UNIVERSITÀ DEGLI STUDI
DELL'INSUBRIA

"Structural characterization of functional material"

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Keywords: synthesis, X-ray diffraction, spectroscopy, solid-state materials, X-ray total scattering

Purpose: Advanced synthesis and structural characterization of microcrystalline functional materials (organic, inorganic, or organic/inorganic hybrids) through powder X-ray diffraction methods under ambient or in situ conditions, both in laboratory settings and at large-scale facilities.

It also focuses on the synthesis and advanced structural and microstructural characterization of functional nanomaterials using powder X-ray diffraction and X-ray total scattering techniques, both in laboratory environments and at large-scale facilities.

Location: Department of Science and High Technology

Organization: The facility integrates a network of research groups with multidisciplinary expertise in Chemistry and Materials Science, together with advanced instrumental and technological resources. As such, it represents a reference point for research and development of structural and microstructural characterization methods for functional materials of high relevance in the fields of energy and environmental sustainability, with potential impact in both academic and industrial contexts.

Connections with CRIETT Technological Platforms and University Scientific Platforms:

CRIETT Technological Platform: *Materials analysis and characterization*.

Scientific Platform: *Technologies for energy, health, and environment*, with a focus on materials and nanomaterials.

Subunit: “Synthesis and characterization of nanoscale materials using X-ray Total Scattering methods”

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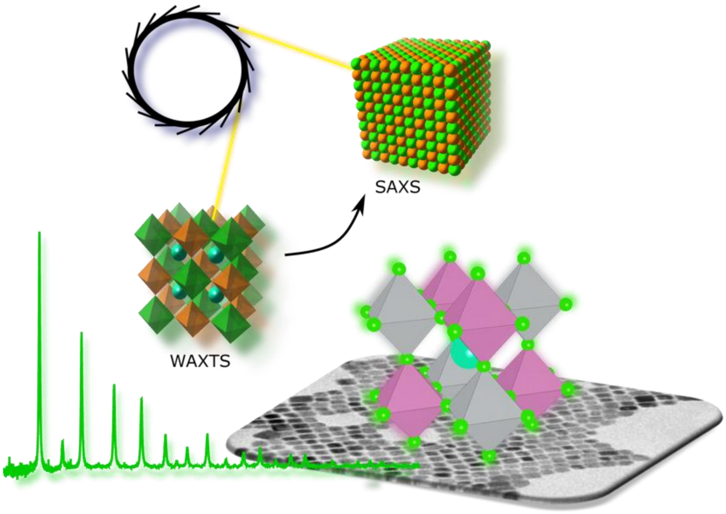
Keywords: total scattering, nanomaterials, quantum dots, optoelectronic properties



The subunit focuses on the preparation and study of nanoscale materials, in particular colloidal semiconductors known as quantum dots. These materials, due to their extremely small size, exhibit unique optical and electronic properties of great interest for advanced technological applications.

The laboratory is equipped for synthesis under controlled atmosphere (nitrogen or argon) and has dedicated instrumentation such as Schlenk lines, vacuum pumps, and heating mantles. This enables the implementation of specific synthetic strategies (such as hot injection and heat-up methods) that allow precise control over the size and shape of nanocrystals. This control is crucial, as it determines the optical absorption and emission properties, which can be tuned from the ultraviolet to the near-infrared region by exploiting quantum confinement effects and compositional modulation.

Once synthesized, the materials are analyzed using advanced small- and wide-angle X-ray scattering techniques, which allow investigation of their atomic structure, microstructure, and morphology. Data analysis and atomic-scale modelling, also supported by the development of open-source software (https://debyeusersystem.github.io), provide deep insight into the structure–property relationships, offering crucial guidance for improving synthesis and directing potential applications.

Currently, research activities are mainly focused on next-generation halide perovskites, including lead-free formulations, and on copper-based ternary quantum dots, which are promising materials for sustainable optoelectronic applications.

