

Creation of structural defects in MgO crystals under irradiation by SHIs or fast neutrons





Neutron-irradiated at 300 K

1-2 MeV, 10^{17} n_f/cm^2

^{238}U-irradiated at 300 K

2.25 GeV, 2×10^{11} U/cm^2

$F^+ + e \rightarrow (F)^* \rightarrow F$ 2.4 eV

$v_a e + e \rightarrow (v_a e\, e)^* \rightarrow v_a e\, e + h\nu$

$v_a + e \rightarrow (F^+)^* \rightarrow F^+ + h\nu +$ 3.15 eV

10^{12} U/cm^2, 2.5 GeV, 300 K

2×10^{11} U/cm^2, 2.5 GeV, 300 K

10^{17} n/cm^2, ~1-2 MeV, 330 K

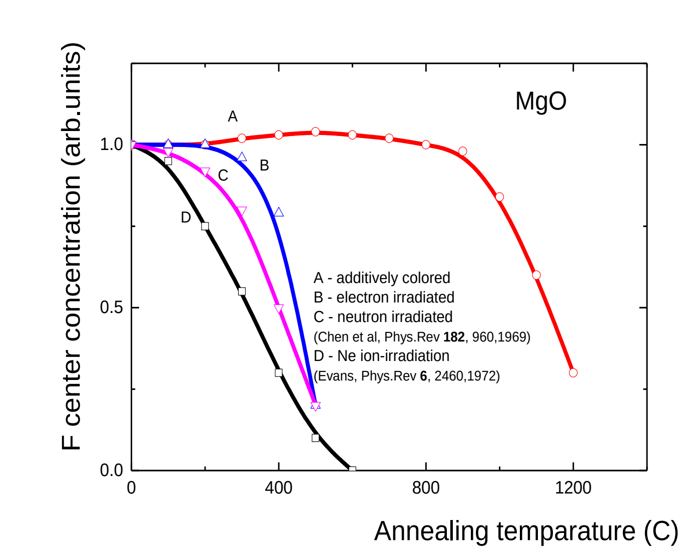
$S(F) > S(F^+)$ $S(F) < S(F^+)$

Emission spectra at the excitation of MgO crystals by 5 keV electrons at 6 K

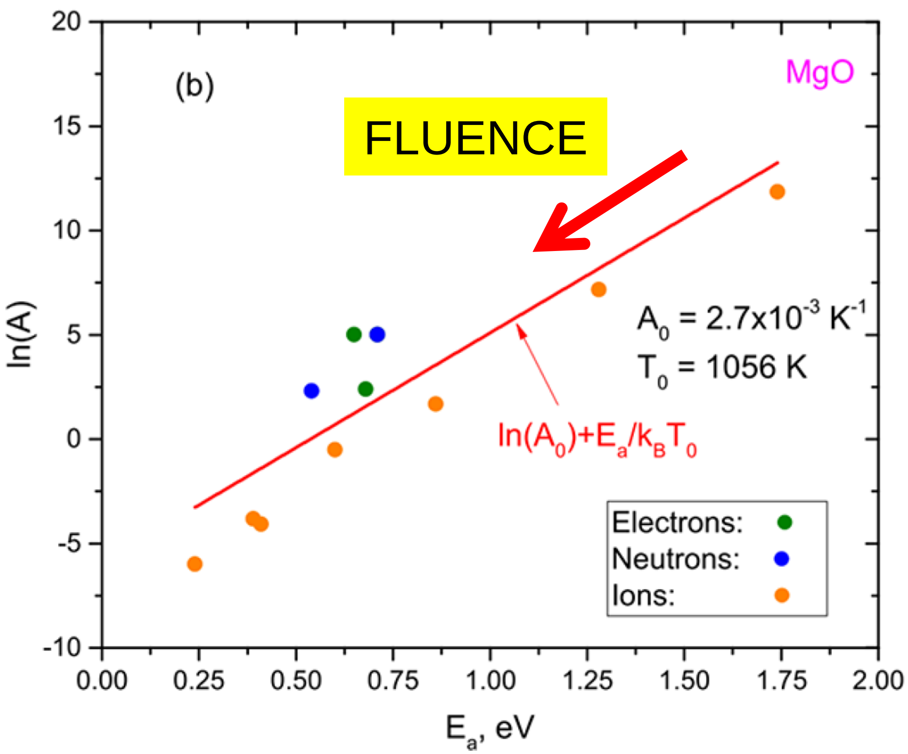
Spectra of induced optical absorption for MgO single crystals irradiated by swift uranium ions (d~100 μm) or fast neutrons (d > 1 mm)

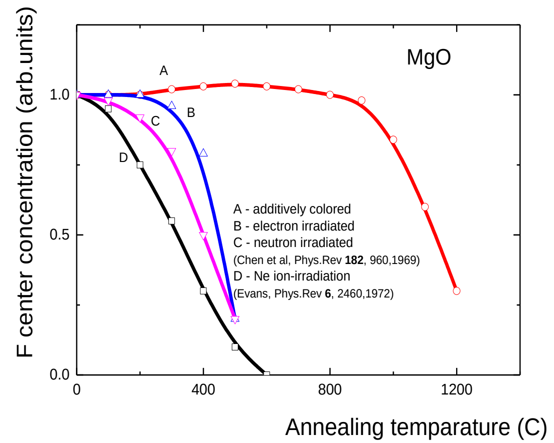
MgO: E_{act} summary (eV)

Thermochemically reduced (or additive colored)	**3.4 (F centers)**	**3.13 (F center) (theor.)** **2.70 (F^+ center)**
Neutron **a) optical absorption (F/F+ centers)** **b) EPR (F+ centers)** **c) EPR (oxygen interstitials)**	**0.23; 0.32** **0.54** **1.70; 1.73**	**1.60 (theoretical)**
Electron irradiated **a) optical absorption ((F/F+ centers)** **b) EPR (oxygen interstitials)**	**0.65; 0.68; 0.68, 0.71** **no data**	
Ion irradiated **a) optical absorption** **b) EPR**	**0.25** **No data**	



The Mayer-Neidel rule - Disordering





The Meyer-Neldel rule
(Phys.Zeits. 1937)

- The rule known in reaction kinetics:

$$ln(X) = ln(X_0) + E_a/k_B T_0\ ,$$

where X_0 is a constant and T_0 some characteristic temperature

It could be also interpreted as the diffusion coefficient with exponentially dependent pre-exponent

$$D \sim exp\left(\frac{E_a}{k_B T_0} - \frac{E_a}{k_B T}\right) \quad , T<T_0$$

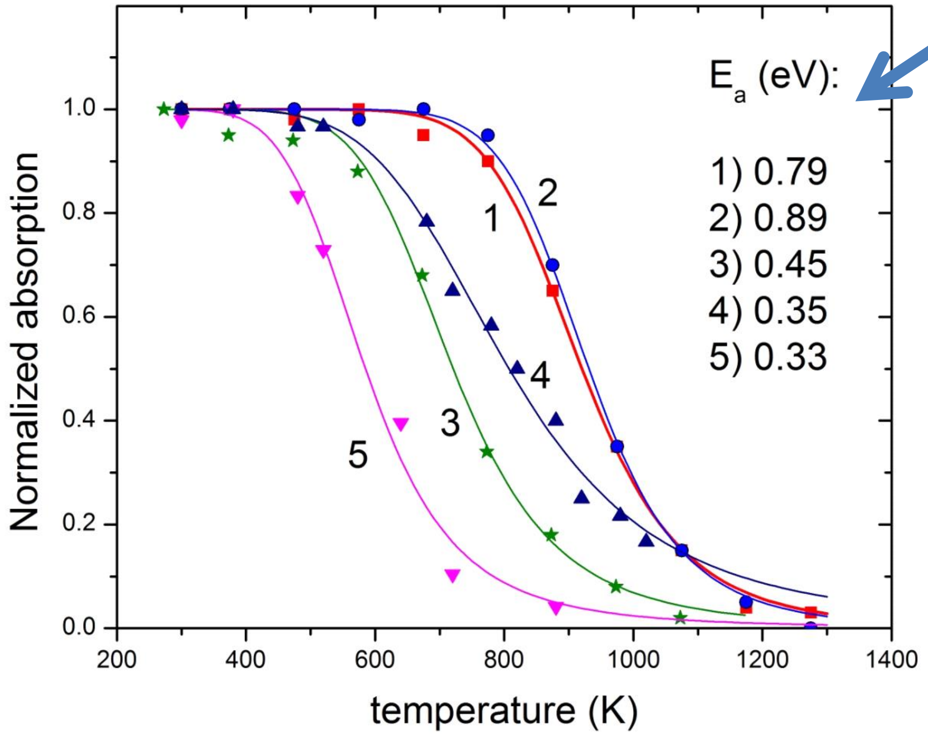
This relation was observed in many disordered systems in chemistry, biology, semiconductors

This equation shows how reduction of the activation migration energy with growing radiation-induced disorder is compensated by orders of magnitude decrease of the pre-factor *X* (or pre-exponent).

Figure clearly demonstrates that this relation indeed is well working for MgO and more importantly, for different types of irradiation (and initial defect spatial distributions).

Understanding of F center annealing in irradiated Al_2O_3

Al_2O_3



close to ab initio calculations

- The obtained *F*-recombination energy is close to that predicted for **charged** Oi interstitials
- Large dispersion due to **dose effect!**

1,2 – F and F^+ centres, neutron irradiation, Ramires et al (2007)

3 – F+ center, neutron, Evans (1995)

4 – F+ center, neutron, Vila et al (1981)

5 – TSDS, neutron, Vila et al (1981)

Comparison of the *F*-type center thermal annealing in heavy-ion and neutron irradiated Al_2O_3 single crystals

A.I. Popov, A. Lushchik, E. Shablonin, E. Vasil'chenko, E.A. Kotomin, A.M. Moskina, V.N. Kuzovkov

Nuclear Instruments Methods B, 2018, **433**, 93-97

The optical absorption of Al_2O_3 (sapphire) single crystals irradiated with swift heavy ions (SHI) ^{238}U with energy 2.4 GeV is studied with the focus on the thermal annealing of the *F*-type centers in a wide temperature range of 400–1500 K. According SRIM 2013 code [36], ion range of used ^{238}U ions approximately equals 90 μm that is significantly smaller than the sample thickness.

Its theoretical analysis allows us to obtain activation energies and pre-exponentials of the interstitial oxygen ion migration, which recombine with both types of immobile electron centers (*F* and F^+ centers).

A comparison of these kinetics parameters with literature data for a neutron-irradiated sapphire shows their similarity and thus supports the use of SHI-irradiation for modeling the neutron irradiation.

