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New dielectric functional materials and interfaces (DFMI) – Theoretical and Experimental analysis (2024-2025)

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Our objectives include the following basic steps:

1. Understanding of the role of impurities in diamond (^{13}C, N, H) related to optical and dielectric properties (loss tangent, dielectric constant, magnetization effects)
2. Influence of doping with boron on electrical conductivity, band gap, dielectric and optical properties with the target of developing a neutron dosimeter for diagnostics
3. Irradiation of boron-doped diamond and determination of physical consequences for the use in nuclear fusion reactors
4. Precise calculations of defect-induced vibrational properties, using first principles methods (comparison of diamond and silicon carbide)
5. Validation of experimental data by RAMAN, IR, UV, VIS and EPR spectra
6. Theoretical investigation of interface structures between diamond and SiO/AlN
7. Experimental verification of interface structure and thin films properties (SEM, EBSD, EDX, FIB, TEM, AFM, nano-indentation/scratch tests)
8. Single crystalline exotic dielectrics: $LaAlO_3$, $NdGaO_3$, Y-ZrO_2 (YSZ) and SiC

Size of the samples: 1x5x10 mm.
We just received: disks with diameter 25-50 mm.

New dielectric functional materials and interfaces (DFMI) – Theoretical and Experimental analysis - Annual Work Plan for 2025 year.

- **Investigation of un-irradiated and irradiated functional materials (pure and B-doped diamond, AlN, SiOx and interfaces) and the related optical and dielectric and magnetic (when applicable) properties, by VUV, UV, Raman, EBSD, TEM techniques.**
- **Detailled comparative studies of exotic dielectrics $LaAlO_3$, $NdGaO_3$, Y-ZrO_2 (YSZ), SiC before and after irradiation.**
- **Detailed analysis of thermal annealing of radiation defects in AlN, diamond, LaAlO3, $NdGaO_3$, Y-ZrO_2 and SiC. Determination of defects parameters as a function of fluence and type of irradiation.**
- **Validation of the experimental results by ab-initio calculations.**
- **Several Irradiation campaigns, using swift-heavy ion radiation accelerator in Kazakhstan and neutrons (Mols reactor)**

Executive Summary

The proposal of DFMI project has the goal to combine experimental investigations of new functional materials used in diagnostics and heating and current drive applications in fusion reactors with theoretical calculations to provide an exhaustive understanding of material behaviour and the corresponding properties which are of high relevance for DEMO development works in the frame of EUROfusion activities taking the fusion roadmap into account. A tremendous emphasis is put on radiation resistant functional materials (FM) used for optical systems and for microwave and THz transmission applications. **The main idea is the physics understanding of that group of crystalline solid state systems.**

In particular, as planned, several **single crystalline exotic** dielectrics: $LaAlO_3$, $NdGaO_3$, Y-ZrO_2 (YSZ) and SiC were studied before and after irradiation with neutrons at SCK CEN, Mol (Belgium) or swift heavy-ion irradiation in Astana at DS-6 accelerator, providing ^{84}Kr and ^{132}Xe in the energy range 0.35 - 1.75 MeV/nucleon. The corresponding radiation effect and the resulting defects were studied in details by X-ray diffraction, Raman, optical absorption, luminescence spectroscopy as well as VUV photoluminescence/reflectivity at synchrotron beamlines at DESY and MAXIV.

Comparison of obtained results with earlier irradiated/obtained MgO, Al2O3, BeO and Si3N4 were done.

Precise ab-initio calculations of defect-induced optical and vibrational properties, using first principles methods (LaAlO3 and diamond).

As a results, four papers were published and few are in preparation

Comments (shortcomings, deviations, etc.)

- In general, only one derivable was not achieved fully. Due to several reasons (see the Table with deliverables and the relevant text), we have not succeeded in measurements with neutron irradiated samples. At the same time, considerable amount of information on swift heavy ion irradiation properties have still been obtained via Raman and FTIR measurement as well as relevant first-principle calculations.
- Ab-initio calculation were not fully completed due to weather emergency at CINECA High Performance Computing center, Marconi supercomputer was not in production in October-December. This has limited the output of WP5 due to lack of computational resources, as well inaccessibility to previously obtained results that were stored there

Scientific deliverable *(annual scientific deliverables as specified in the Task Agreement)*	**Achieved: Fully/Partly/Not**	**Evidence for achievement, brief reason for partial or non-achievement**
1. Detailed comparative analysis of radiation-induced polymorphic transformation in ZrO2 ceramics.	Fully	Results published in *Optical Materials 156 (2024) 115994*
2. Swift heavy ion /neutron irradiation campaine (SiC, LaAlO3 and NdGaO3	Partly/Fully	SiC and LaAlO3 both from 2 different suppliers were successfully irradiated by swift-heavy ions, NdGaO3 was not irradiated. Neutron irradiation is in progress
3. Analysis of general picture about OA, PL, RAMAN properties of heavily irradiated materials SiC and LaAlO3	Partly/Fully	Experiments were successfully performed. Data treatment and paper preparation are in progress.
4. Ab initio calculations of Boron-doped diamond	Fully	Calculation are completed. Paper is in prepation
5. Ab initio calculation of pure and defective LaAlO3	Partly	Due to weather emergency at CINECA High Performance Computing center, Marconi supercomputer was not running in October-December. This has limited the output of WP5 due to lack of computational resources, as well inaccessibility to previously obtained results that were stored there

