SOLID21
Research program 3
Photonics and energy conversion

Martin Nikl

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The project Solid state physics for the 21st century – SOLID21 CZ.02.1.01/0.0/0.0/16_019/0000760 is co-funded by the European Union.

EVROPSKÁ UNIE
Evropské strukturální a investiční fondy
Operační program Výzkum, vývoj a vzdělávání

MINISTERSTVO ŠKOLSTVÍ, MLÁDEŽE A TĚLOVÝCHOVY

RP3: Research Activities

RA1: Phosphors for solid state light sources

RA2: New material concepts and technologies of scintillation materials

RA3: Luminescence of nanostructures of silicon and other semiconductors

RA4: Nanostructures for photovoltaic solar energy conversion

RA5: Thermoelectric materials, heat transfer and thermoelectric applications

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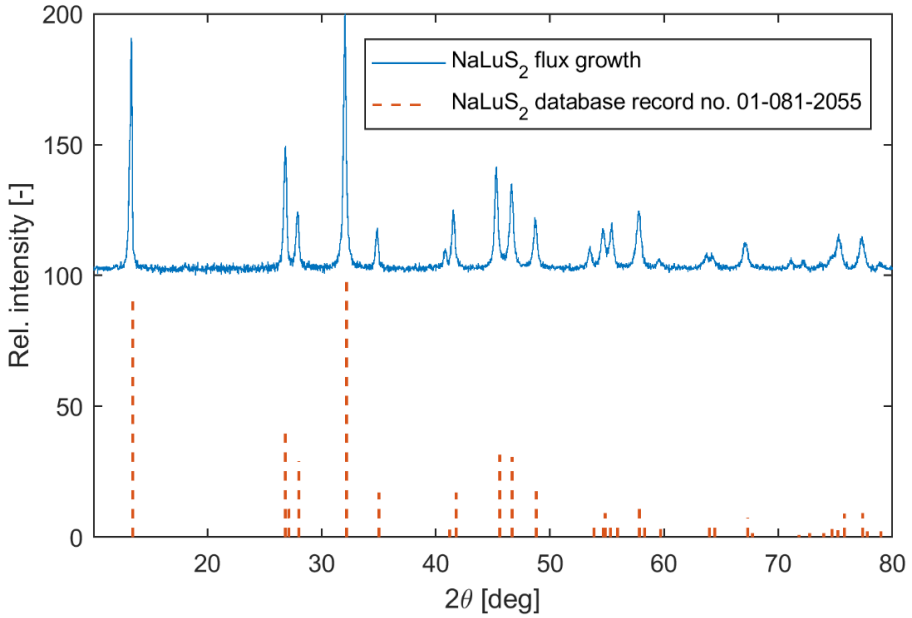
- This research programme merges FZU groups studying energy conversion. This includes the phosphors for solid state light sources, scintillating materials for ionising radiation detection, and research of photovoltaic and thermoelectric energy conversion.
- The teams involved have been participating in a number of domestic and international projects in H2020 and Horizon Europe and collaborate with world-known institutions over the globe.
- The involved groups have also established a number of application-minded collaborations with domestic and foreign industrial companies (Crytur, ASML, HVM plasma, On Semiconductors, Škoda Auto a.s.).

RA1: New sulfidic material forms for light conversion

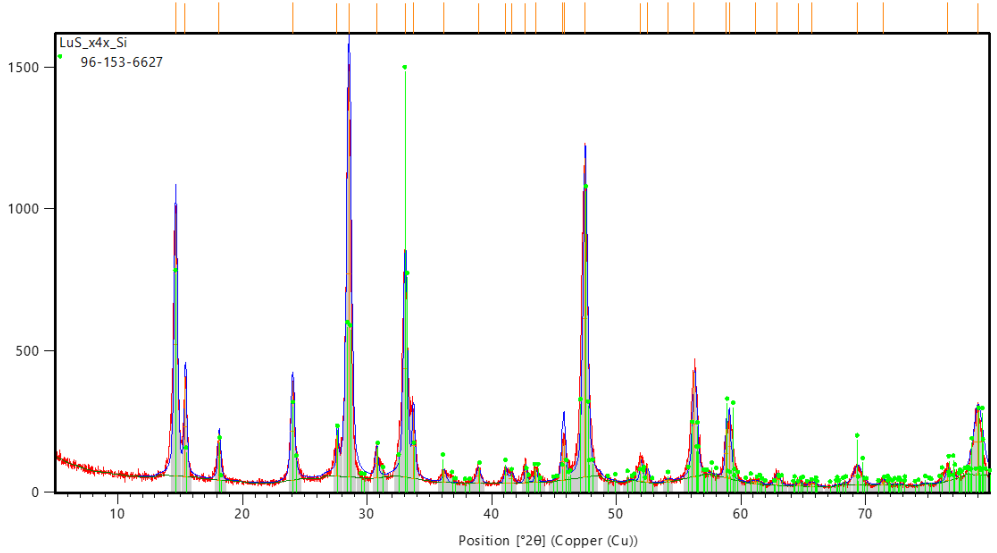
Single crystals – from thin crystalline platelets to a bulk material – **using modified halide μ-PD**

- **undoped $NaLuS_2$** – first time in the world

Unique in Europe



Thin layers – using plasmatic reactive sputtering deposition technique (in **RP5**) – undoped Lu_2S_3,



V. Jarý et al. Physical Review Applied 19, 2023, 034092
M. Brik et al. Chemical Engineering Journal 418, 2021, 129380.

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Novel persistent luminophores

- Novel garnet-based materials fully comparable to the state-of-the-art $SrAl_2O_4:Eu^{2+},Dy^{3+}$
- Excitable by blue light (indoor light based on LEDs) + emission in the maximum of eye sensitivity
- Collaboration with industry

Collaborative research with Gent university (Prof. P. Smet) based on visit of Jary in Q3 2022 – new set of samples under investigation + synchrotron in Grenoble measurement planned (Q2 2023)

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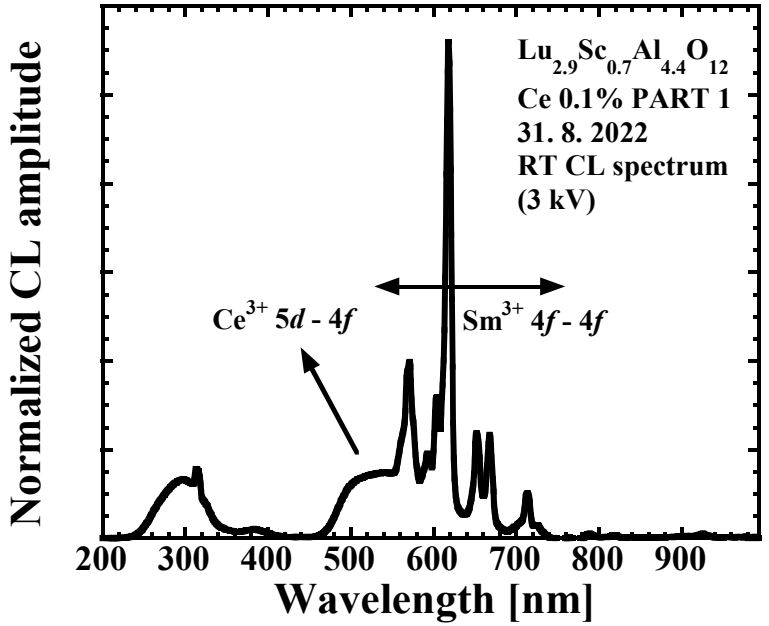
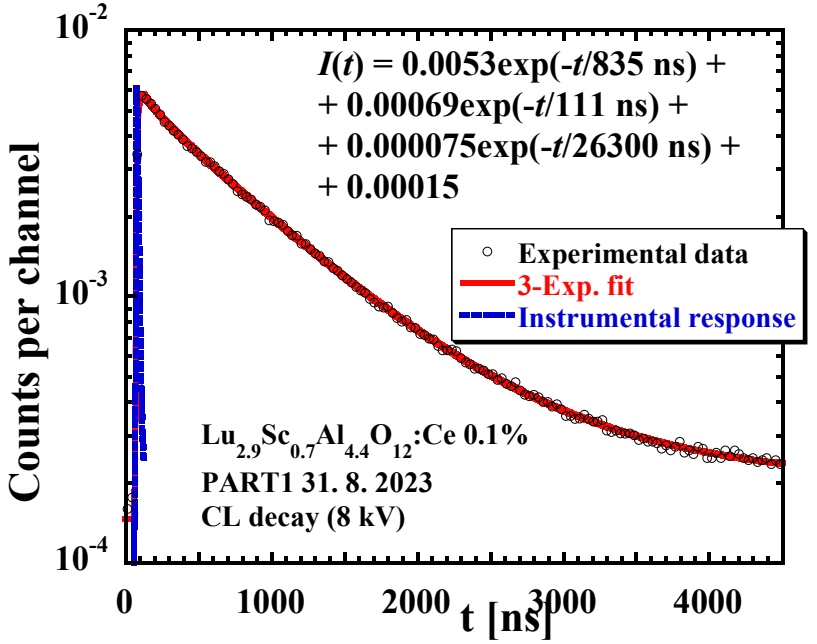
Time-resolved cathodoluminescence setup