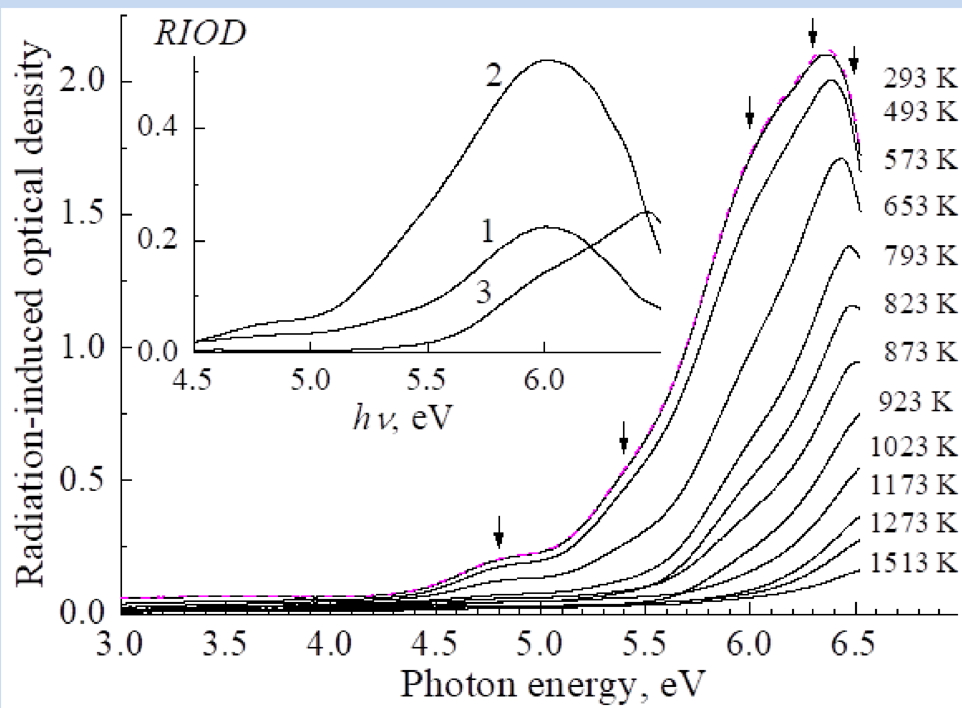
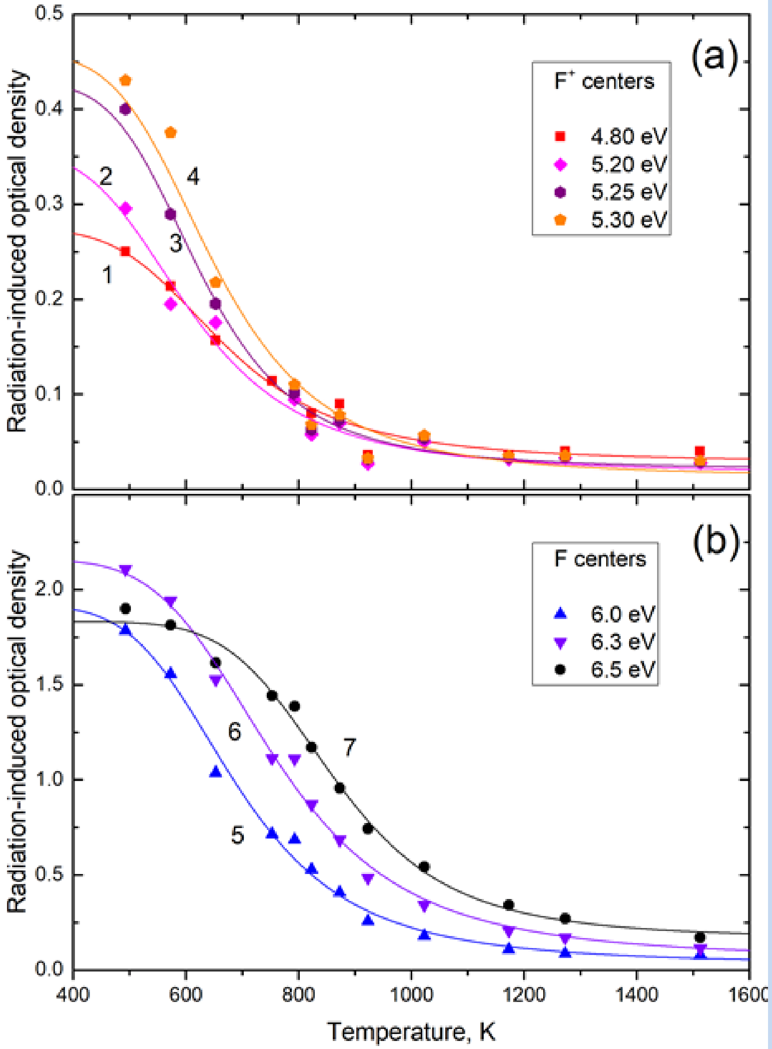


Figure 1. The absorption (actually, RIOD) spectra of an α-Al_2O_3 single crystal measured after irradiation with 2.4-GeV SHIs (RT, 10^{12} U/cm^2) and after additional preheating of the irradiated sample to depicted temperatures.

Insert depicts difference spectra representing the decreases of RIOD due to the preheating of the irradiated sample from 493 to 573 K (curve 1), 573 → 653 K (curve 2) and 823 → 873 K (curve 3). All spectra are measured at RT.

Comparison of the *F*-type center thermal annealing in heavy-ion and neutron irradiated Al_2O_3 single crystals



- **F – center = O vacancy with 2e**
- **F^+ - center = O vacancy with 1e**

Dependences of the RIOD measured for the F anf F+ centers on the preheating temperature for a SHI-irradiated α-Al_2O_3 single crystal (2.4-GeV, 10^{12} U/cm^2, RT) and their theoretical fitting

The obtained results of the theoretical fitting are presented in Table.

N.	Type	E_a (eV)	X (K^{-1})
1	4.80 eV (F^+)	0.26	6.9×10^{-2}
2	5.20 eV (F^+)	0.22	5.1×10^{-2}
3	5.25 eV (F^+)	0.29	2.1×10^{-1}
4	5.30 eV (F^+)	0.28	1.1×10^{-1}
5	6.0 eV (F)	0.29	1.0×10^{-1}
6	6.3 eV (F)	0.31	7.5×10^{-2}
7	6.5 eV	0.49	5.8×10^{-1}

Comparison of the *F*-type center thermal annealing in heavy-ion and neutron irradiated Al_2O_3 single crystals

The calculated migration energies of interstitial oxygen ions E_a and pre-exponential factors *X* for several kinetics from the literature (see references).

close to ab initio calculations

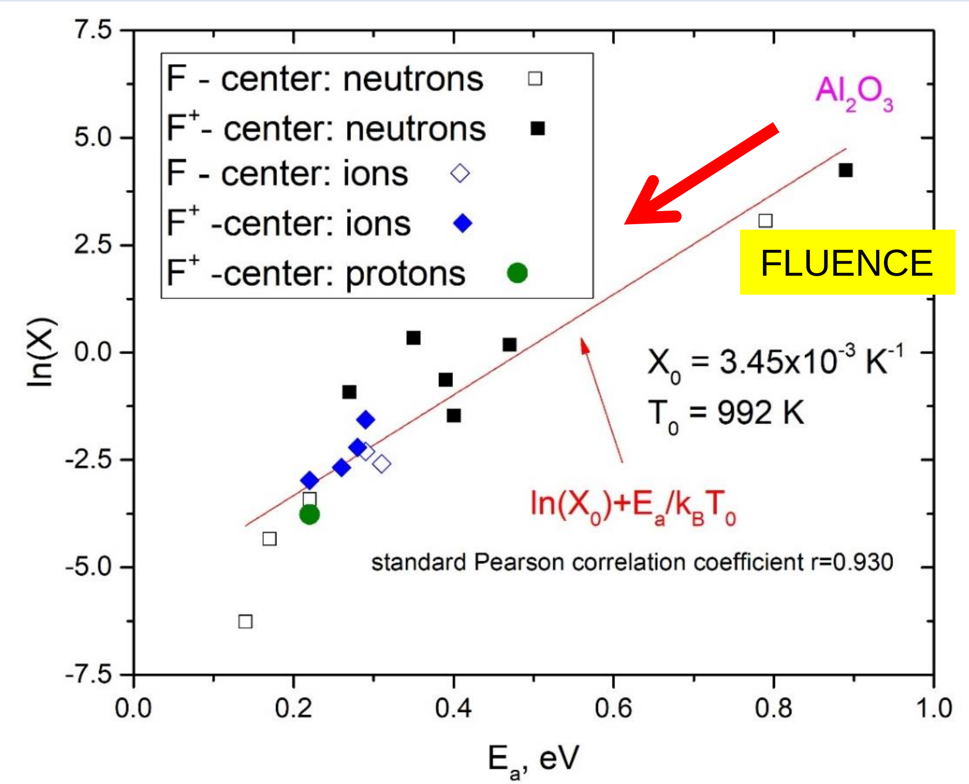
Nr.	Irradiation	Type	E_a (eV)	X (K^{-1})	Reference
1	neutron	F	0.79	$2.1x10^1$	Ramírez et al, 2007
2	neutron	F^+	0.89	$7.0x10^1$	Ramírez et al, 2007
3	neutron	F^+	0.40	$2.3x10^{-1}$	Vila et al, 1991
4	neutron	F^+	0.47	$1.2x10^0$	Izerrouken et al, 2010
5	neutron	F^+	0.39	$5.3x10^{-1}$	Atobe et al, 1985
6	neutron	F^+	0.27	$4.0x10^{-1}$	Bunch et al. 1974
7	neutron	F	0.22	$3.3x10^{-2}$	Bunch et al, 1974
8	neutron	F	0.17	$1.3x10^{-2}$	Atobe et al, 1985
9	neutron	F	0.14	$1.9x10^{-3}$	Izerrouken et al, 2014
10	neutron	F^+	0.35	$1.4x10^0$	Evans. 1996
11	proton	F	0.22	$2.3x10^{-2}$	Draeger and Summers 1979
12	^{238}U ion	F^+ F	0.27 0.30	See Table 1.	This work

The obtained F center thermal annealing energies

1. are much lower than F center diffusion energy
2. show large dispersion due to dose effect
3. the largest values are close to the predicted for charged oxygen interstitials
4. Ratio *Ea(F)/Ea(F+)* is different !!!

Comparison of the *F*-type center thermal annealing in heavy-ion, neutron, proton irradiated

The calculated migration energies of interstitial oxygen ions E_a and pre-exponential factors X for several kinetics from the literature (see references).



Nr.	Irradiation	Type	E_a (eV)	X (K^{-1})	Reference
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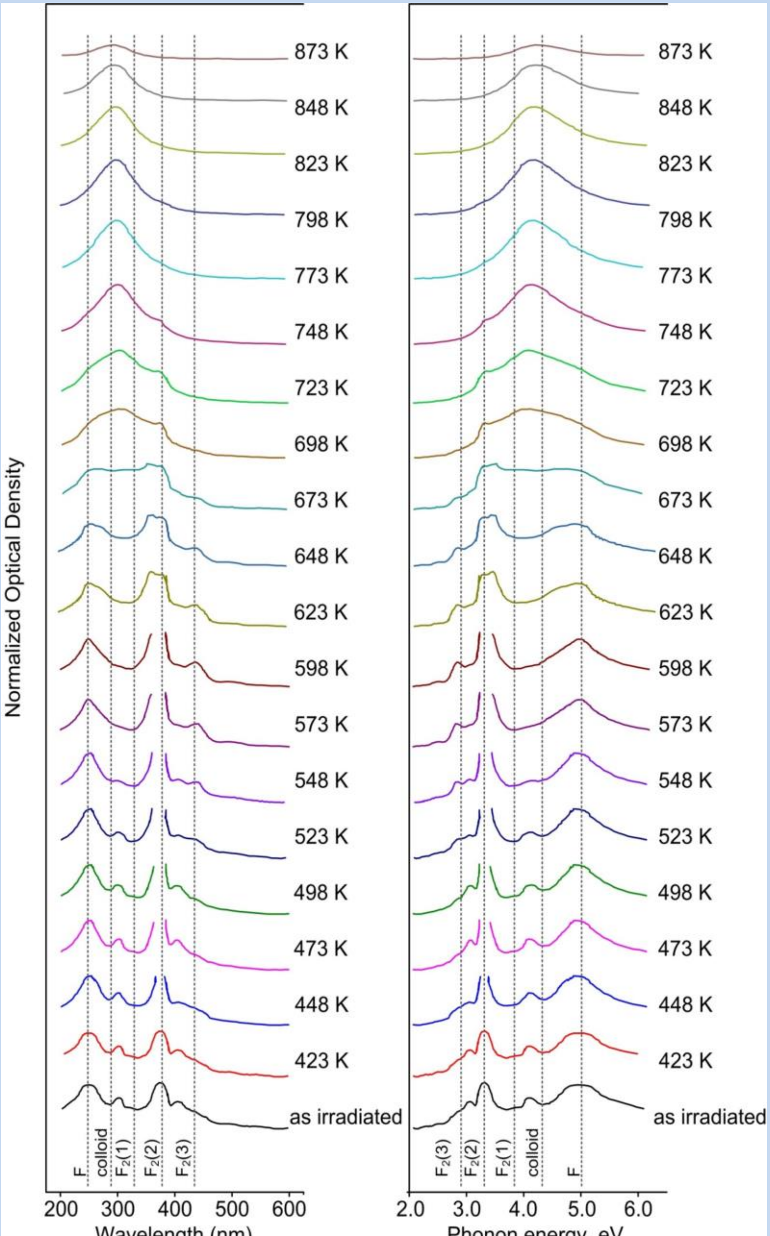
11	proton	F	0.22	2.3×10^{-2}	Draeger and Summers 1979
12	^{238}U ion	F^+ F	0.27 0.30	See Table 1.	This work

This equation shows how reduction of the activation migration energy with growing radiation-induced disorder is compensated by orders of magnitude decrease of the pre-factor *X*.