4. Publications/presentations

Provide the list of publications produced by your project, **EUROfusion Pin board ID** is essential for cross-check of publications

First Author	Initials	Title of work	Journal / Conference	Doc. Type	DOI or status of paper	Pinboard ID
Kozlovskiy	**A**	Study of irradiation temperature effect on radiation-induced polymorphic transformation mechanisms in ZrO2 ceramics	*Optical Materials 156 (2024) 115994*	*Paper*	*published*	*1022*
Kozlovskiy	**A**	Study of the effect of nanostructured grains on the radiation resistance of ZrO2 ceramics during gas swelling in the case of high-dose irradiation with He2+ ions	*ES Materials and Manufactoring 24 (2024) 1165*	*Paper*	*published*	*1023*
Ryskulov	**A.**	The effect of residual mechanical stresses and vacancy defects on the diffusion expansion of the damaged layer during irradiation of BeO ceramics	*Optical Materials X 24 (2024) 100375*	*Paper*	*published*	*1024*
Borbekov	**D.**	The effect of oxygen vacancies on the optical and thermophysical properties of (1-x)Si3N4 – xAl2O3 ceramics	*Optical Materials 157 (2024) 116056*	*Paper*	*published*	*1025*

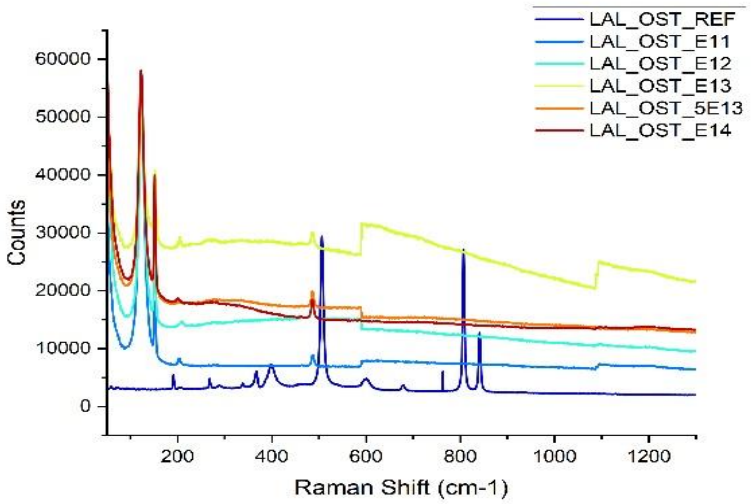
The following samples were studied:

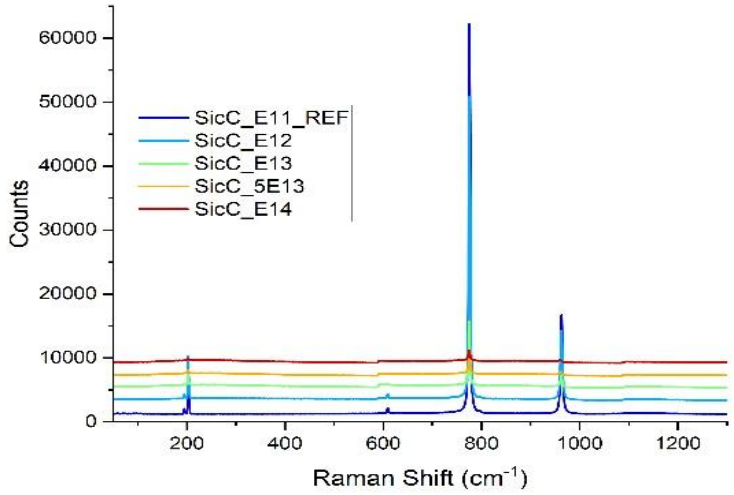
Un-doped materials: single and poly-crystalline diamond samples (SCD, PCD),

Un-doped materials: $LaAlO_3$, $NdGaO_3$, Y-ZrO_2 (YSZ) and p-Boron doped diamond.

In 2024 for deep understanding of functionality in new dielectric materials for diagnostics in fusion reactors (engineering solution approach and theoretical undertanding) we performed their full characterization by RAMAN, XRD, UV, VUV, OA, including corresponding VUV luminescence/reflectivity measurements at synchrotrons DESY (Hamburg) and MAXIV (Lund). Furthermore, most of the samples were irradiated 231-MeV ^{132}Xe ions with four fluences from 10^{10} to 10^{14} cm^{-2} (DC-60 accelerator in Astana, Kazakhstan) and then characterized and compared with non-irradiated reference samples as well as with the samples from our previous ENR projects. Some obtained results were already published (see the publication list), but the most obtained data are under treatment and corresponding publication are in preparation. The most complete results relate to ZrO2, as a results two papers were already published.