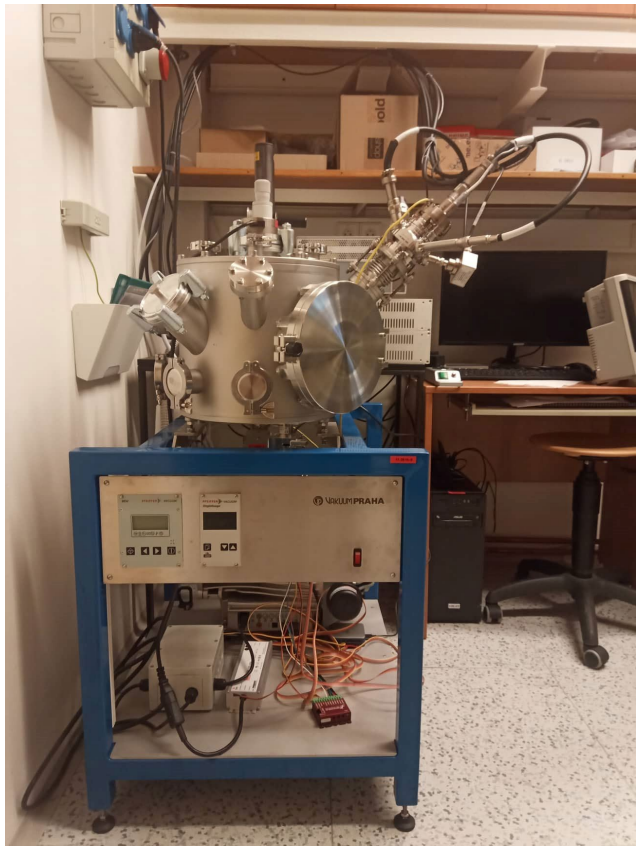
- **For both RA1, RA2** – complementary technique to investigate new materials in various forms
- Tailored vacuum chamber (Vacuum Praha) and Kimbal Physics EGG-3101 electron gun, steady-state and pulsed (**down to 5 ns FWHM**) regime, fiber optics&CCD spectrometer
- Both steady-state CL spectra and CL decays (precious for industrial collaborations)



Example of the steady-state cathodoluminescence spectrum (RT)



Example of the cathodoluminescence decay (RT)



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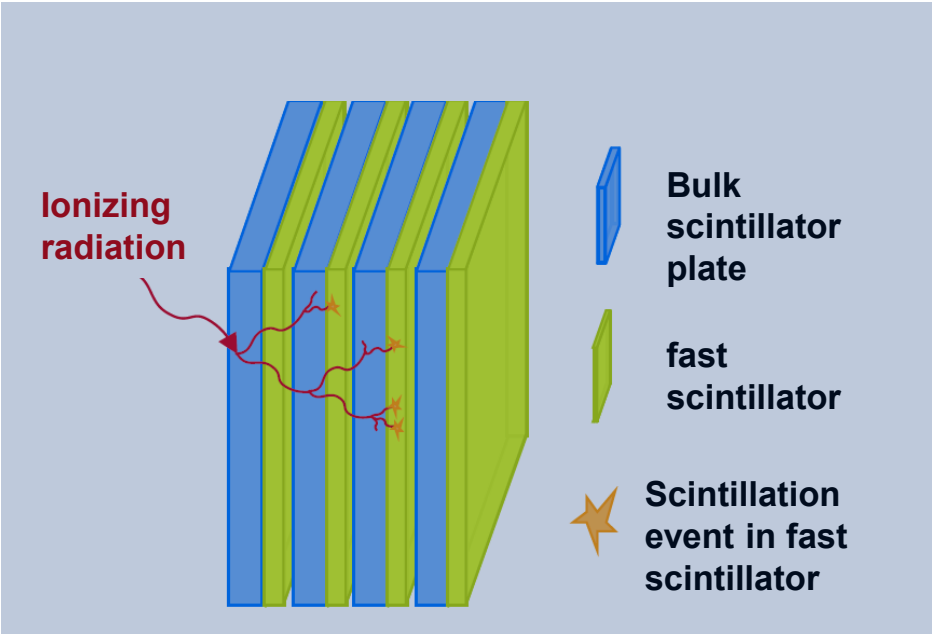
RA2: Nanoscintillators for fast detection systems

- Collaboration with FNSPE, Czech Technical University, CERN and other partners in Crystal Clear Collaboration
- Fast scintillation detection systems required especially in **medical imaging**, the Time-of-flight Positron emission tomography (TOF-PET), and **high energy physics**
- **Coincidence time resolution** – key parameter of fast timing when e.g. time-of-flight techniques are used

→ impossible to achieve with conventional bulk scintillators, ultrafast scintillators – building up **heterostructures**



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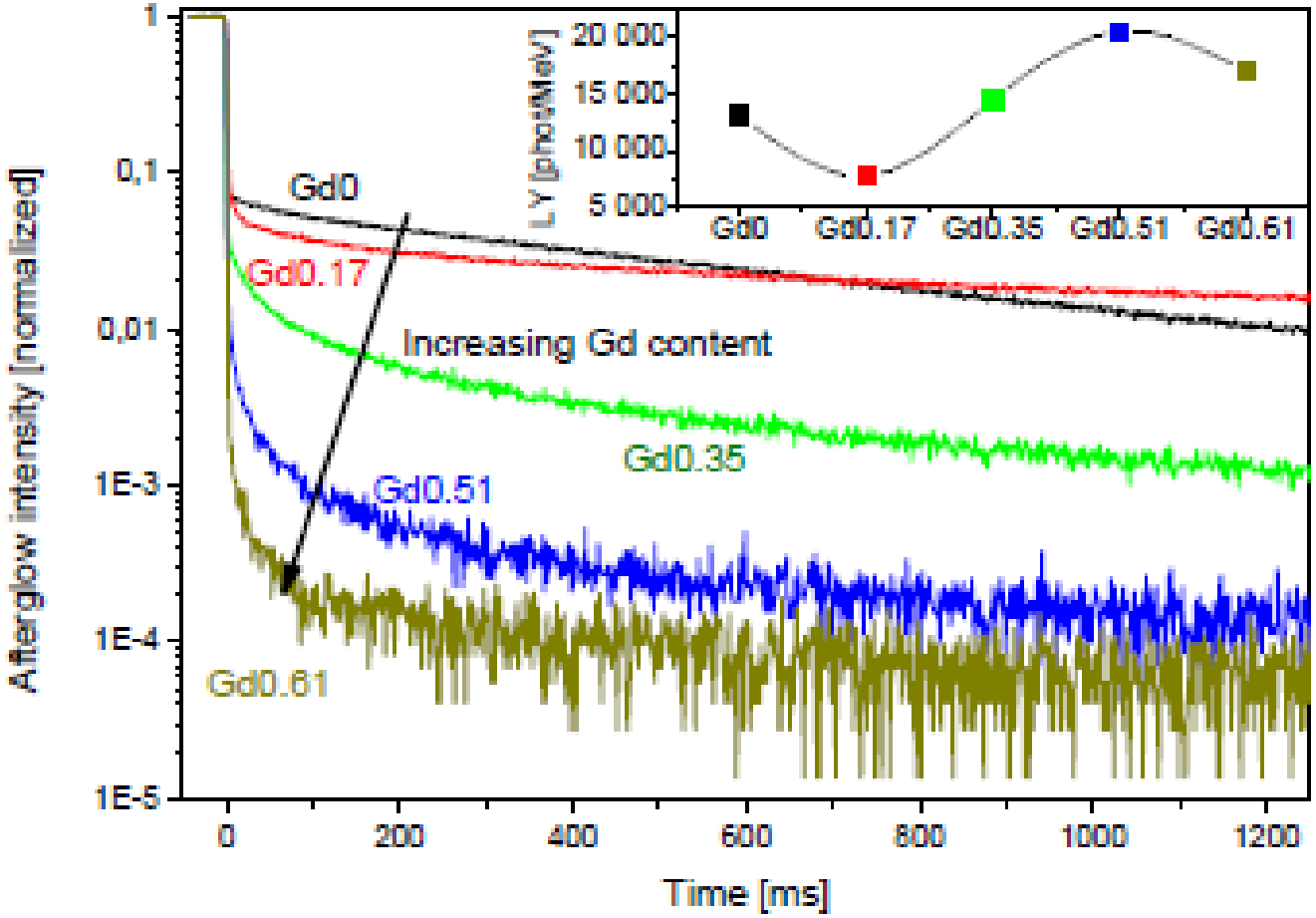
Awarded European project in EIC Pathfinder Open 2022 call, UNICORN, coordinated by University of Milano-Bicocca, starting from June 2023 (4 years duration), consortium of 7 academic and industrial partners from 5 countries.