Figure clearly demonstrates that this relation indeed is well working for Al_2O_3 for SEVERAL different types of irradiation (and initial defect spatial distributions).

Thermal annealing of radiation defects in MgF_2



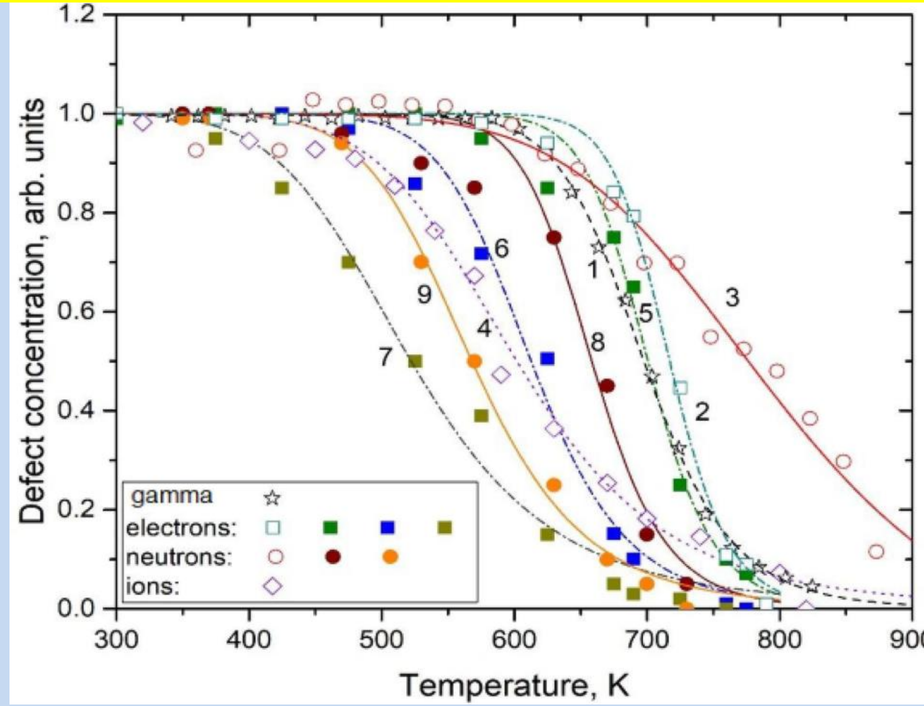


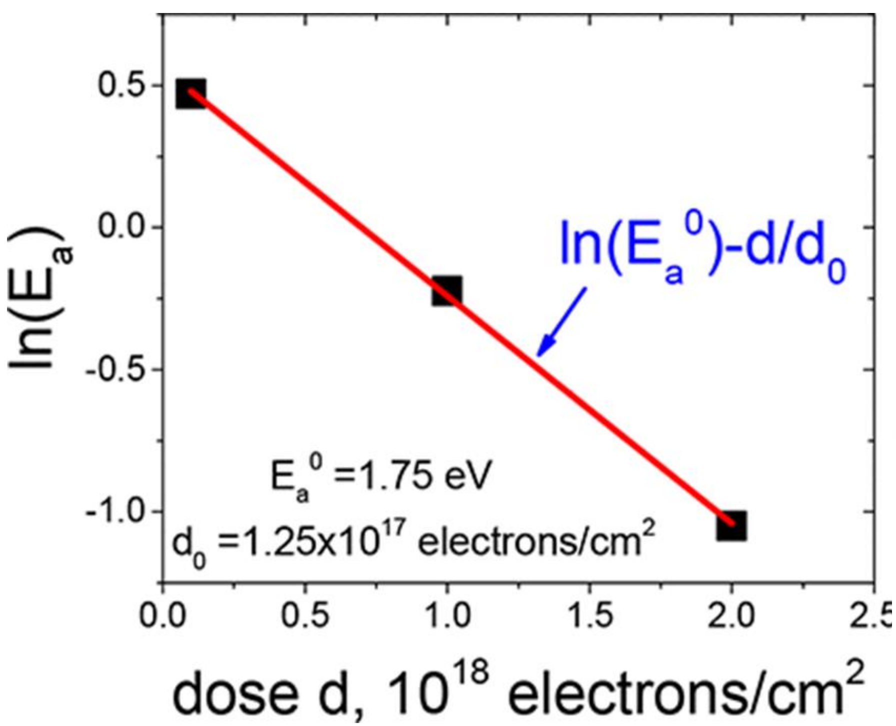
Fig. 1. Optical absorption spectra of neutron irradiated MgF_2 as a function of annealing temperature in nm and eV horizontal scale (left and right, respectively).

Fig. 2. The kinetics of the *F* center annealing after exposure to four different types of radiation

A.I. Popov, E. Elsts, E.A. Kotomin, A. Moskina, Z.T. Karipbayev, I. Makarenko, S. Pazylbek, V.N. Kuzovkov. Thermal annealing of radiation defects in MgF_2 single crystals induced by neutrons at low temperatures. *Nucl. Instrum. Methods Phys. Res. B*, 2020, **480**, pp. 16–21.

Thermal annealing of radiation defects in MgF_2

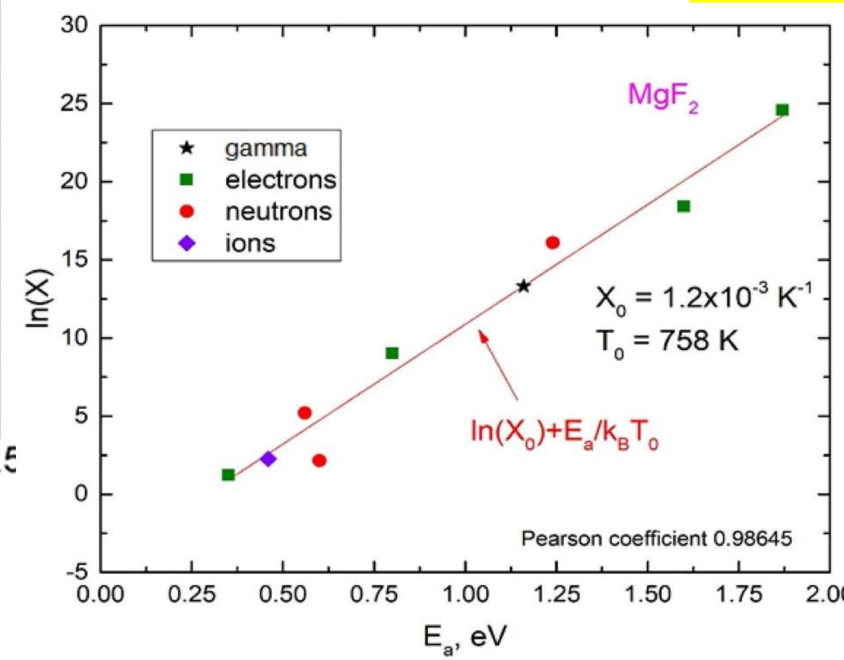
The kinetics of the *F* center annealing in MgF_2 exposed to different types of radiation;
Correlation of the effective energies and pre-exponents (fast neutron, electron and heavy ions), compilation of the data from: E.A. Kotomin, V.N. Kuzovkov, A.I. Popov, J. Maier, R.Vila (2018). Anomalous kinetics of diffusion-controlled defect annealing in irradiated ionic solids. *J. Phys. Chem. A,* **122**, 28-32.



$E_a(0) = 1.75$ eV

The Mayer-Neidel rule - Disordering

FLUENCE



Note: Theoretical values for F center diffusion in MgF2 are 1.5-1.7 eV.

The decrease of both the migration energy and pre-exponential *A* with radiation fluence

A.I. Popov et al. Thermal annealing of radiation defects in MgF_2 single crystals induced by neutrons at low temperatures. *Nucl. Instrum. Methods Phys. Res. B*, 2020, **480**, pp. 16–21.

Thermal annealing of radiation defects in $MgAl_2O_4$

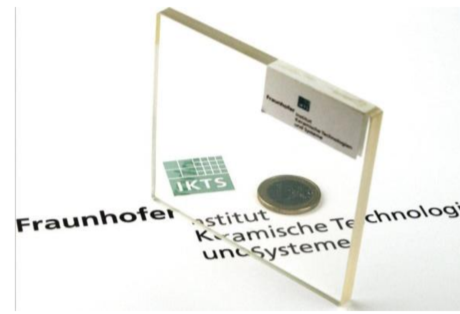
Structural damage was induced by:

Irradiation with fast neutrons

fluence of 10^{17} n/cm^2, 10^{18} and 2.6×10^{18} n/cm^2 , >0.1 MeV, <100°C

Irradiation with protons H^1, 100 keV, 10^{15}–8×10^{17} p/cm^2 KIIA 500 kV implanter at Ion Beam Lab, Helsinki University,

Irradiation with swift heavy ions Xe^{132}, 0.23 GeV (1.75 MeV/n), 10^{12}–10^{14} Xe/cm^2, R ~20 μm, cyclotron DC-60 at Eurasian National University, Astana



The following samples have been investigated:

- $MgAl_2O_4$ optical ceramics with different grain size from IKTS, Fraunhofer (0.5-12 μm); Ciemat-Nanoker; and LSPM-CNRS (Paris)
- $MgO\cdot2.5Al_2O_3$ (1:2.5) and $MgAl_2O_4$ (1:1) single crystals from different suppliers (Oak Ridge, ALINEASON, MTI, etc.)