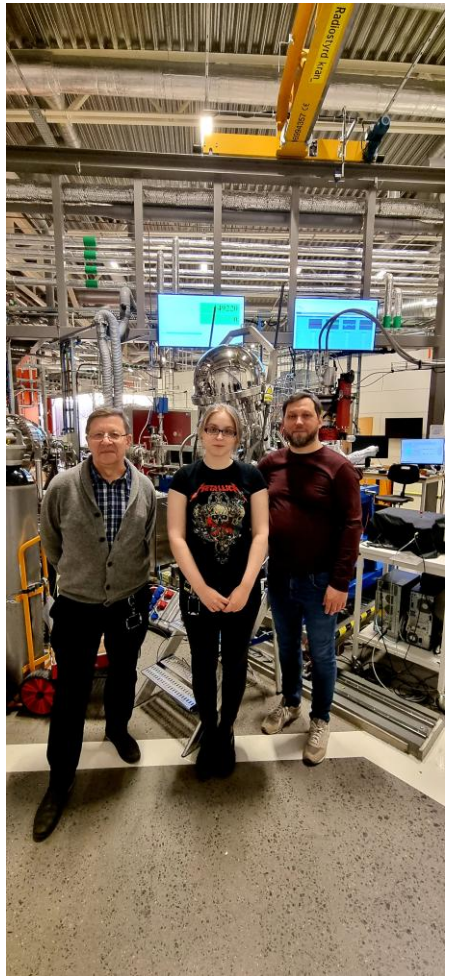
Some the most interesting results are shown below:

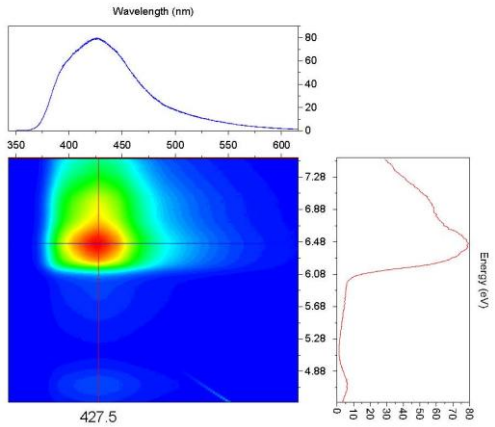




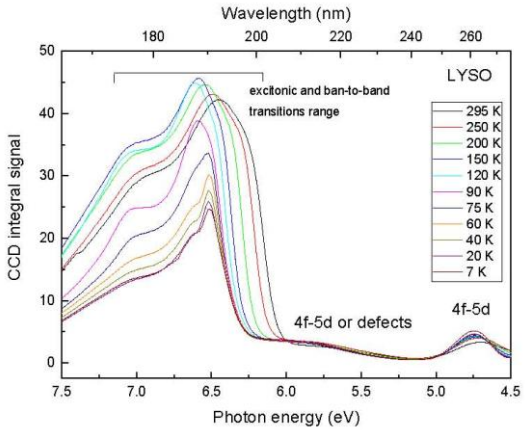
While in case SiC only suppression of the main Raman peaks is observed, in the second case of LaAlO3 the formation of new (for the first time) so-called defect-induced Raman modes is found.

VUV measurements at MAXIV synchrotron radiation facility, LUND, SWEDEN



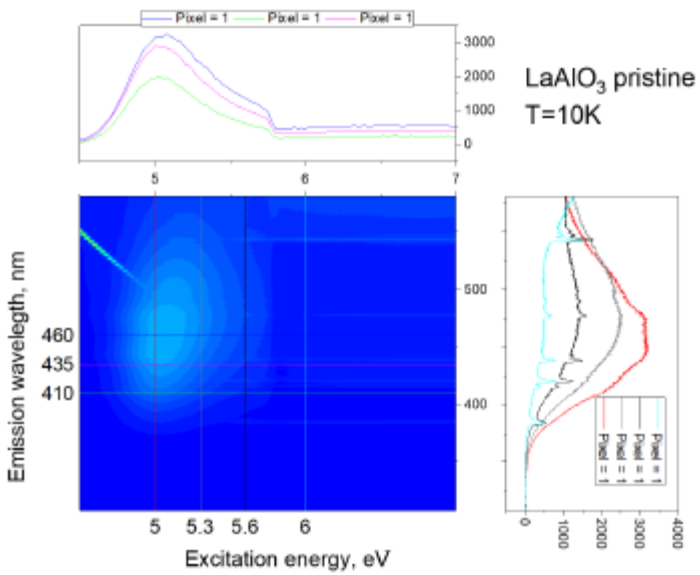


Contour map of the excitation and emission spectra centers at 295 K. The profiles of the emission spectra (top) and excitation spectra (right) in the maximum intensity are shown.