The goal of UNICORN is to develop unprecedented nanocomposite scintillator (SL) detectors based on engineered nanomaterials for transformative breakthroughs in strategic radiation detection areas spanning homeland security and medicine to industrial, nuclear, and environmental monitoring to cosmology and high energy/particle physics.

RA2: Composition engineered $Lu_{1-x}Gd_xAP$:Ce large single crystals: desired breakthrough?



Successful Bandgap Engineering!

Industrial collaboration with CRYTUR company

Pokorny et al, The Gd-admixed (Lu,Gd)AlO_3 single crystals: Breakthrough in heavy perovskite scintillators.
NPG Asia Materials ***13*** *(2021) 66.*
DOI: 10.1038/s41427-021-00332-w

The best performing composition $(Lu_{0.5}Gd_{0.5})AlO_3$:Ce has light yield value of 21 000 phot/MeV exceeding high quality commercial YAP:Ce. **Compared to $LuAlO_3$:Ce it shows 60% increase in light yield.** The afterglow decreases by two orders of magnitude .

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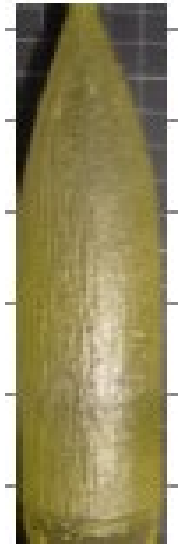
Adapted for CRYTUR technology: (Gd,Y)AP:Ce single crystal scintillator for environmental applications

Cost effective technology based on Mo crucible, crystal size currently with ∅**2.5cm and length above 10 cm** (cylindrical part)
Achieved light yield up to 24000 ph/MeV (130% of YAP:Ce standard), energy resolution is not deteriorated compared to YAP:Ce
Joint national patent filed in 2022, report obtained from Patent Office in May 2023 without essential objections
Granted project from TACR, call TREND2022, coordinated by CRYTUR with another industrial partner Georadis, *"Ionizing radiation detectors in the environment"*, started from Jan 2023, 4 years duration



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RA1&RA2: Links to universities and industry, projects, international collaborations

Running national projects with university and/or industry partners in 2023:

1) CSF – Three projects with university (CTU, CU, Univ. of Chemistry and Technology) and Academy partners
2) TACR – Four projects, coordinated by **CRYTUR**, with another industrial and university partners

International projects and collaborations in 2023:

1) **Title:** Advancement and Innovation for Detectors at Accelerators (AIDAinnova)
EU call: H2020-INFRAINNOV-2019-2020, started 4/2021
Coordinated by CERN, FZU is partner (PI J. Kvasnicka), **RA2 from RP3 participates** in WG8,
2) **Title:** **I**ntegration of processes and mo**D**ules for the **2**nm node meeting **P**ower **P**erformance **A**rea and **C**ost requirements (ID2PPAC)
EU ECSEL call: H2020-ECSEL-2020-1-IA-two-stage, 6/2021-5/2024
Coordinated by ASML, FZU is partner (PI M. Nikl), **RA2 from RP3 participates** in WG3
3) Just starting:
Title: Hybrid Nanocomposite Scintillators for Transformational Breakthroughs in Radiation Detection and Neutrino Research (UNICORN), Horizon Europe, EIC Pathfinder Open 2022, 6/2023 – 5/2027,
Coordinated by University of Milano-Bicocca, FZU is partner (PI M. Nikl), leader of WP3

We are members of Crystal Clear Collaboration coordinated from CERN (30 partners around the globe)

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RA1&RA2:Outreach &young generation education

- V. Jary participates in the “Open Science (https://www.otevrenaveda.cz/)” project of CzAS focused on education of high school students

- Many popular lectures at high schools, supervising high school science works

- Participation in Science Fair – the largest scientific even for public in the Czech Republic – V. Jary presents new phosphors (https://www.veletrhvedy.cz/)

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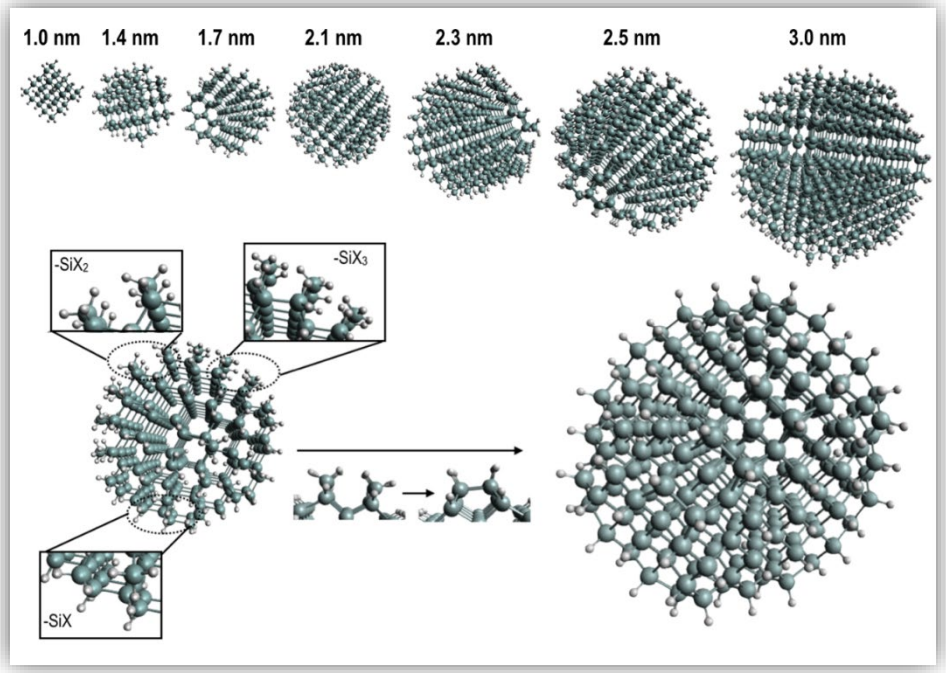
RA3: DFT study of light emission in SiQDs

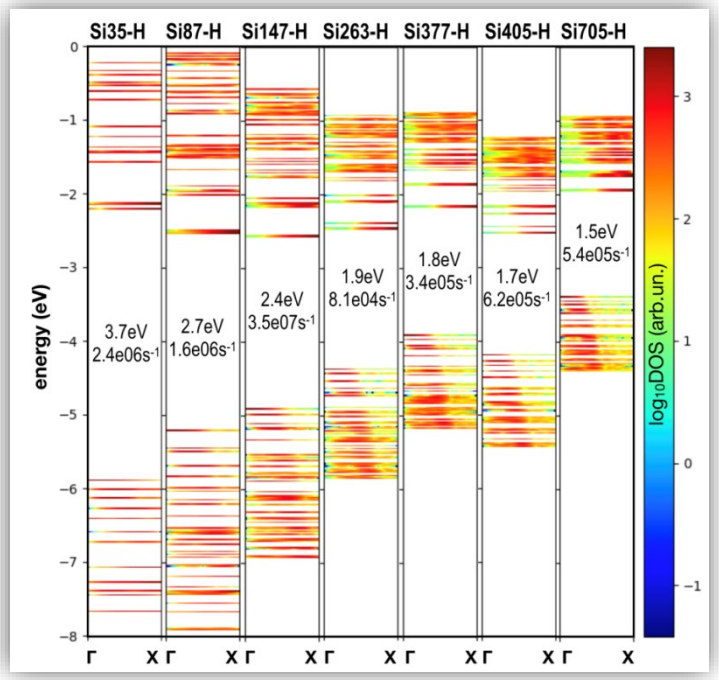
collaboration with the University of Amsterdam