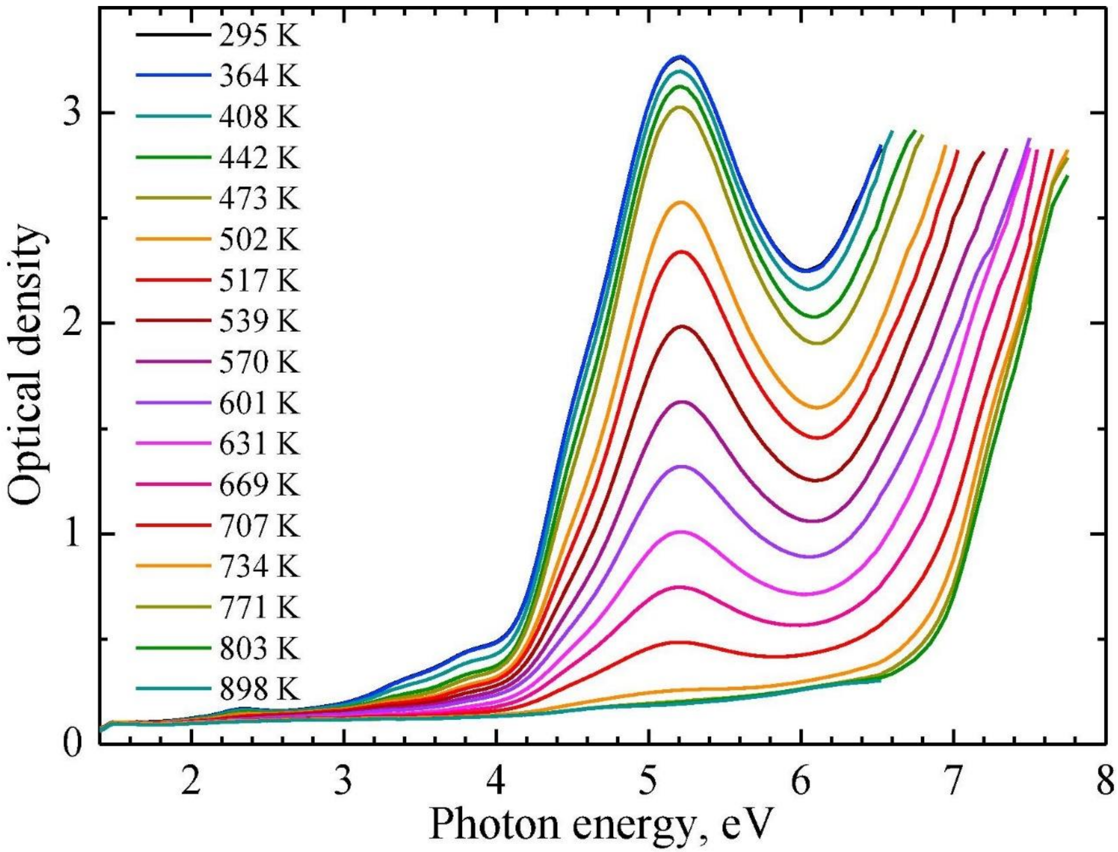
EUROfusion

This work has been carried out within the framework of the EUROfusion Consortium and has received funding from the Euratom research and training programme 2014-2018 under grant agreement No 633053. The views and opinions expressed herein do not necessarily reflect those of the European Commission.

Thermal annealing of radiation defects in MgAl2O4

The absorption spectra of an $MgAl_2O_4$ single crystals (d = 0.3 mm) measured after irradiation with fast neutrons (2.59×10^{18} n/cm^2) and after additional preheating of the irradiated sample to depicted temperatures. All spectra are measured at RT.:

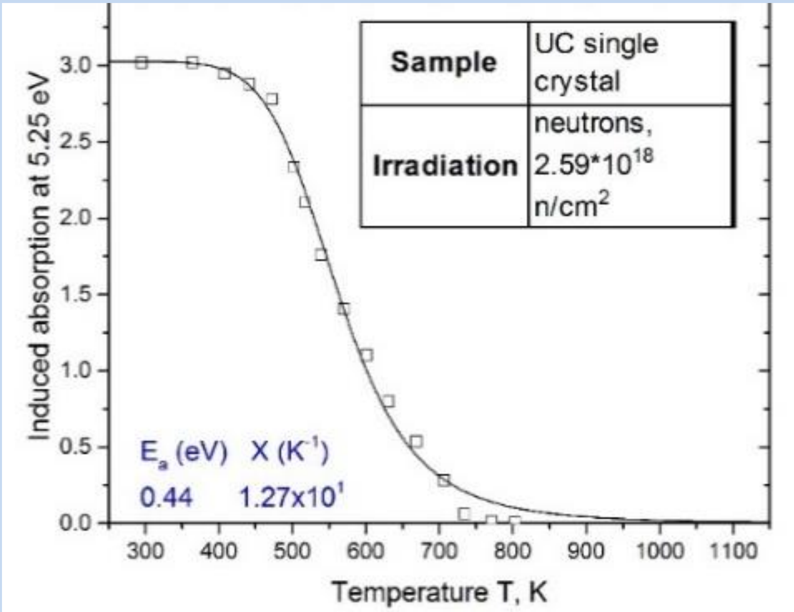
Creation and thermal annealing of structural defects in neutron-irradiated MgAl2O4 single crystals
A.Lushchik, S.Dolgov, E.Feldbach, R.Parej, A.I.Popov, E.Shablonin, V.Seeman NIMB, 2018, **435,** 31-37.

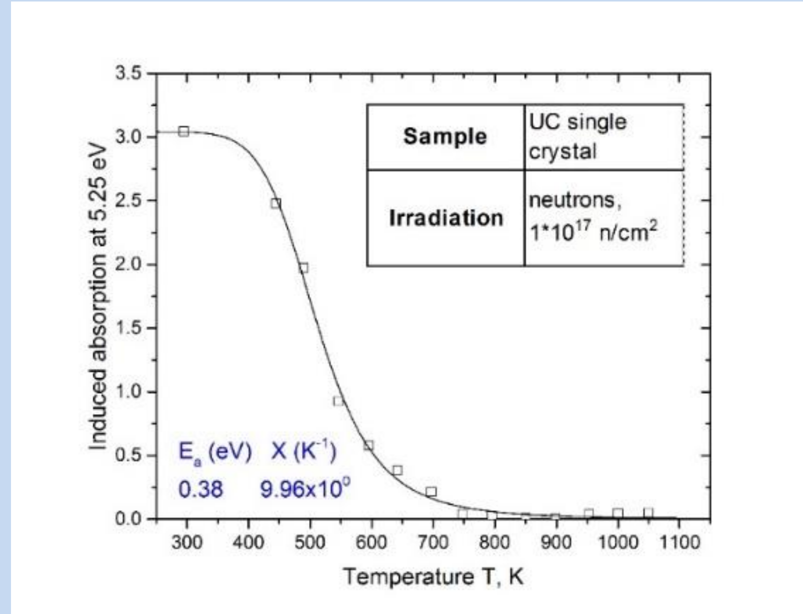


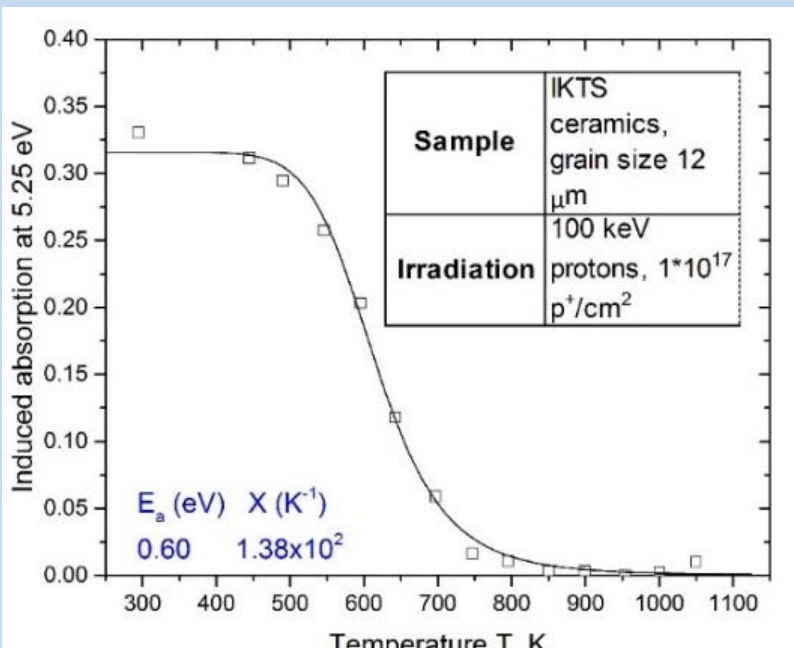
Stoichiometric $MgAl_2O_4$ (**1:1**) were grown by Union Carbide Corporation using the Czochralski method.

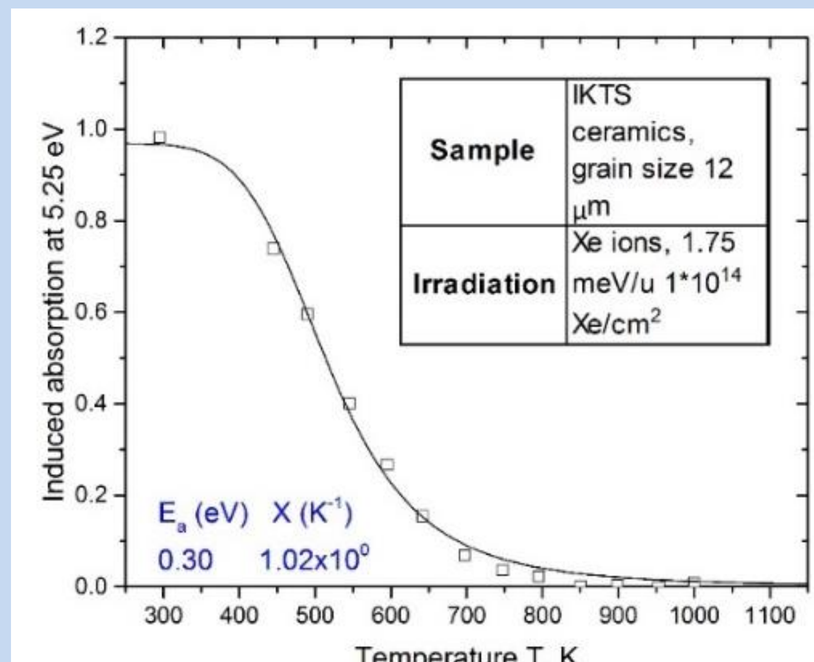
electron-type F^+ and F centers (~4.6 and ~5.3 eV)

F center thermal annealing in $MgAl_2O_4$ - 5.25 eV band

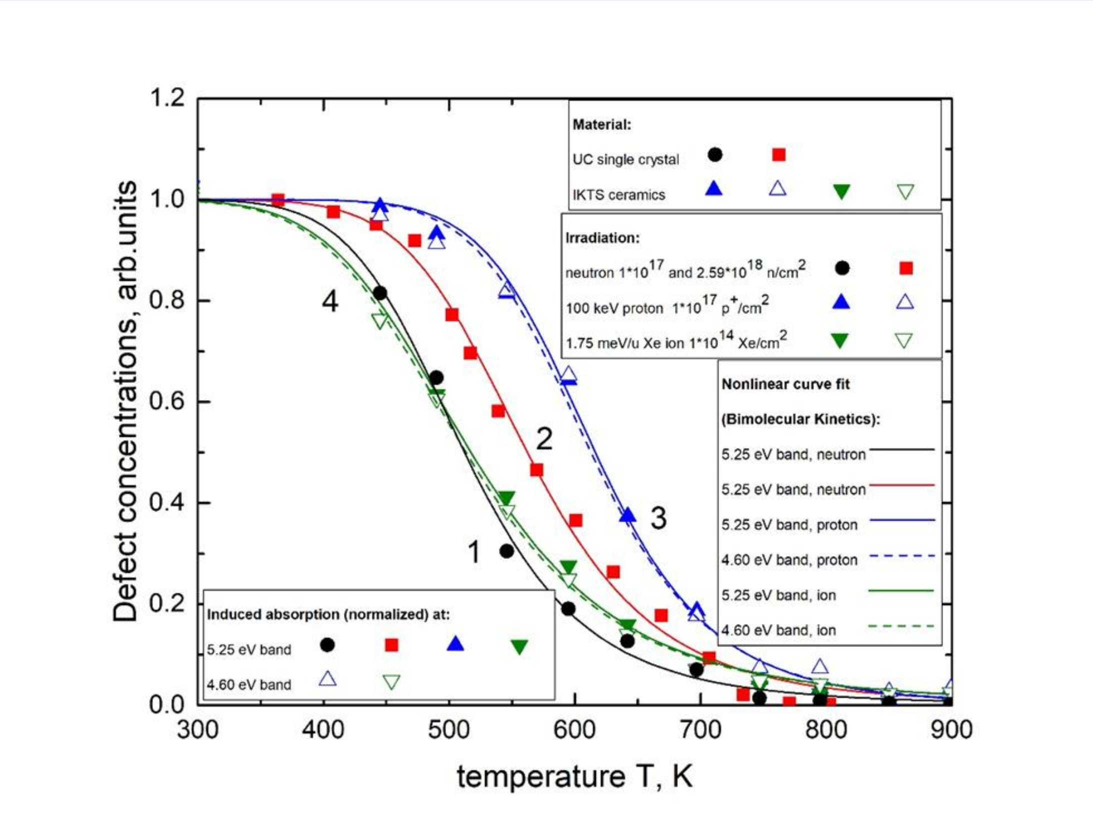








Defect recombination kinetics in irradiated $MgAl_2O_4$



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Distinctive features of diffusion-controlled radiation defect recombination in stoichiometric magnesium aluminate spinel single crystals and transparent polycrystalline ceramics