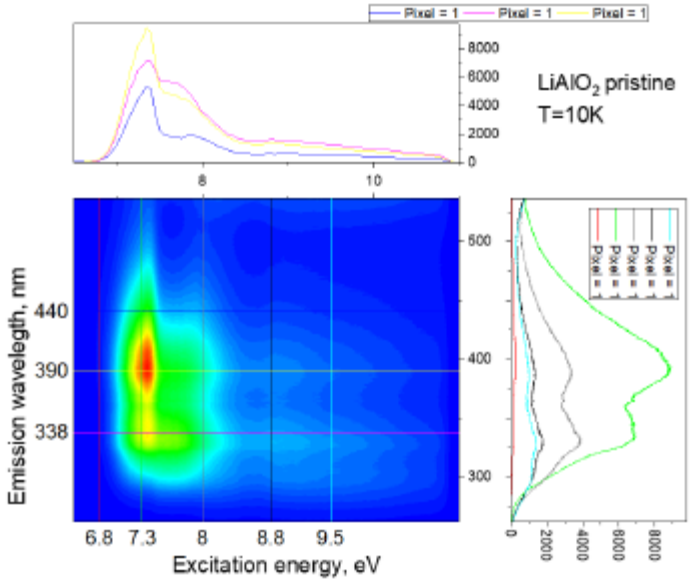


Temperature dependency of the excitation spectra monitored at specific wavelengt

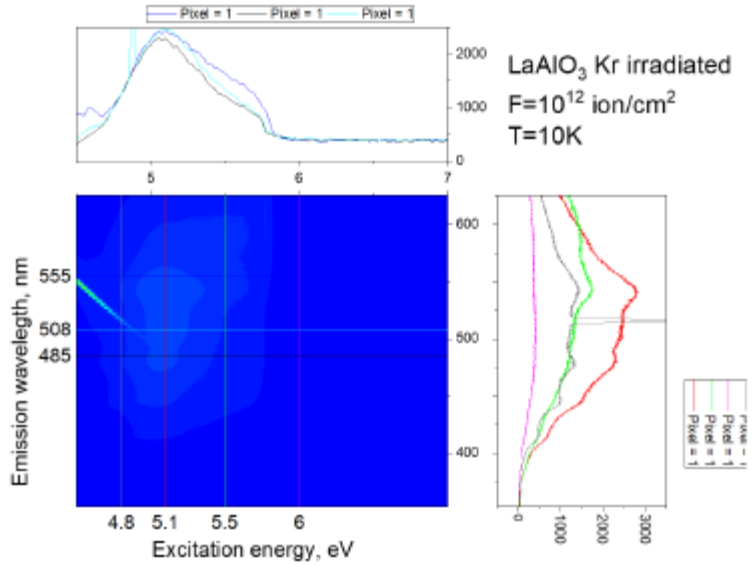
VUV synchrotron study (MAXIV, Lund, Sweden)