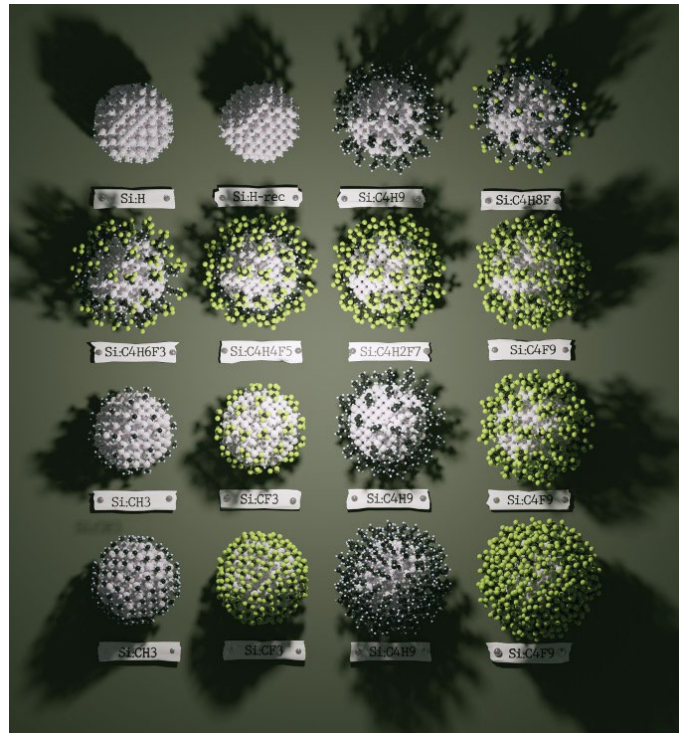
theoretical study to reveal the effects of a phenomenon on the radiative rate

the resulting radiative rate is an intricate interplay of many factors

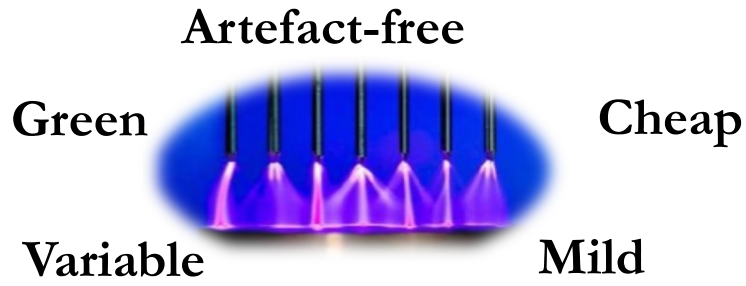
Dohnalová, K., Hapala, P., Kůsová, K., & Infante, I. (2020). Electronic Structure Engineering Achieved via Organic Ligands in Silicon Nanocrystals. *Chemistry of Materials*, *32*, 6326. https://doi.org/10.1021/acs.chemmater.0c00443







Surface modification using Plasma Activated Water



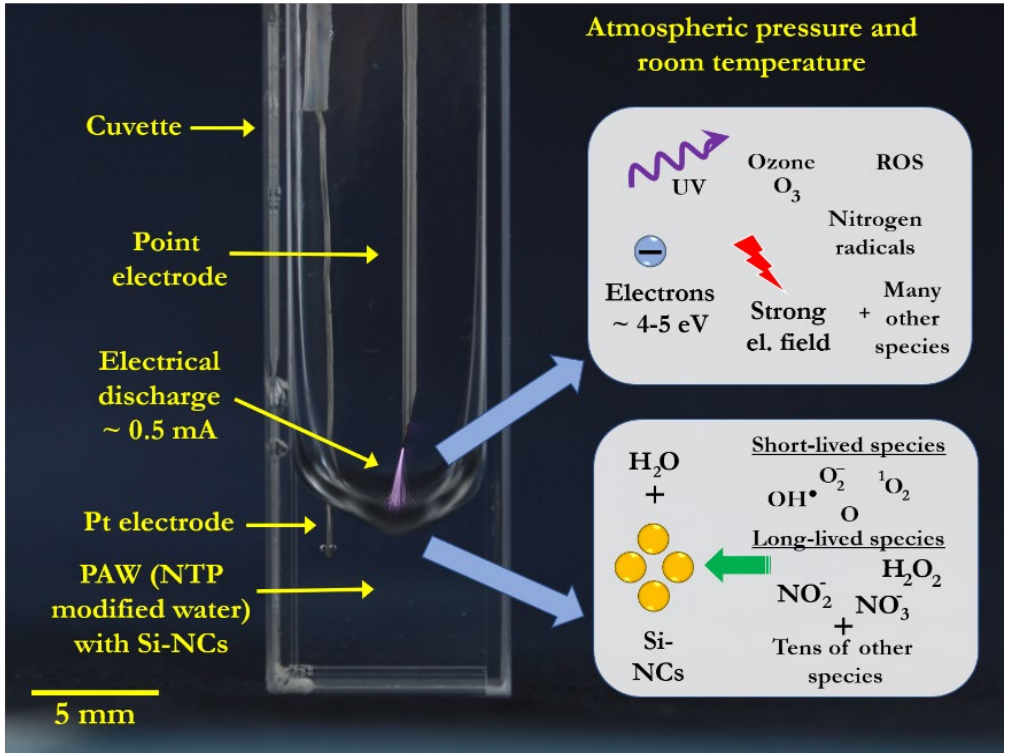
new simple technique for surface modification of nanoparticles

uses only water and air as the source of passivating species

enriches the surface with nitrogen-related species

in SiQDs, improves dispersibility in water and photoluminescence quantum yield

potentially useful in bioimaging



Galář, P., et al (2021). Non-thermal pulsed plasma activated water: environmentally friendly way for efficient surface modification of semiconductor nanoparticles. *Green Chemistry*, *23*, 898.

Matějka, F., et al (2023). Mechanisms leading to plasma activated water high in nitrogen oxides. *Physica Scripta*. https://doi.org/10.1088/1402-4896/acc48e

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Other activities

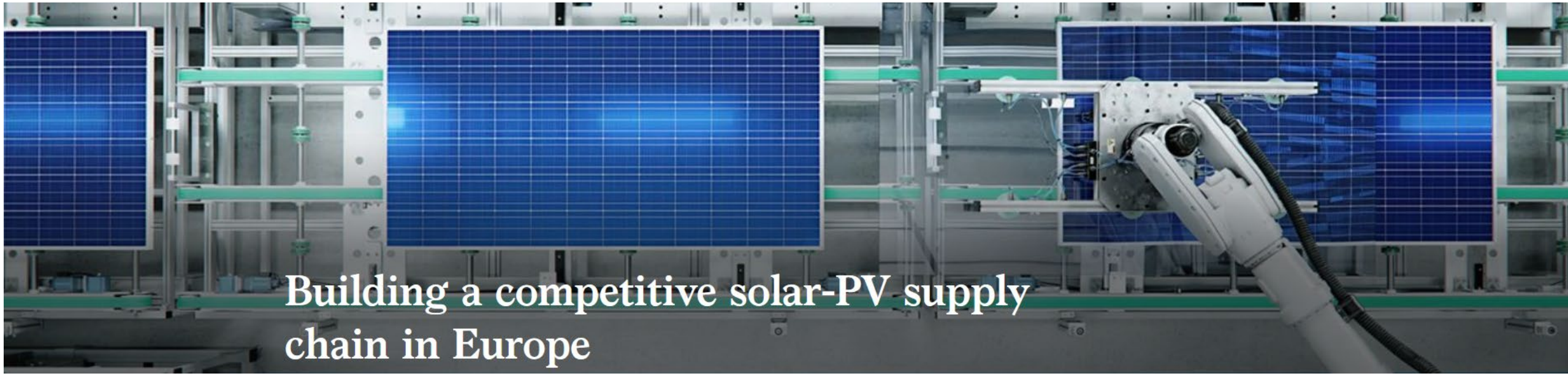
Co-organization of Symposium EL07-Group IV Nanostructures for Emerging Optoelectronic Applications at the MRS Spring Meeting, 2023, San Francisco, California, Apr 10-14

Student theses:

- F. Matejka: Surface modification of plasma synthesized silicon nanocrystals using non-thermal plasma activated water, bachelor thesis, defended 2022
- J. Kopenec: Flamability of nanosilicon, bachelor thesis, defended 2022
- F. Matejka: Plasma activated liquids and their application for surface modification of silicon nanocrystals, diploma thesis, defended 2023
- J. Kopenec: Synthesis of silicon nanoparticles in non-thermal plasma, diploma thesis, to be defended 2023
- D. Kafka: The influence of fabrication conditions on the photoluminescence of silicon nanoparticles, bachelor thesis, to be defended 2023

RP4: Nanostructures for photovoltaic solar energy conversion

the Solid21 activities led to 2 international projects, aiming at:



1) HORIZON-CL5-2021-D3-03-13 **Digitalised pilot lines for silicon heterojunction tunnel interdigitated back contact solar cells and modules** (Pilatus) (2022-2025)

2) LUASK project with Slovak Academy of Sciences: **Perovskite layers with improved structure and passivation** (2022-2025)

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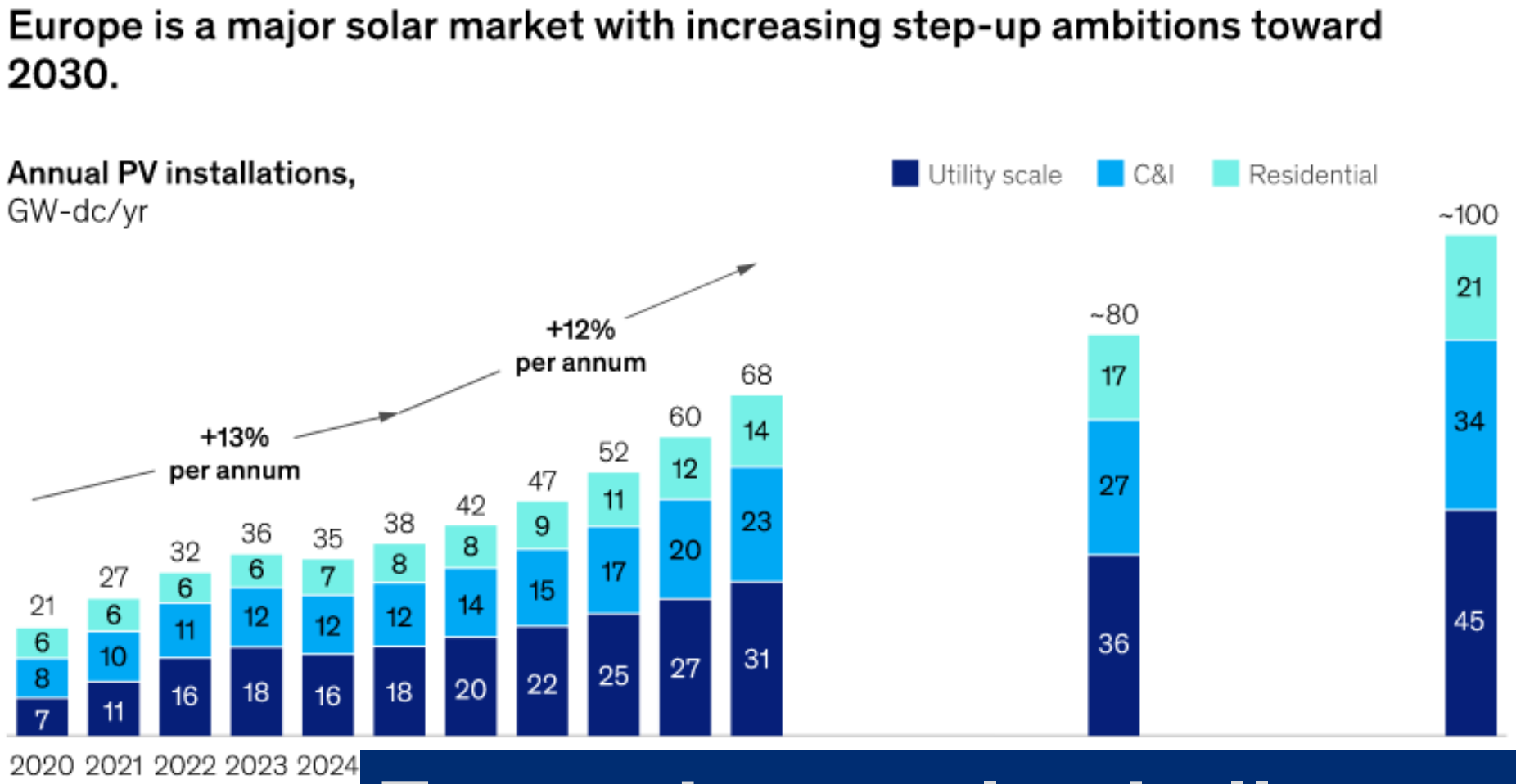
Motivation



Europe’s supply challenge: It’s all imported

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RP4: Horizon Europe project PILATUS has started in November 2022

Digitalised pilot lines for silicon heterojunction tunnel interdigitated back contact solar cells and modules

PILATUS

3 year project is coordinated by Meyer Burger Germany with a **consortium of 19 partners** (e.g. EPFL, CSEM, Fraunhofer ISE, Norwegian Crystals, Wacker Chemie, Cambridge Photon Technology, TNO, Pasan etc.).

Targets: by 2025 **three digitalised pilot lines** for the production in Europe of silicon wafers, solar cells, and modules, with patented and already proven “tunnel-IBC” technology.

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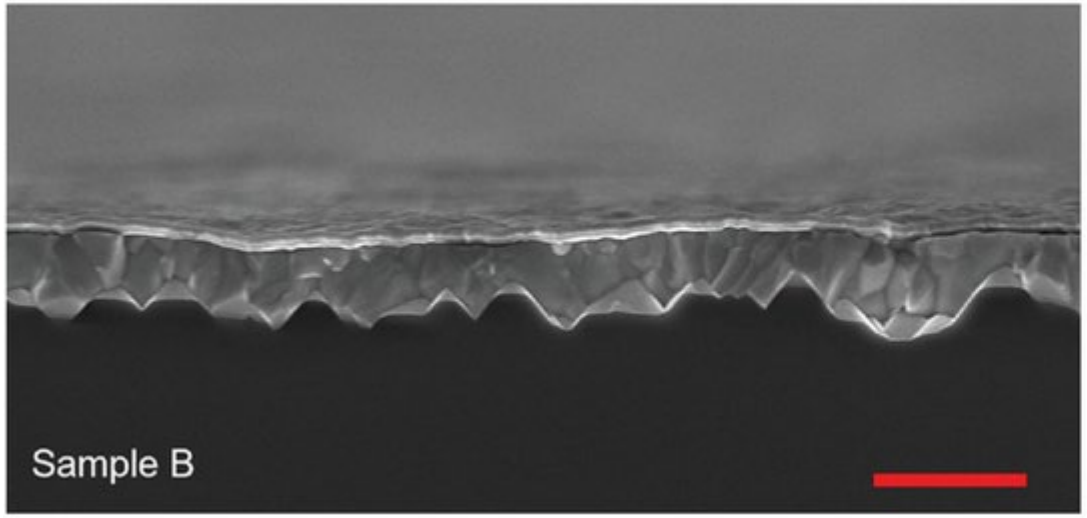
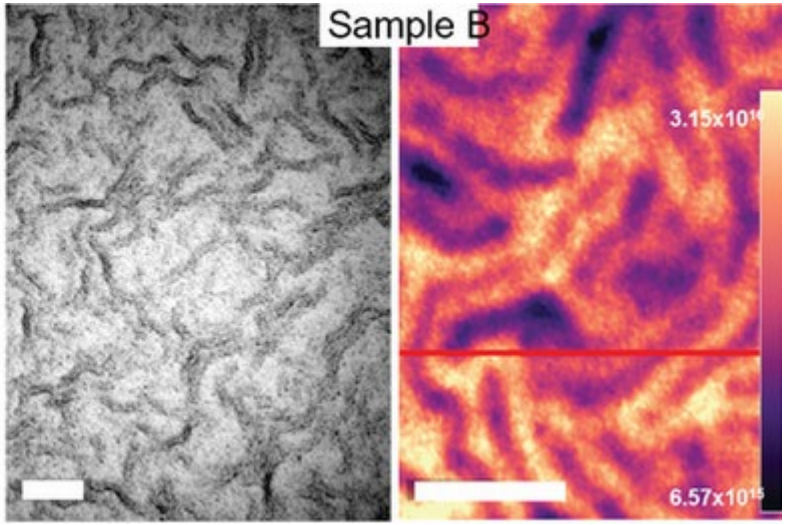
Funded by the European Union

LUASK project with Slovak Academy of Sciences: Perovskite layers with improved structure and passivation (2022-2025)

Triple cation perovskite films on silicon substrates with pyramidal texturing.