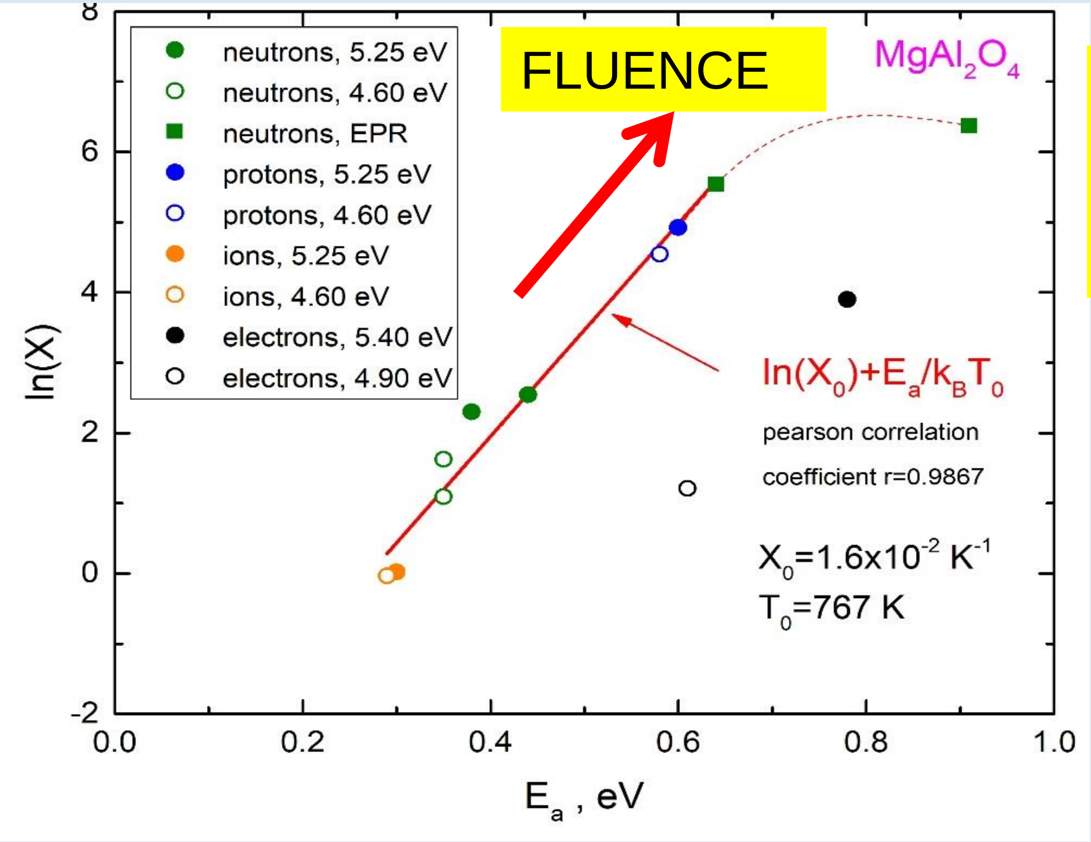
A. Lushchik[1], E. Feldbach[1], E. A. Kotomin[2], I. Kudryavtseva[1], V. N. Kuzovkov[2], A. I. Popov[2], V. Seeman[1] & E. Shablonin[1,2]

Table 1. Explanation of curves I-V in Fig. 3 and the values of calculated migration energy E_a and pre-exponential factor X obtained under different irradiation conditions for the electron (Nos.1-12) and hole (Nos. 13 and 14) centers.

No.	Irradiation	Defect	E_a (eV)	X (K^{-1})	Legend
1 (I)	neutron	F	0.38	1.0×10^{1}	Optical absorption, single crystal, 1 MeV, $\Phi = 1.0\times10^{17}$ n/cm^2
2	neutron	F^+	0.35	5.1×10^{0}	same as No. 1
3 (II)	neutron	F	0.44	1.3×10^{1}	Optical absorption, single crystal, 1 MeV, $\Phi = 2.6\times10^{18}$ n/cm^2,
4	neutron	F^+	0.35	3.0×10^{0}	same as No. 3
5 (III)	protons	F	0.60	1.4×10^{2}	Optical absorption, ceramics with grain size 12 µm, 100 keV, $\Phi = 1.0\times10^{17}$ p/cm^2
6	protons	F^+	0.58	9.4×10^{1}	same as No. 5
7 (IV)	proton	F	0.24	8.5×10^{-2}	Optical absorption, ceramics with grain size 1.4 µm, 100 keV, $\Phi = 1.0\times10^{17}$ p/cm^2
8	proton	F^+	0.24	8.7×10^{-2}	same as No. 7
9	proton	F	0.29	3.4×10^{-1}	Optical absorption, ceramics with grain size 1.4 µm, 100 keV, $\Phi = 5.0\times10^{17}$ p/cm^2
10	proton	F^+	0.22	9.3×10^{-2}	same as No 9
11	proton	F	0.34	1.1×10^{0}	Optical absorption, ceramics, grain size 0.5 µm, 100 keV, $\Phi = 2.0\times10^{17}$ p/cm^2
12	proton	F^+	0.38	3.1×10^{0}	same as No. 11
13 (V)	neutron	V_2	0.64	2.5×10^{2}	EPR signal, single crystal 1 MeV, $\Phi = 2.6\times10^{18}$ n/cm^2
14	neutron	V_1	0.63	1.9×10^{5}	same as No. 13

The normalized experimental (symbols) and theoretical (full and dashed lines) annealing kinetics for **defects in single crystals and ceramics after different types of irradiation** (see legend) for the F (5.25 eV) and F^+ (4.60 eV) optical absorption bands.

The Mayer-Neidel rule (MNr) - Disordering



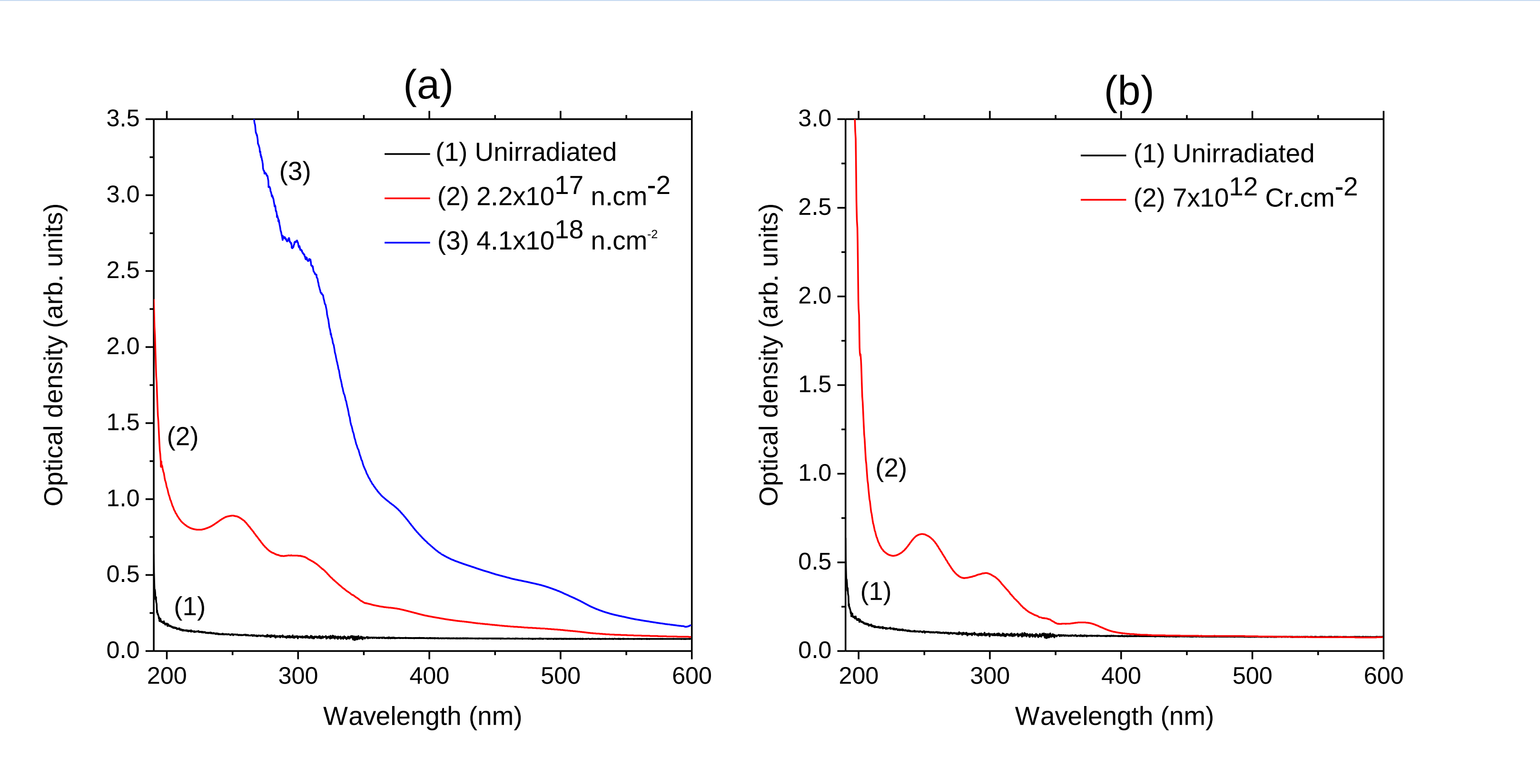
Good fit of data for both single crystals and ceramics, as well as under different irradiations: Universal law!

Here MNR shows how INCREASE of the Ea activation energy with growing radiation-induced disorder is compensated by orders of magnitude INCREASE of the prefactor *X*.

Figure clearly demonstrates that this relation indeed is **also well working for $MgAl_2O_3$**, and more **importantly, for different types of irradiation (and initial defect spatial distributions**).