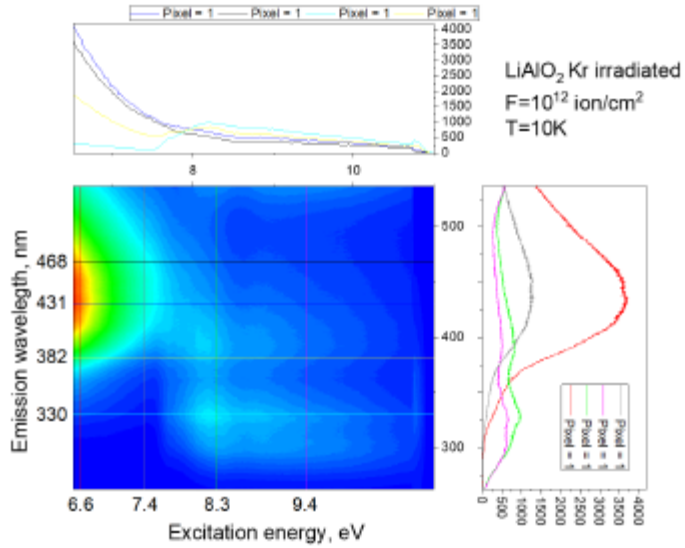
$LaAlO_3$ pristine
T=10K



$LiAlO_2$ pristine
T=10K

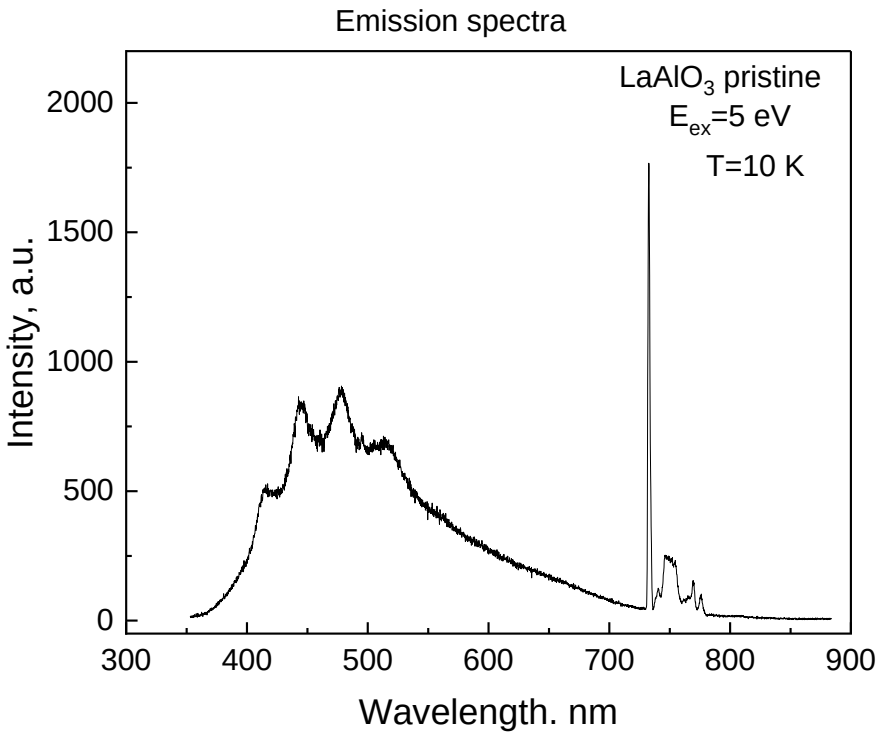


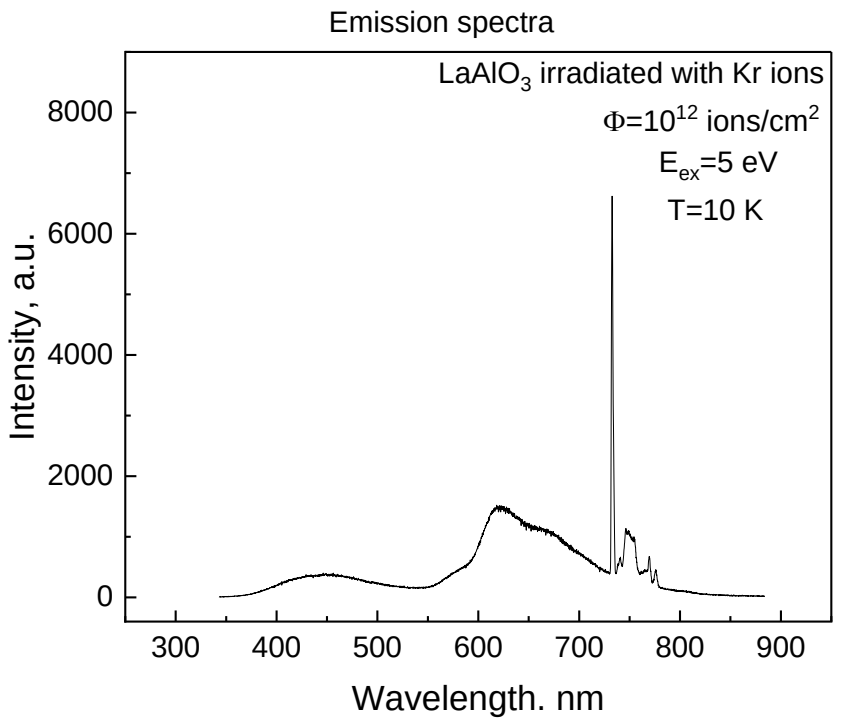
$LaAlO_3$ Kr irradiated
$F=10^{12}$ ion/cm^2
T=10K



$LiAlO_2$ Kr irradiated
$F=10^{12}$ ion/cm^2
T=10K

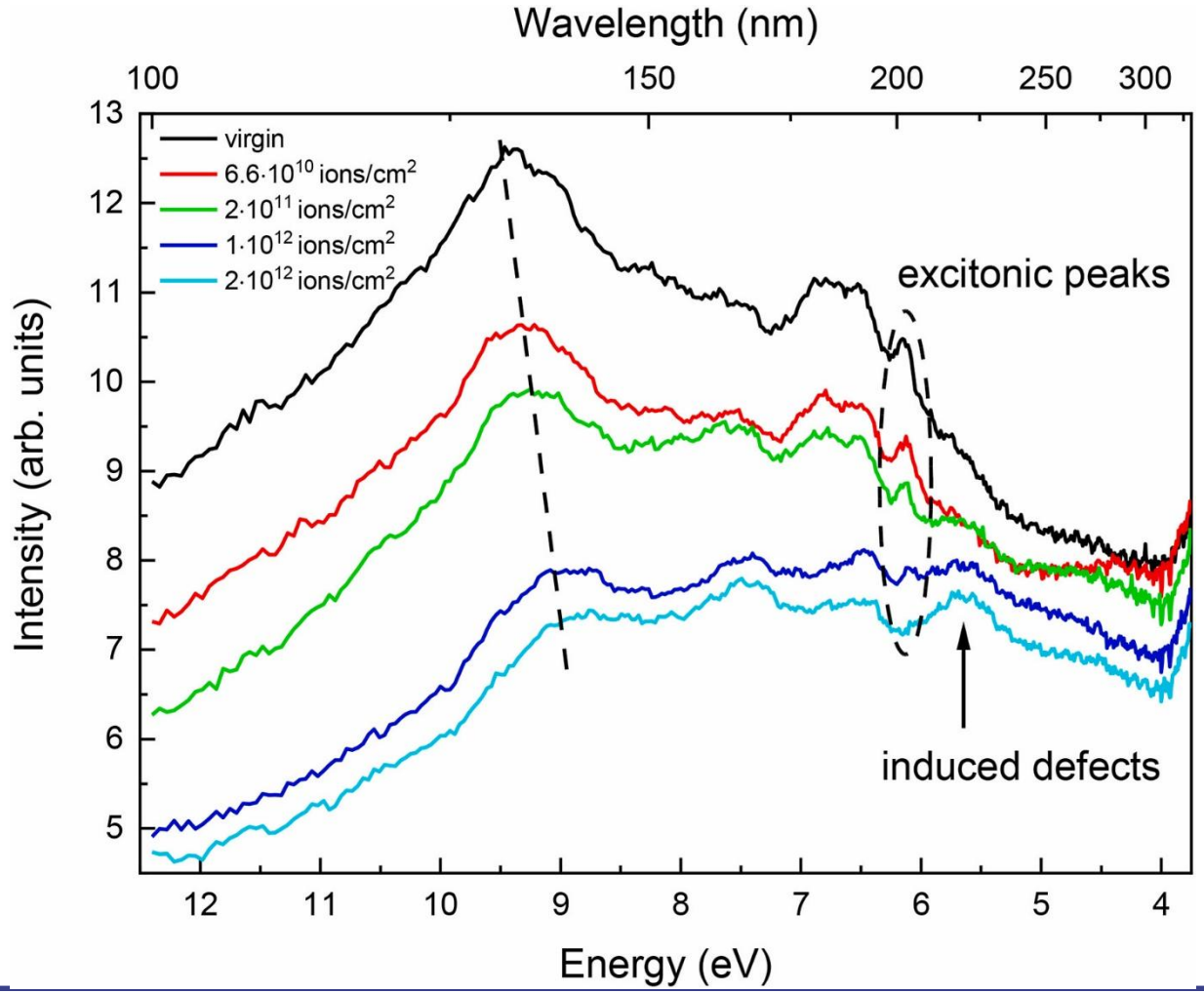
The next series of experiments relates this behavior to the optical and dielectric properties in the process of the data analysis. In particular, we have performed detailed comparative measurement of their luminescence properties at synchrotrons MAVIV and DESY at 10-300 K.