SEM cross-section image of the perovskite film Si substrate with the perovskite film capped with the top contact for tandem integration.
Red scale bar: 2 µm.



Optical microscopy image

Hyperspectral PL imaging

De Bastiani, Michele, Rawan Jalmood, Jiang Liu, Christina Ossig, Aleš Vlk, Karol Vegso, Maxime Babics, et al. “Monolithic Perovskite/Silicon Tandems with >28% Efficiency: Role of Silicon-Surface Texture on Perovskite Properties.” *Advanced Functional Materials* 33, no. 4 (2023): 2205557. https://doi.org/10.1002/adfm.202205557.

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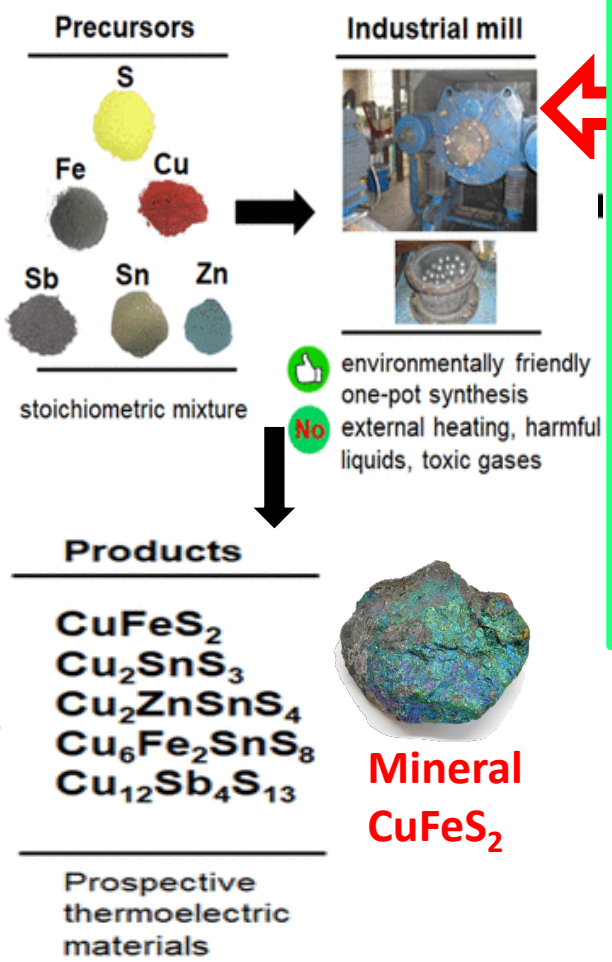
*with KAUST, Thuwal, holder of the current world record in tandem efficiency of 32.3 %.

RA5:Thermoelectricity in chalcogenides – towards low cost and eco-friendly applications



Mineral $CuFeS_2$

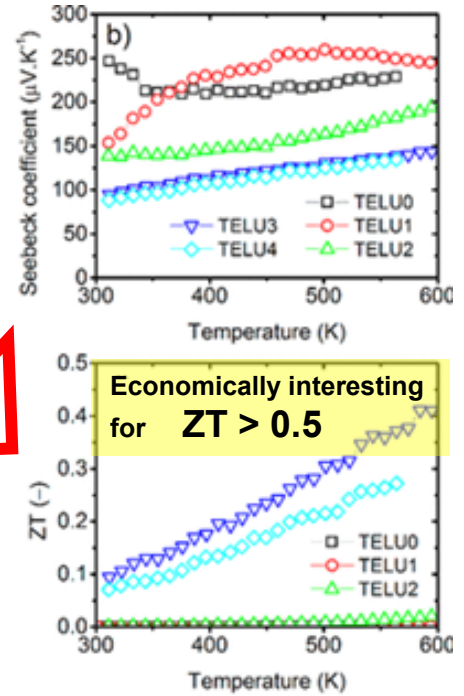
- Cu-based **thermoelectric sulfides** ($CuFeS_2$, Cu_2SnS_3, $Cu_{12}Sb_4S_{13}$, $Cu_6Fe_2SnS_8$, Cu_2ZnSnS_4) synthesized by **industrial milling in an eccentric vibratory mill** to demonstrate the **scalability of their synthesis**.
- Comparison of the thermoelectric characteristics resulting in the figure-of-merit ZT shows that the **scaling process of mechanochemical synthesis leads to similar thermoelectric parameters as compared to standard laboratory methods**.

Figure of merit:

$$ZT = \frac{S^2}{\rho\kappa}T$$

S: Seebeck - thermoelectric coefficient; ρ: electrical resistivity; κ: thermal conductivity

Thermoelectric characteristics:



Baláž P. et al, Enhanced thermoelectric performance of chalcopyrite nanocomposite via co-milling of synthetic and natural minerals, **Materials Letters 275 ,2020, 128107**

Baláž P. et al., Thermoelectric Cu–S-Based Materials Synthesized via a Scalable Mechanochemical Process, **ACS Sustain. Chem. Eng. 9 ,2021, 2003 – 2016**

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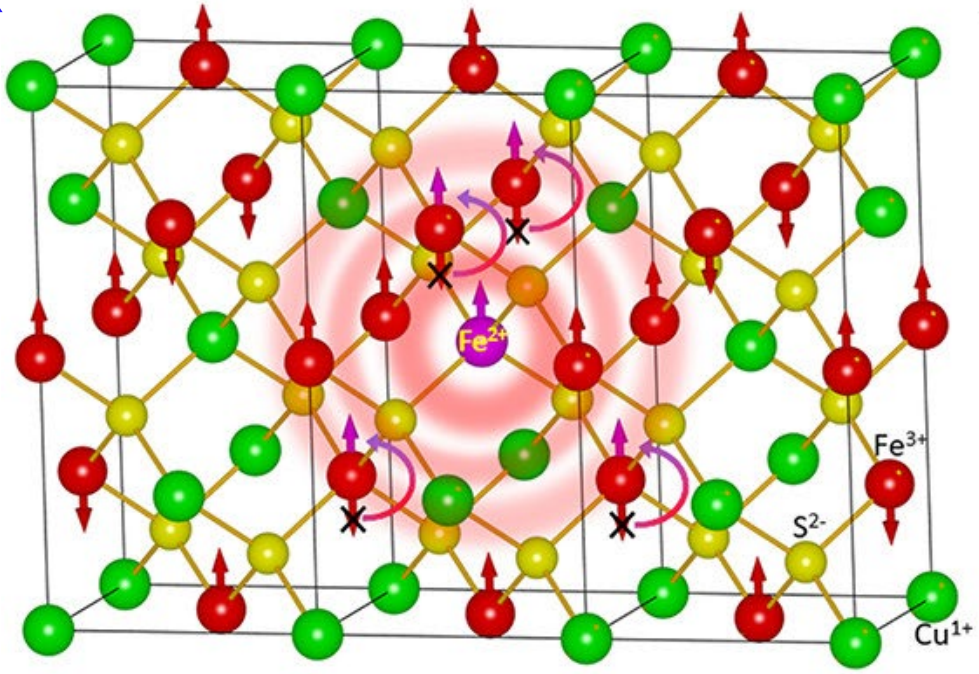
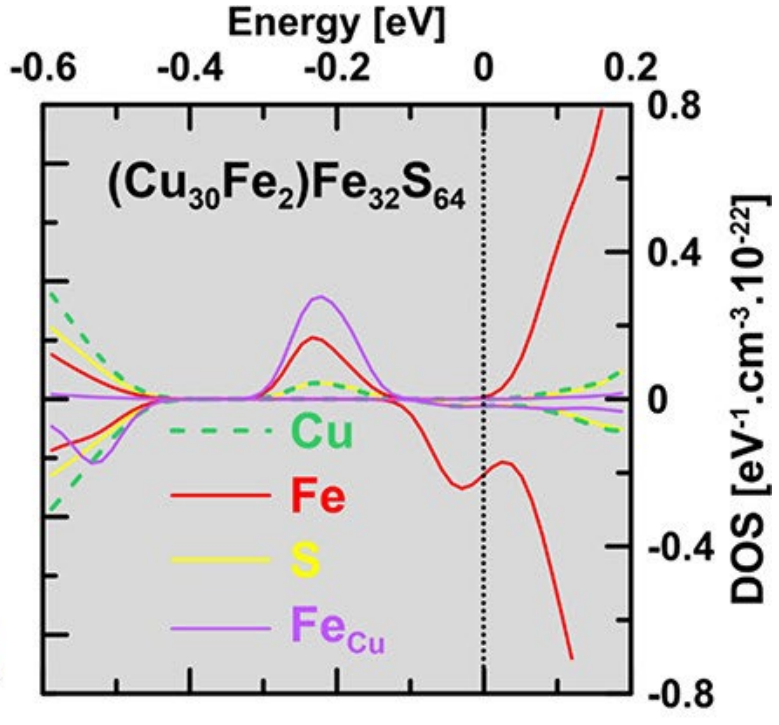
Peculiar Magnetic and Transport Properties of $CuFeS_2$

- Our model addresses weak ferromagnetism and the high mobility of charge carriers on the background of a rigid antiferromagnetic structure.
- The charge "cloud" partially delocalized around antisite defect Fe^{2+} is visualized by the **red concentric circles** – see the figure on the left.