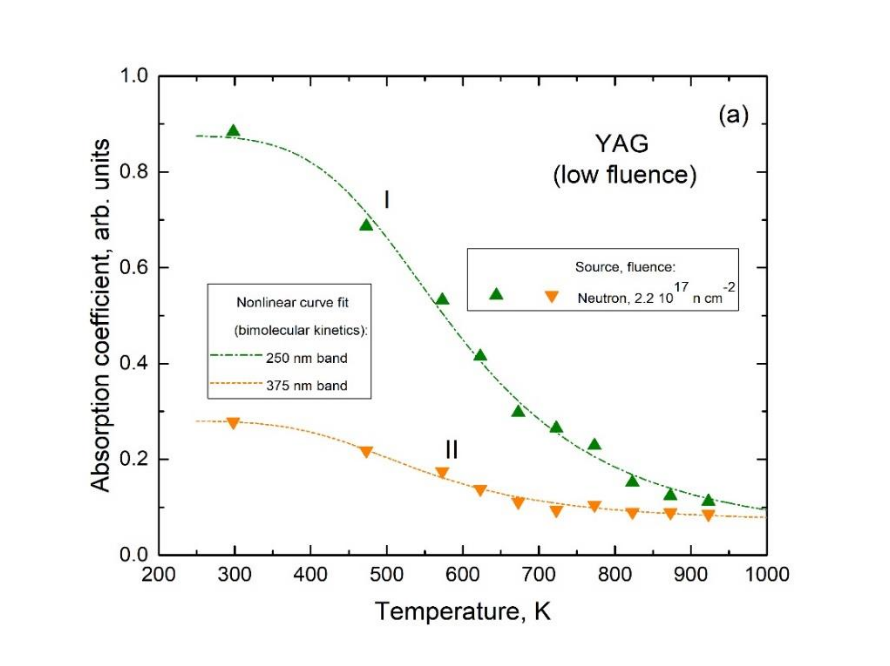
Defect recombination kinetics in irradiated $Y_3Al_5O_{12}$

A.I. Popov , E.A. Kotomin, M. Izerrouken, V.N. Kuzovkov, R. Villa
(ISSP, Latvia; *Nuclear Research Center of Draria, Algiers* and *CIEMAT, Spain*)



Optical absorption spectra of YAG before and after irradiation. (a) YAG irradiated with neutrons and (b) YAG irradiated with 6.6 MeV/u Cr ions

Defect recombination kinetics in irradiated $Y_3Al_5O_{12}$



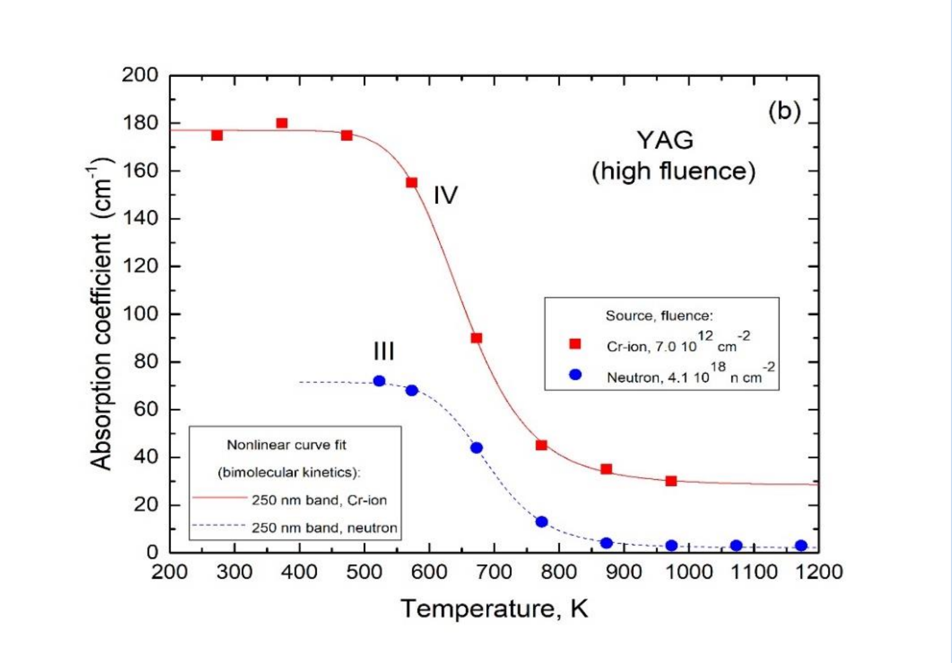
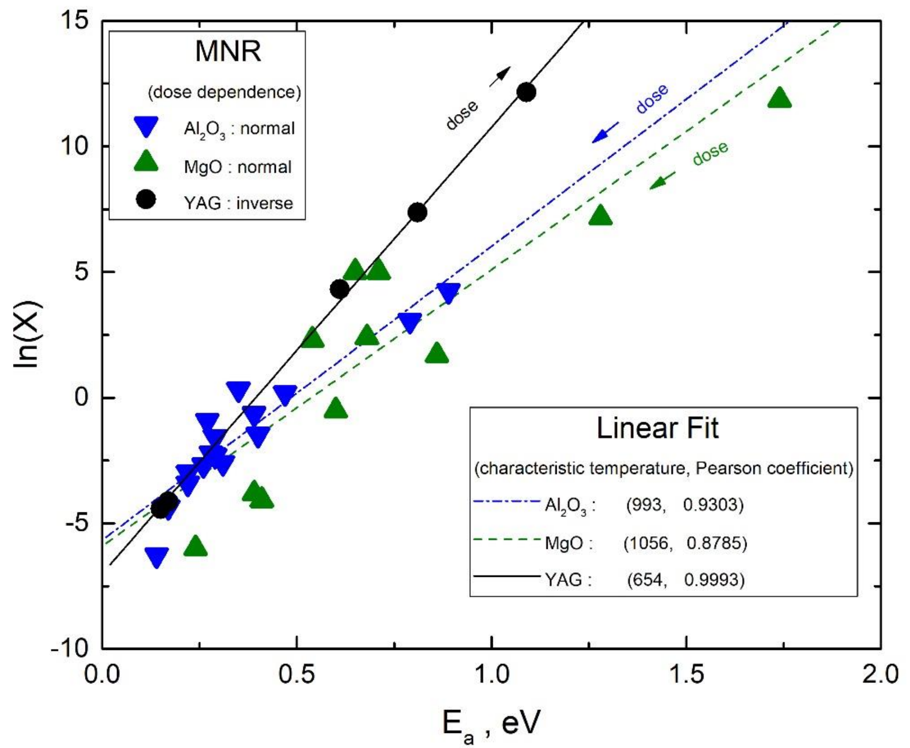
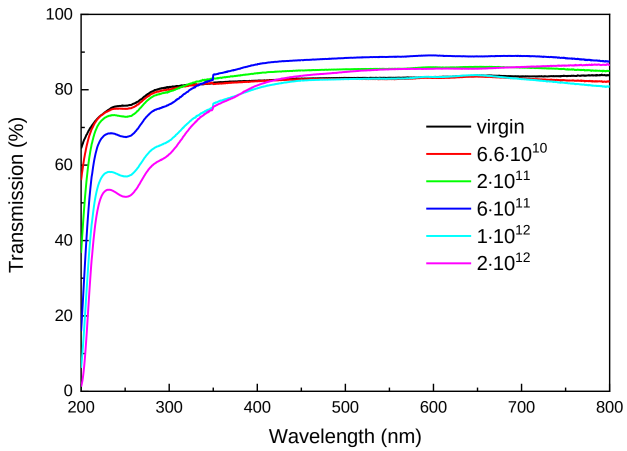


Table . The calculated migration energies E_a and pre-exponential factors X obtained from analysis of experimental data. The experimental and theoretical kinetics (points and full lines I-IV) for the four typical cases are shown in Figure.

Nr.	Type	E_a (eV)	X (K^{-1})	Legend
1	F^+(375 nm)	1.09	$1.9x10^5$	Fast neutrons (>1.2 MeV), fluence 4.1 x 10^{18} n cm^{-2}
2 (I)	F (250 nm)	0.17	$1.6x10^{-2}$	Fast neutrons (>1.2 MeV), fluence 2.2 x 10^{17} n cm^{-2}
3 (II)	F^+(375 nm)	0.15	$1.2x10^{-2}$	Fast neutrons (>1.2 MeV), fluence 2.2 x 10^{17} n cm^{-2}
4 (III)	F (250 nm)	0.81	$1.6x10^3$	Fast neutrons (>1.2 MeV), fluence 4.1 x 10^{18} n cm^{-2}
5 (IV)	F (250 nm)	0.61	$7.5x10^1$	Cr ions, fluence 7.0 x 10^{12} cm^{-2}

Meyer-Neldel rule in $Y_3Al_5O_{12}$





Xe ions (E=156 MeV) irradiations were performed at fluences ranging from 10^{10} to 10^{12} cm^{-2} at the IC-100 cyclotron at FLNR JINR

YAG shows the same MNR but in opposite dose direction

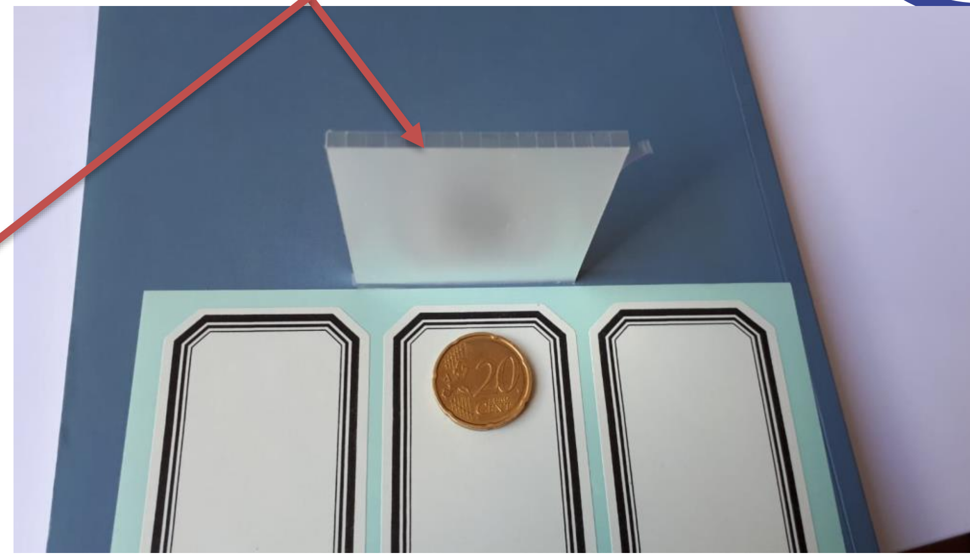
The correlation between the migration energy and pre-exponential factor (the Meyer-Neldel rule) for YAG, as well as Al_2O_3 and MgO.

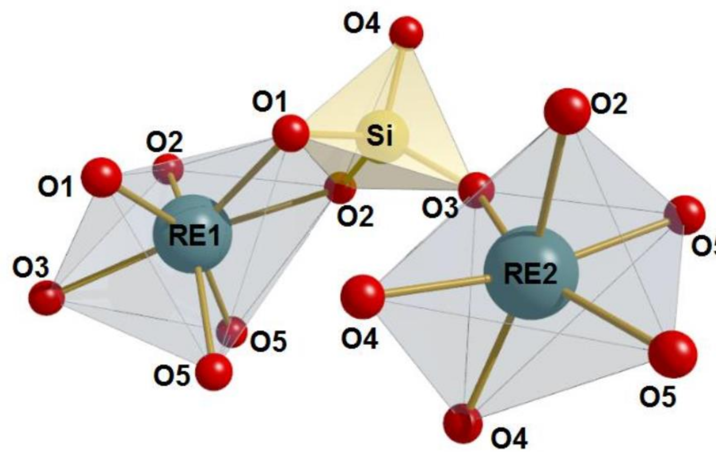
Directions of the radiation fluence (dose) increase are shown by arrows. YAG shows the same MNR but in opposite dose direction

Reference crystals

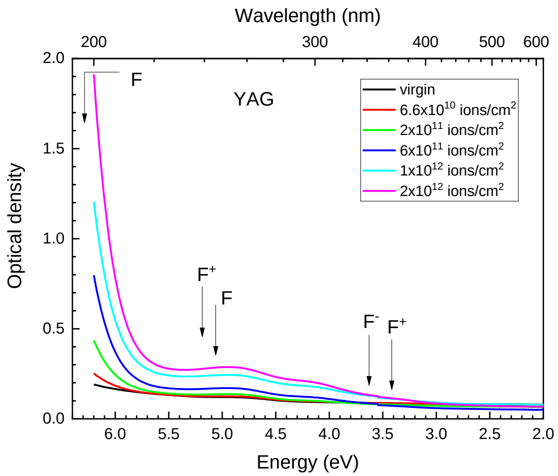
- YAG
- $PbWO_4$
- PbF_2

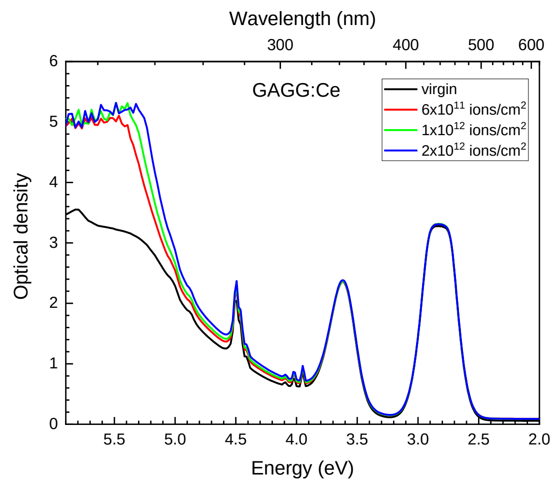
LYSO Detector unit – 16 crystals from CALTEH (USA)