Clear appearance of new defect states is observed not only in the luminescence spectra (shown above), but also in their excitation spectra (not shown) at all applied Kr ion flunce.

The reflection spectra at 12 K in virgin and irradiated crystals under different fluences (the fluences in ions/cm^2 are shown in legend). The dashed area indicates the excitonic peaks.



P66 beam line (DESY):

Main conclusion:
The radiation damage induced by swift heavy ion irradiation of the results in the significant damage of the crystal surface.

Surface amorphization
Metallization.
Detailed analysis by Ellipsometry, Reflectivity, Excitation Luminescence

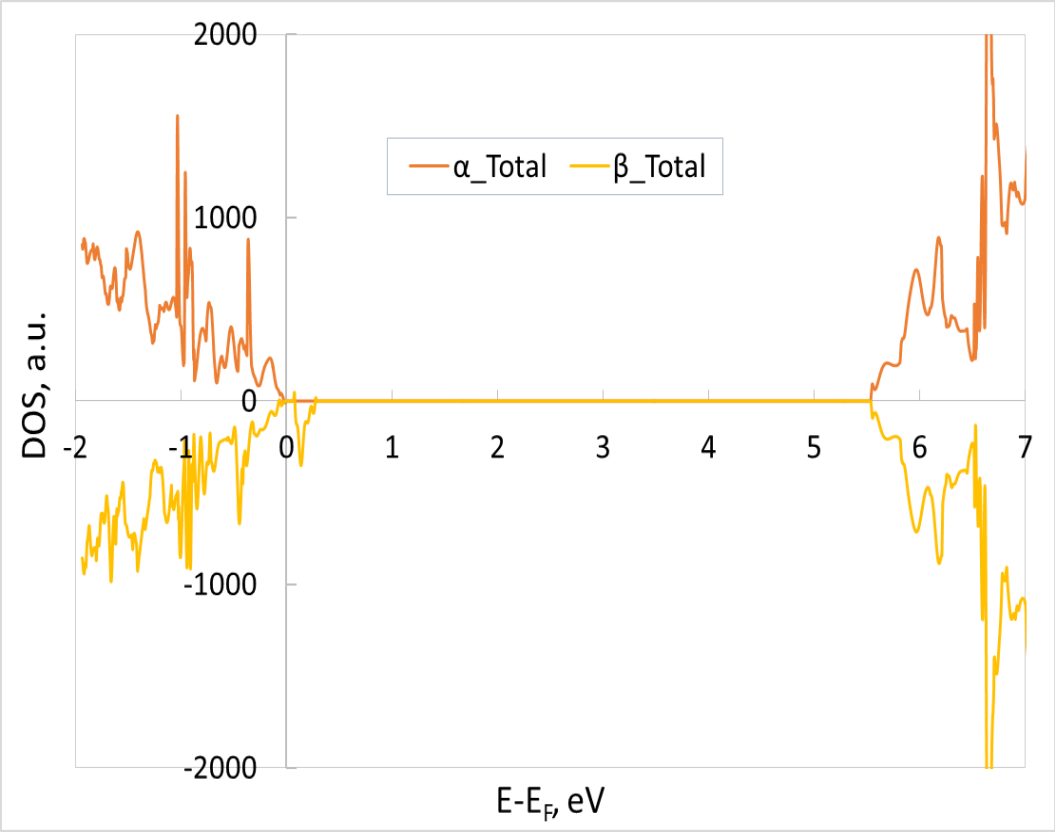
We have also performed a detailed characterization of $NdGaO_3$ and completed comparative corresponding optical measurements with MgO, BeO and Si_3N_4-Al_2O_3 ceramics.