Crystal structure



Electronic structure



Point defect induced FM and high-mobility states in AFM $CuFeS_2$

A unique situation where the defect structure can, counterintuitively, **boost the carrier mobility** due to **defect-modified charge transfer** inducing the weak ferromagnetism in the Cu- and Fe-sublattices.

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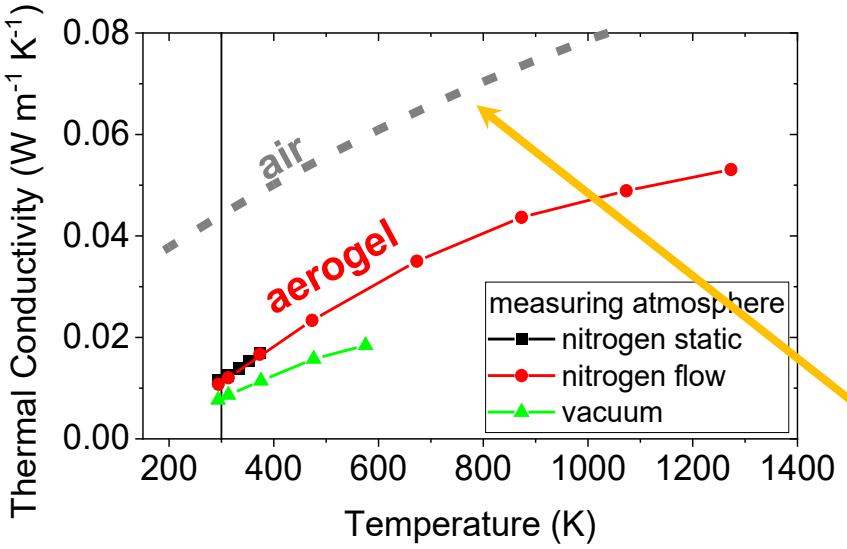
Navratil J. et al, Peculiar Magnetic and Transport Properties of CuFeS2: Defects Play a Key Role, **J. Phys. Chem. C 124 ,2020, 20773–20783**

RA5: Key instrumental aquisition

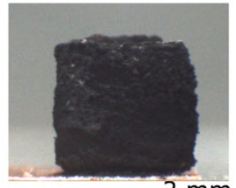
Characterization

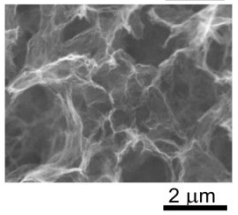
- **Light Flash Analysis (LFA)**
- **Thermal conductivity 170-1500 K**
- Models Netzsch LFA 467&LFA 467 HT



Measurement example

- **Graphene aerogel**
- Succesfully measured despite **extremely low** thermal conductivity (see graph)
- **Density 0.007 g·cm^{-3}**
- Pressure-dependent measurements





The versatility of **thermal diffusivity-conductivity** analysis using the **LFA** method demonstrated by unique measurement of **graphene aerogel;** its thermal conductivity is **well below the conductivity of the air** …

Promotes cooperation at all levels:

International (e.g. CNRS (France)), national (e.g. IPP CAS), within FZU (e.g. Dept. of Thin Films and Nanostructures), internal use

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RA5: Collaborations, outreach, future research

Key partners in CR and abroad:

-Faculty of Chemical Technology, Univ. of Pardubice, UCT Prague,
- Faculty of Mathematics and Physics, Charles University
- SAS in Košice, Slovakia
- Institute Jean Lamour, Universite de Lorraine, France

Scientific community - outreach..

As co-organizer we prepare with UPCE the 19-th European Conference on Thermoelectrics (September 2023- https://thermoelectric-conference.eu)

Future research…

(i) The thermal conductivity in real materials- role of defects, grain boundaries,… Experimental insight via **low temperature** experiments **under magnetic field, theoretical calculations**
(ii) the active role of **magnetic excitations** in electron and heat transport
(iii) Transverse and longitudinal thermomagnetic effects – **both theory and experiment**- FM $CdCr_2Se_4$, $CuCr_2Se_4$, …

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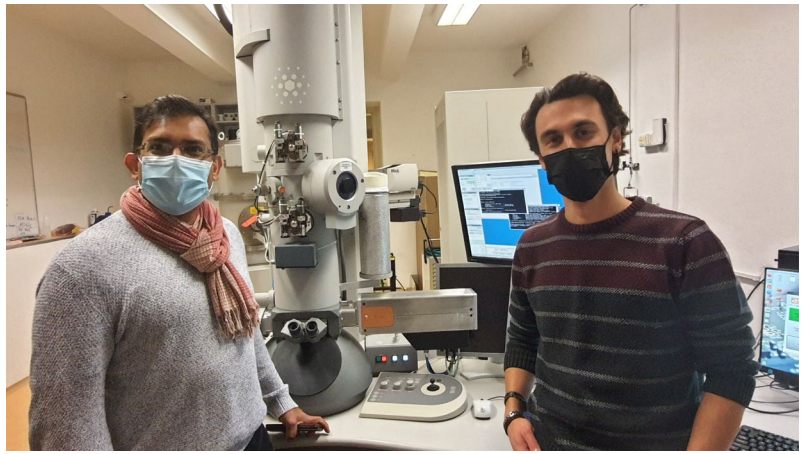
Joint Experimental Base: Upgrade of transmission electron microscope for 3D electron diffraction

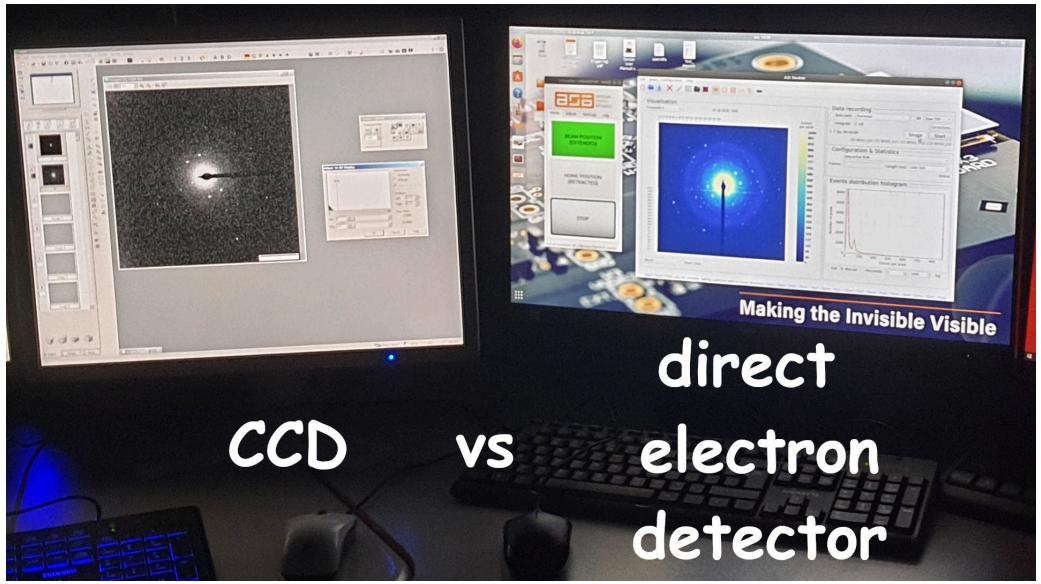
The TEM was upgraded with a hybrid pixel direct electron detector. This upgrade provides a qualitative leap forward in our ability to analyze nanocrystals of pharmaceuticals and other electron-beam-sensitive compounds

The new instrument opens up the door for scientific and industrial collaborations.