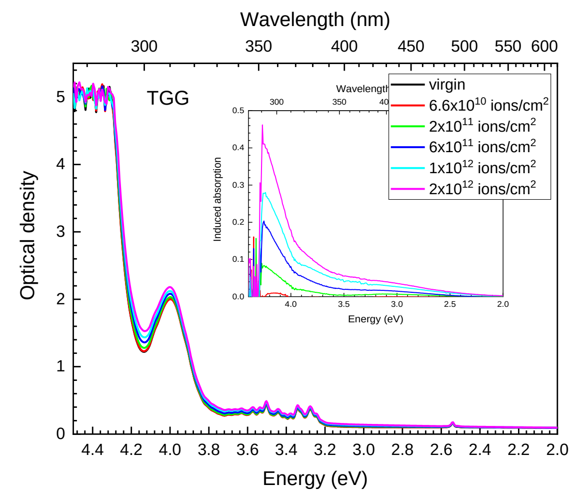


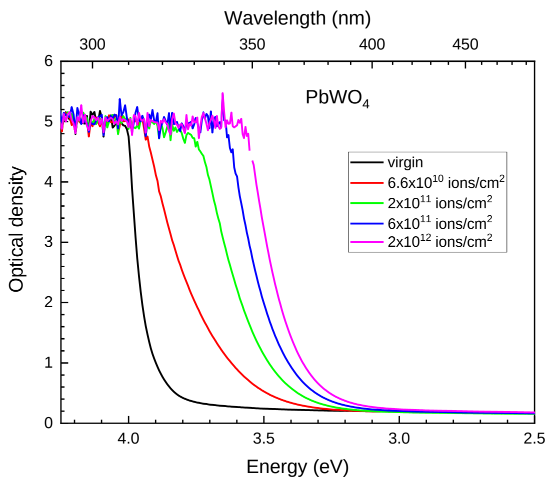


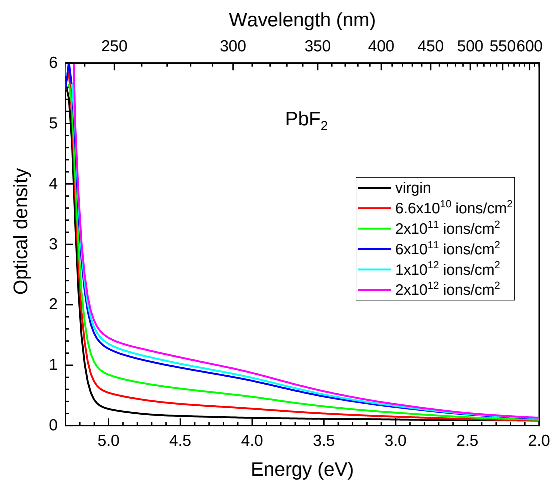
Radiation Induced Optical Absorption

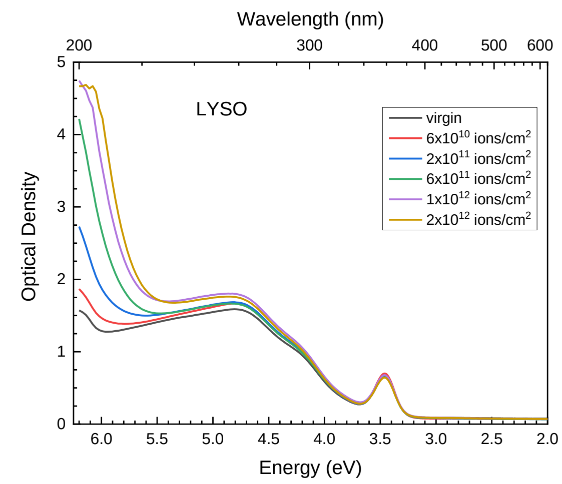






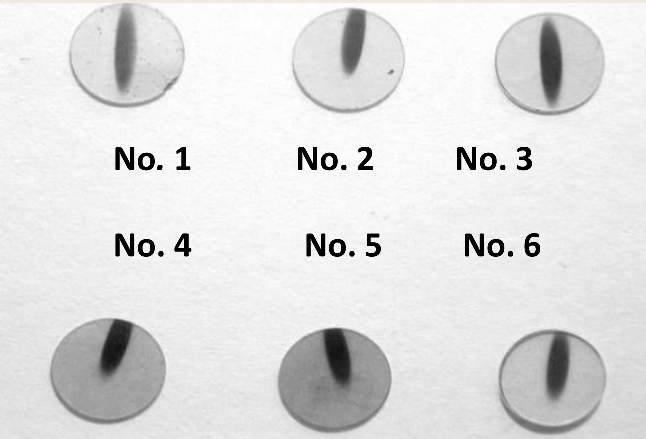




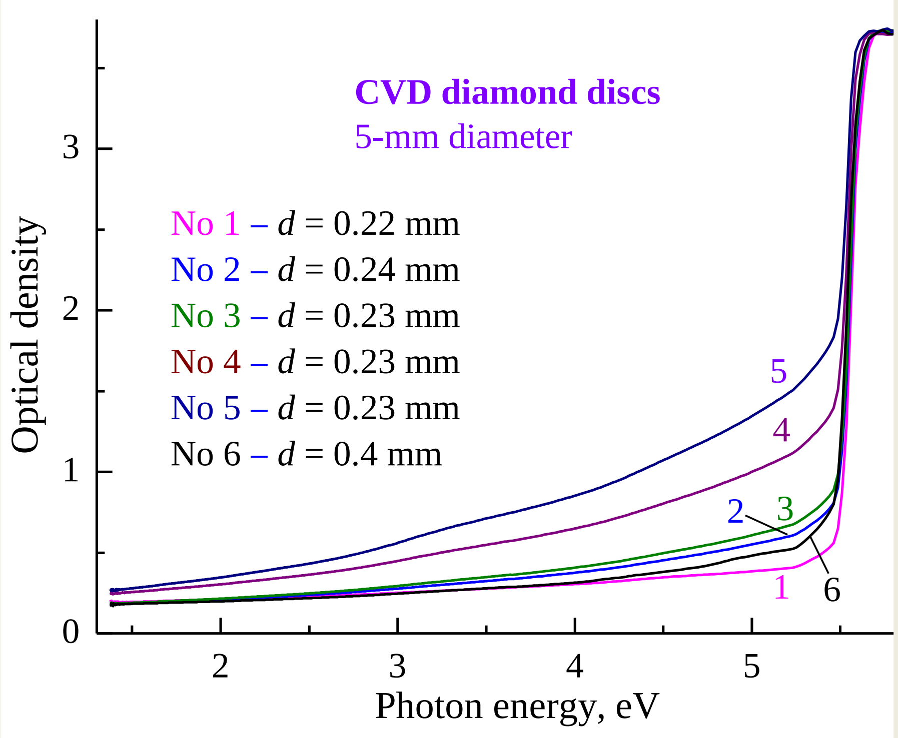


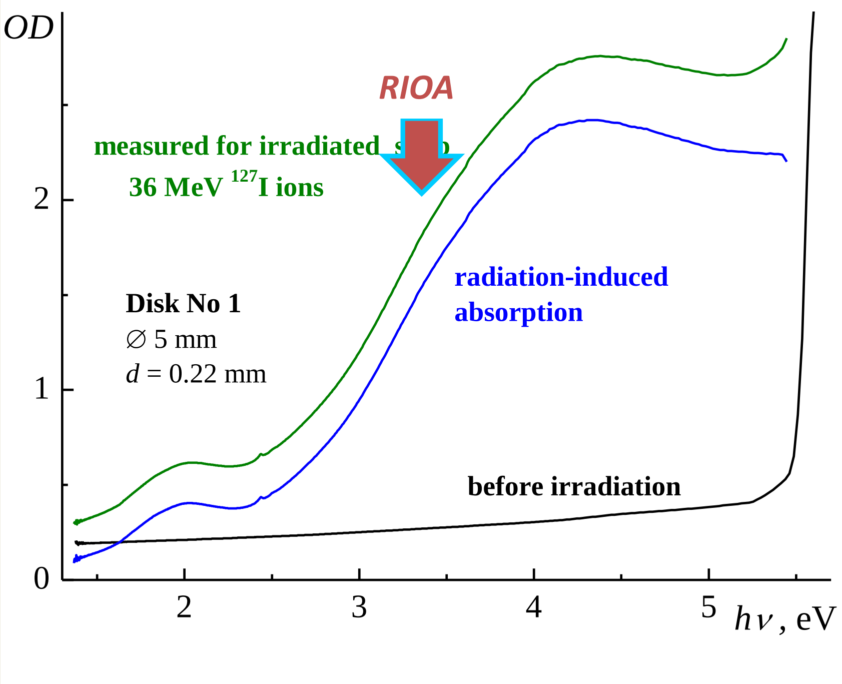
EUROfusion ENR – DDRM

Six 5-mm-diameter discs of SVD diamond have been analyzed **before and after** irradiation with 36-MeV ^{127}I ions (Elastic Recoil Detection Analysis (ERDA) measurements using Tandem accelerator in Angström-Lab, Uppsala).



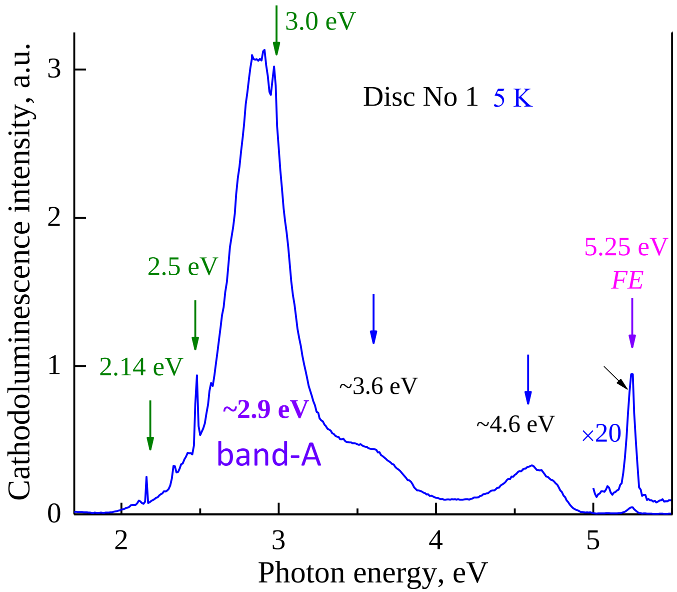
Optical absorption spectra for nonirradiated Diamond discs, JASCO-V660 spectrophotometer





Modeling of thermal defects annealing (IN PROGRESS)

Mapping: CL spectroscopy of virgin/irradiated diamonds



Band A - recombination of *e* and *h* bound separatly to donors (N) and acceptors (Al)

Narrow lines at 2.14, 2.5, 3.0 eV are zero-phonon annihilation of various ***bound excitons***.