- 1. X-ray diffraction
- 2. Optical absorption
- 3. Luminescence
- 4. Raman

According our objectives we have performed

ab-initio calculation of diamond with boron dopant.

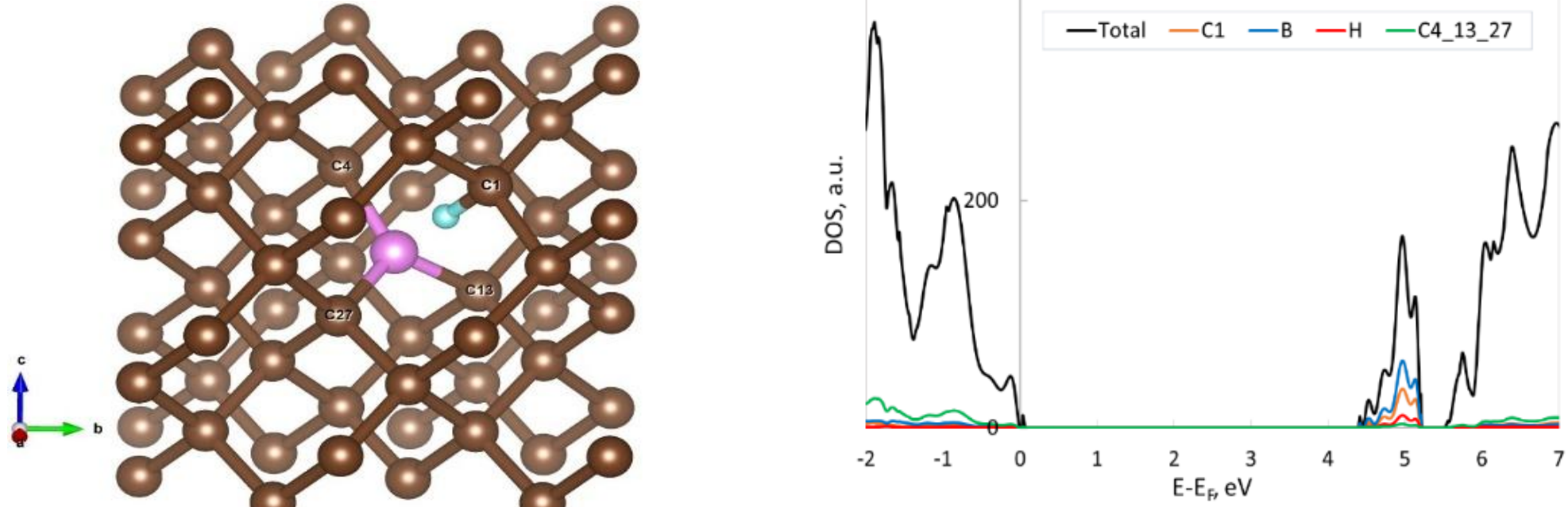
Figure shows the Total electronic DOSs of α- and β-electrons for diamond with boron dopant. Spin state S_z = 1/2. Part of valence band (VB), in-gap unoccupied defect band near VB band and part of conducting band (CB) are shown. The zero energy value corresponds to the Fermi level.



The second subject of our research was ***ab initio* study of the boron-hydrogen complex defect in diamond**.

We have also performed ab initio simulations of diamond crystal with defect B+H on the base of 64- and 216-atom SC. Boron atom was considered as a substitutional atom, hydrogen as an interstitial atom. All calculations were performed in the framework of space group 1 (without taking into account symmetry of system). Our calculations revealed that diamond crystal with B+H defects really remains as dielectric system. Results of simulations of defective diamond system on the base of 64-atom SC are presented in Figure below.

Fig. Defective diamond system with B+H defect. **(a)** Fully relaxed structure with 65 atoms: 63 carbon atoms (brown balls), 1 boron atom (pink), 1 hydrogen atom (blue). **(b)** Projected



We performed computational studies on several materials employing hybrid density functional theory (DFT) as implemented in CRYSTAL23 code.

Various diamond surfaces – clean and hydrogen-terminated – were analyzed in terms of surface free energy, Debye temperature, surface atoms and hydrogen electronic energy levels, polarizability and induced dipoles in constant electric field. The influence of surface termination on the dielectric and vibrational properties was assessed and compared with each other and with literature data.