Synthon a.s. (CR), TEVA a.s. (CR), Eldico (Basel, Switzerland), Crystallise! (Villingen, Switzerland), GSK (UK), NIS (US)

US and EU patents pending for our methods for absolute structure determination. Licensing is on the way…





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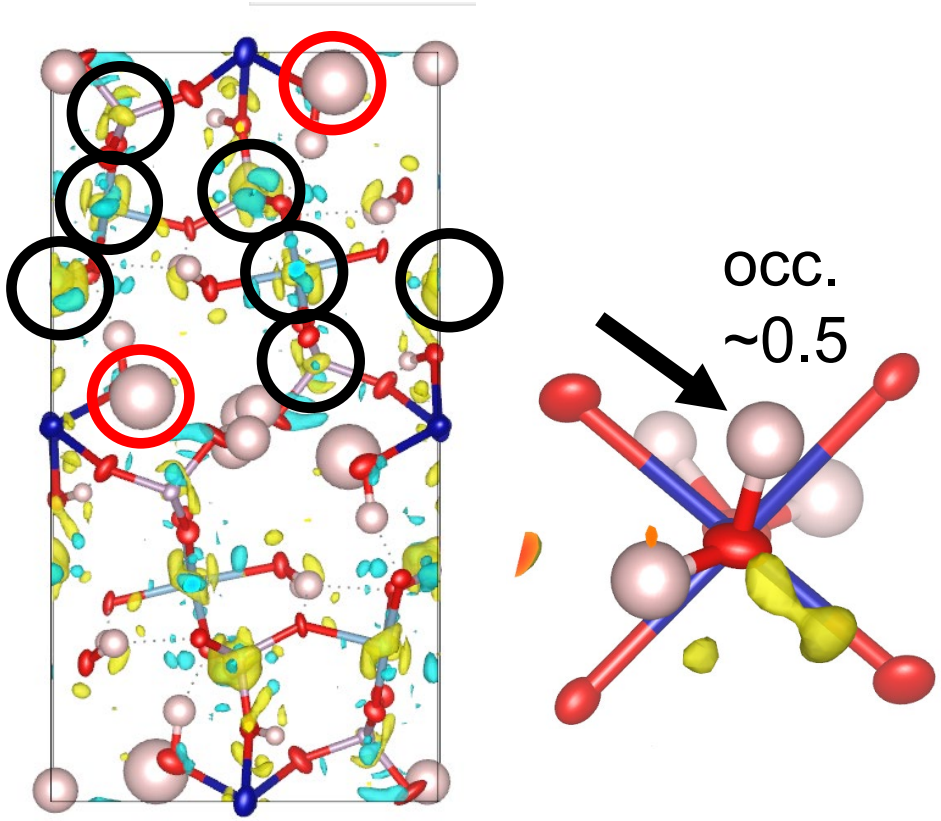
Electron diffraction tomography: From a curiosity towards a routine method reaching accuracy of X-ray diffraction



2017

Electron diffraction can determine hydrogen positions

Science 2017, **355**, 166-169

2019

Electron diffraction can determine the absolute structure

Science 2019, **364**, 667-669

2022 (Left)

Electron diffraction can detect a disorder of water molecule

IUCrJ 2022, **9**, 735–755

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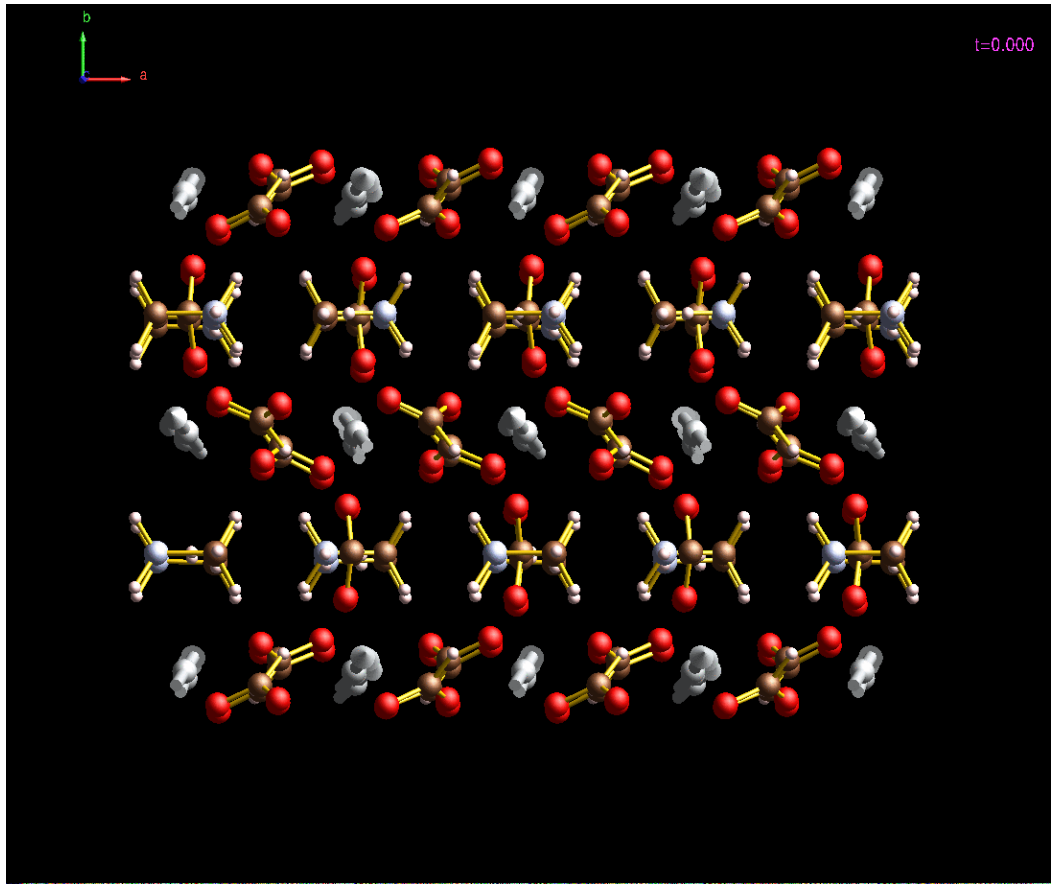
Crystallographic computing: new program Jana2020



Jana2020 solves standard, modulated and magnetic structures from X-ray, neutron and electron diffraction data.

Z. Kristallogr. 2023, ahead of print
https://doi.org/10.1515/zkri-2023-0005

(Left) The first structure with simultaneous modulation of the nuclear and magnetic structure. The structure was solved and refined in Jana2020.

Inor. Chem. 2020, 59, 17896-17905

Outreach activities connected with Jana software:

Jana workshops in Prague and international events – 200 participants every year.

How RP3 met the goals of Solid21 project?

Strengthening the international standing of IoP, internationalization of research:

♦Largest number of papers with foreign coauthors (91) among RPs, their share on overall RP3 publication output is 91/118= 77%! Increasing share of publications in Q1 journals and few in very top ones (Science).

♦ Extended participation in international projects (4 from total 8 counted in related MEYS indicator comes from RP3), H2020, Horizon Europe, COST, NATO, specific calls to support bi- and multi-lateral collaboration in CSF, CzAS, MEYS, ERA-NET, etc. Many invited talks at international conferences, invited review papers.

Consolidation of IoP's own research teams, strengthening of the cooperation with universities:

♦ Long term collaboration with leading Czech universities (CTU, CU, Univ.Chem.Tech., UPOL,…) in joint projects, leading student thesis (bachelor, master, PhD, in total about 15-20 each year) and lecturing

Long-term sustainability and top-quality research in IoP – new laboratory premises&instruments:

♦ Each RA acquired/set up at least one new costly instrument during last 5 years which substantially improve experimental background and international competetiveness

Fulfilment of specific goals using efficiently all existing capacities within IoP:

♦ It goes without saying …XRD and chemical analysis, optical and mechanical workshops, all IT background, support for project preparation from Grant and Central Administration offices…crosslinking with other RPs

Creation of conditions for commercialisation of research results, cooperation with industry:

♦ Very strong position of RP3 due to a number of domestic projects awarded from TA CR and coordinated by industrial partners (pure applied research), joint participation in large European projects (ID2PPAC, Pilatus), and in emerging breakthrough technologies R&D (UNICORN). Patents, technology transfer and licencing.

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THANK YOU FOR YOUR ATTENTION!