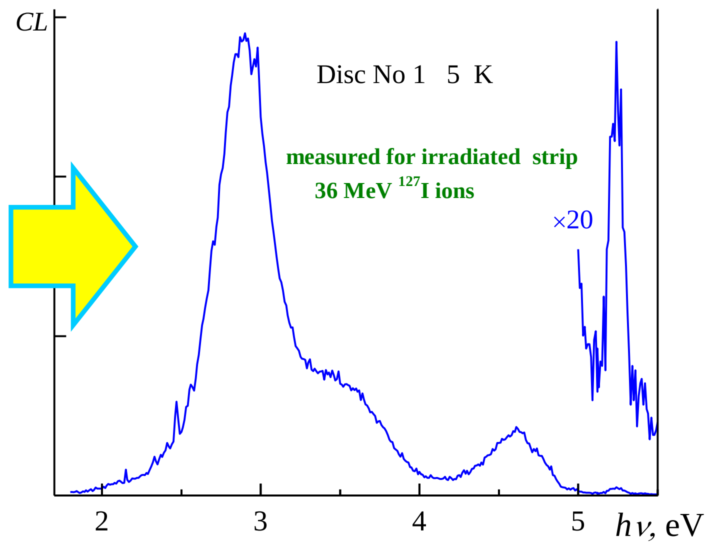
Lines around 5.25 eV (close to fundamentaal absorption edge) belongs to ***free excitons*** and phonon replicas (TO 87 meV, TA 141 meV and LO 163 meV).

Broad bands at ~3.6 and ~4.6 eV not clear yet

Dean PJ, 1965 *Phys. Rev. Review* 139(2A), A588.
Collins AT *et al.,* 1989 *J. Phys.: Cond.Matter*. 1 4029
Takeuchi et al., 2001 *PRB* 63, 245328

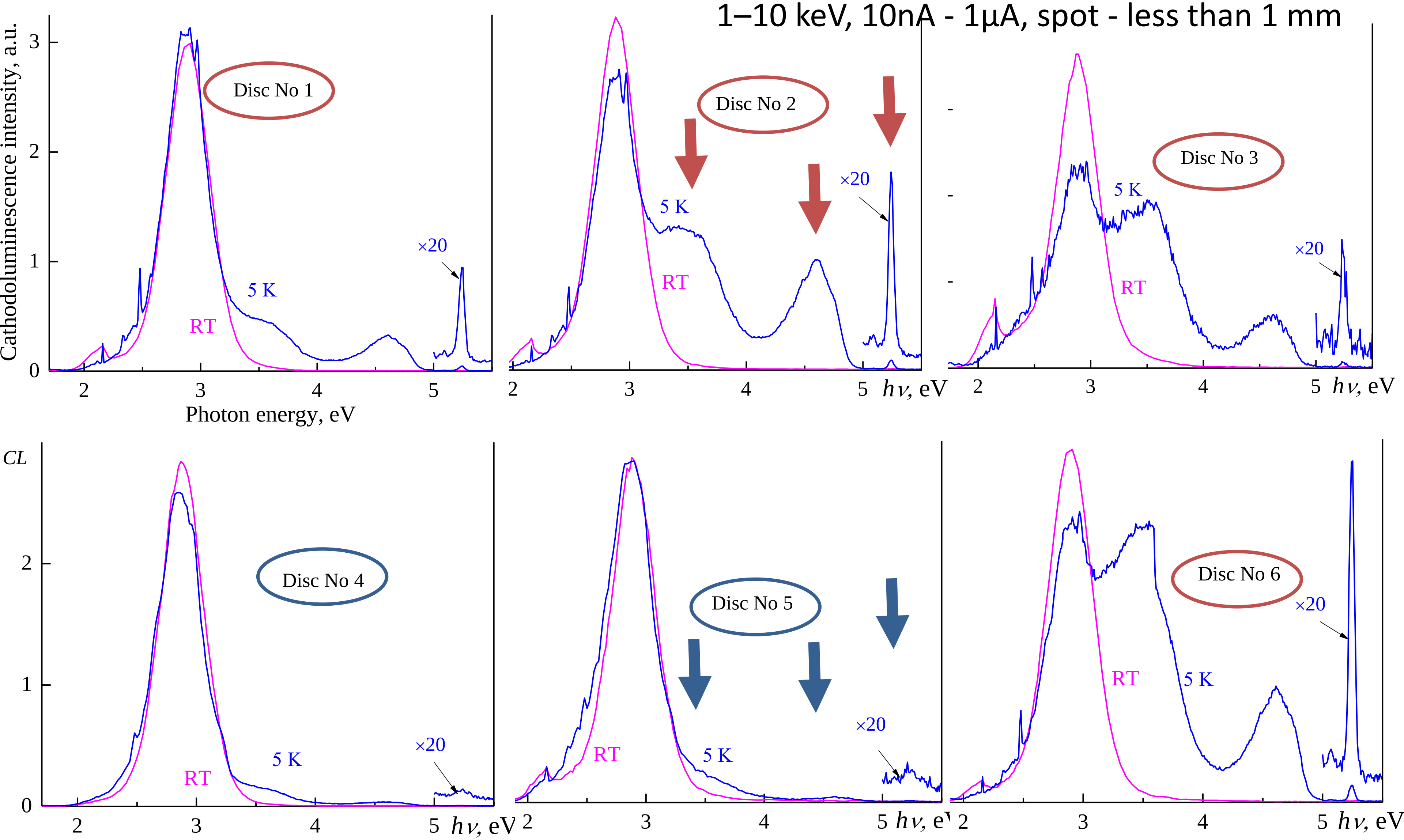
Drastic (at least by **2 orders of magnitude**) and **spectrally not** considerably **selective** drop of CL intensity.

Range of 36-MeV ^{127}I ions is around 5 μm (via SRIM)

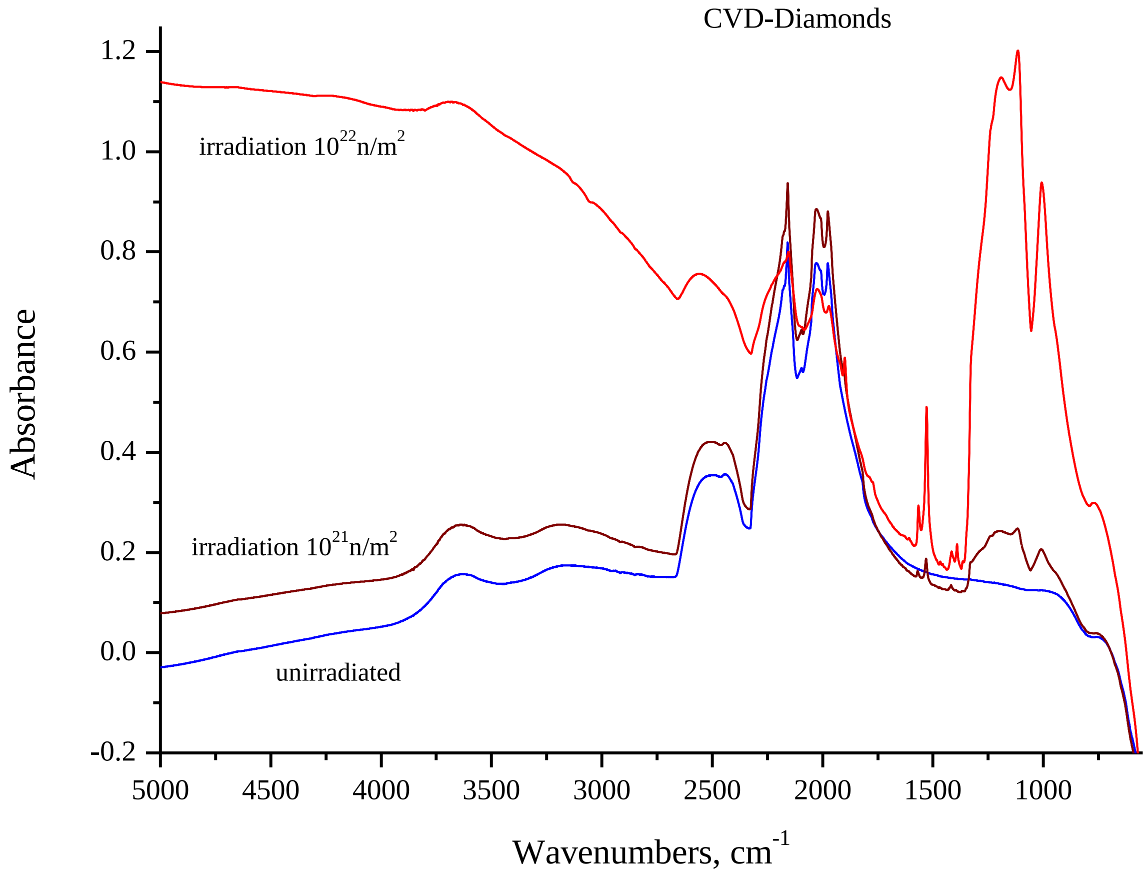


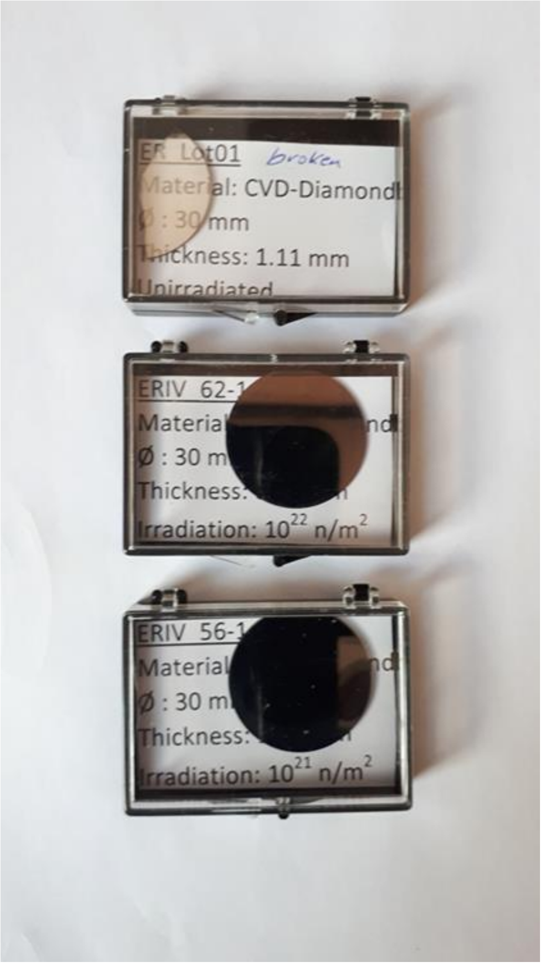
Comparative CL spectroscopy of virgin diamonds

Electron gun: steady 1-30 keV or 10-ns pulsed 1–10 keV, 10nA - 1μA, spot - less than 1 mm



Infrared spectroscopy of neutron irradiated diamond





Conclusion

- **We have performed a detailed analysis of the kinetics of F-type center thermal annealing in the irradiated MgO, MgF_2, Al_2O_3, $MgAl_2O_4$ etc**
- **F center annealing depends on the type of the irradiation as well as fluence**
- **Macroscopic disordering of the crystalline structure (cf. electron and neutron/ion irradiation results) Meyer–Neldel rule in MgO, MgF_2, Al_2O_3 and $MgAl_2O_4$**
- **In strongly irradiated ionic solids radiation defect migration is not necessarily characterized by unique migration energy with constant pre-exponent!**
- **<u>In some cases, the experimental data allows to obtain the activation energy for migration. This makes data analysis complicated</u>**
- **Similar results are in progress for many other materials: $Y_3Al_5O_{12}$, CeO_2, BeO etc., We need more experimental data. We need more samples.**
- **Note that this is one of few first attempts to quantify the kinetics of the defect annealing in these materials which needs further detailed analysis.**
- **Short progress report on EUROfusion ENR project "Investigation of defects and disorder in non-irradiated and irradiated Doped Diamond and Related Materials for fusion diagnostic applications (DDRM) – Theoretical and Experimental analysis“.**