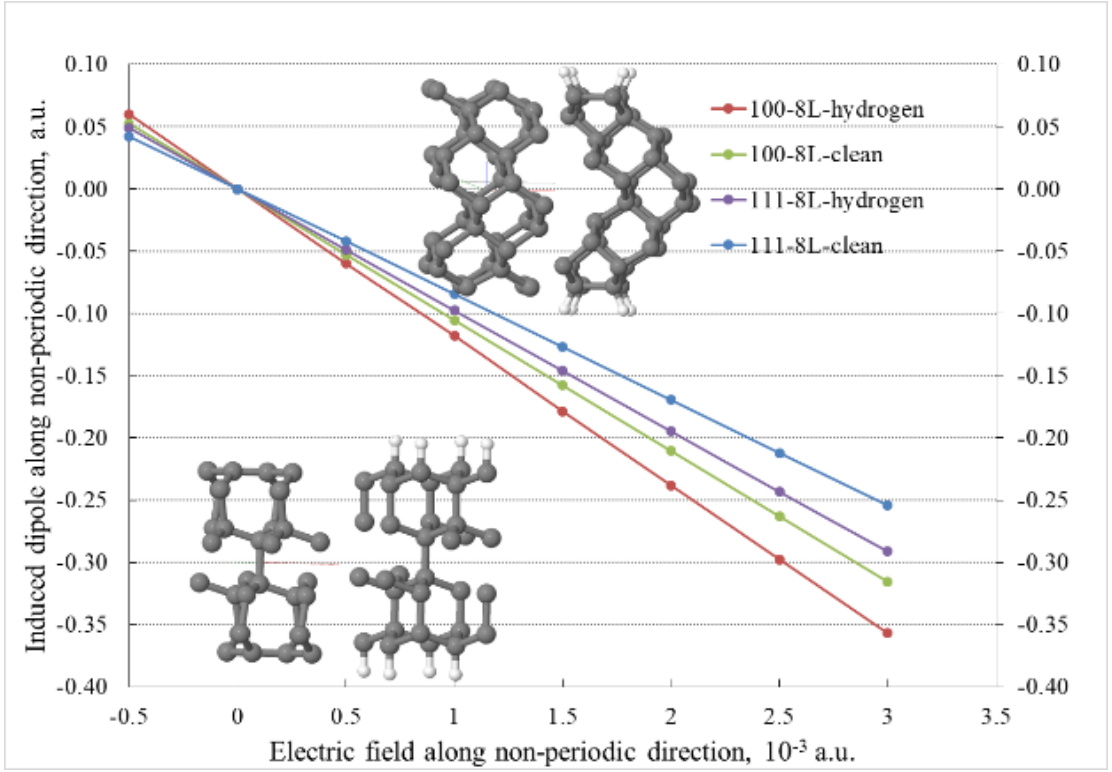
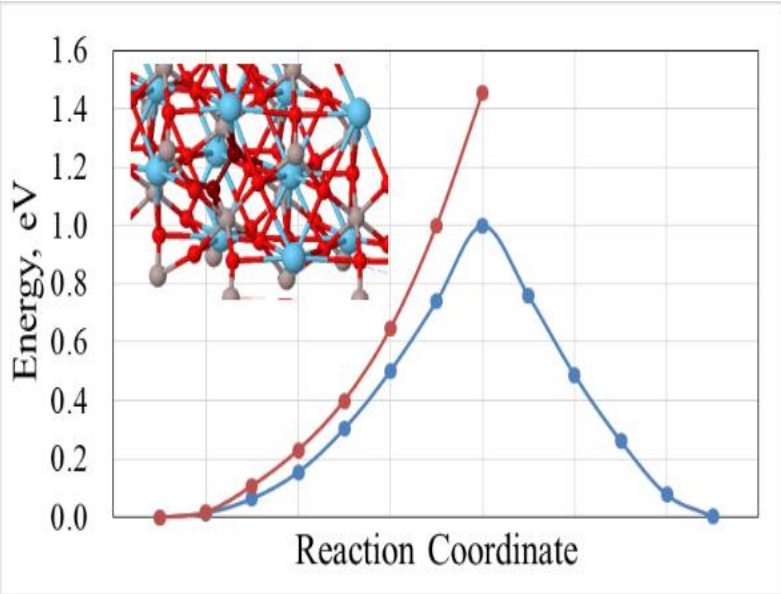


Figure 1. Optimized <100> (top) and <111> (bottom) surface models and induced dipole along non-periodic direction in different diamond slabs.

LaAlO3

- For $LaAlO_3$ we modelled series of point defects: oxygen vacancies, oxygen interstitials and cation antisite defects. From our previous experience, irradiated oxide materials contain Frenkel pairs of oxygen defects – vacancy + interstitial. In MgO and Al_2O_3 these defects have optical absorption bands (5.0-6.5 eV) in the band gap.
- $LaAlO_3$ has a band gap of ~5.7 eV, we found that defect levels of oxygen interstitials are positioned very close to or in the conduction band, which will make them undetectable with optical absorption technics. Our calculations revealed, that interstitial defects have pronounced vibrational modes: at ~1070 cm^{-1} for neutral oxygen defect, and ~900 cm^{-1} for negatively charged one.
- The mobility of oxygen interstitial defects were evaluated using Distinguished Reaction Coordinate method as implemented in CRYSTAL23 code. Several paths were picked as potential diffusion trajectories. In Figure 2 energy curve along two paths for neutral oxygen interstitial is shown. The obtained value is ~1.0 eV, which is by 0.3-0.4 eV smaller than for same defect in MgO and Al_2O_3. From this we can expect higher mobility and lower annealing temperatures for such defects. The results will be compared with experimental data for $LaAlO_3$ which is already obtained within the project.



Energy curves along the path for neutral oxygen interstitial in $LaAlO_3$ and local structure of oxygen interstitial defect (inset).

Due to weather emergency at CINECA High Performance Computing center, Marconi supercomputer was not in production in October-December. This has limited the output of WP5 due to lack of computational resources, as well inaccessibility to previously obtained results that were stored there.

Thank you very much