Subunit: “Synthesis and characterization of microcrystalline functional materials by powder diffraction methods under ambient and non-ambient conditions”

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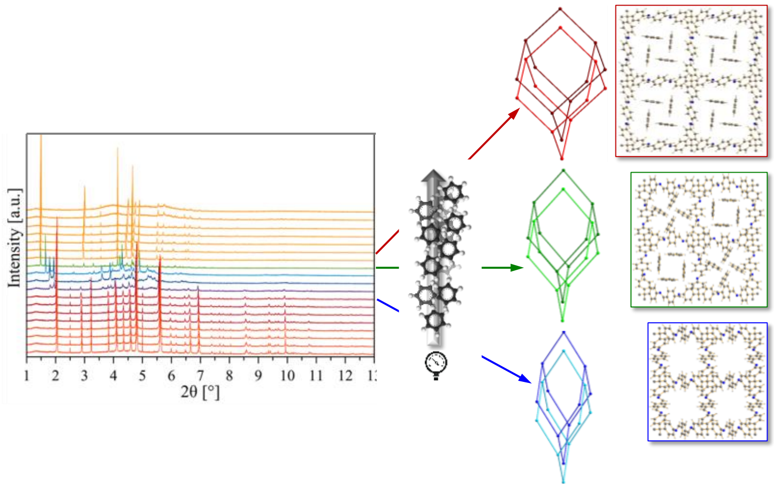
Keywords: (*in situ*) powder diffraction, functional materials, porous materials, structure–property relationships



The subunit is mainly focused on the synthesis and structural characterization of microcrystalline functional materials of organic or organic/inorganic hybrid nature, both non-porous (e.g. coordination compounds or coordination polymers) and porous (e.g. metal–organic frameworks, covalent organic frameworks). These materials can find applications in diverse fields such as nonlinear optics, magnetism, heterogeneous catalysis, selective storage of vapours or gases, capture and potential reuse of emerging pollutants from air or water, and sensing technologies. The structural and functional properties of these materials can be strategically tuned by adjusting the chemical nature and size of their organic and inorganic building units.

Regarding synthesis, the laboratory is equipped for working under inert atmosphere (nitrogen or argon) and has dedicated instrumentation such as Schlenk lines, solvothermal reactors, vacuum pumps, and magnetic stirring and heating systems.

Regarding structural characterization, the subunit relies on advanced powder X-ray diffraction methods, operating under ambient or non-ambient conditions, using laboratory equipment or large-scale facilities. Through this approach, the subunit performs: (i) crystal structure determination of the aforementioned materials, synthesized in-house, by collaborating research groups, or on industrial-scale systems; (ii) characterization of, inter alia, phase transitions, structural flexibility, adsorption–desorption processes, identification of primary adsorption sites, and adsorbent–adsorbate interactions.

In this way, it contributes to the rationalization of the observed functional properties, with short-term impact on the investigated materials and medium- to long-term impact on the development of next-generation materials for the targeted application areas.

In general, for the comprehensive characterization of solid-state materials, the subunit promotes a multi-technique approach. Powder diffraction is complemented by additional characterization techniques available within the facility (e.g. X-ray fluorescence spectroscopy, conductivity and resistivity measurements) or within CRIETT (e.g. thermogravimetric analysis, differential scanning calorimetry, infrared spectroscopy, fluorescence emission spectroscopy, electronic absorption spectroscopy, and nuclear magnetic resonance spectroscopy).

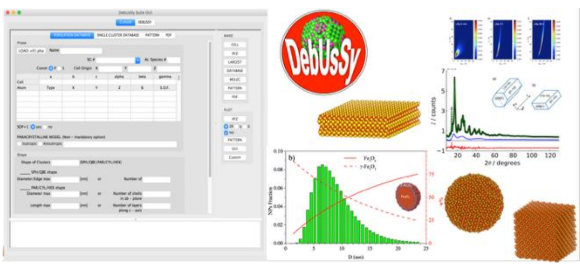
Relevant Publications (2022-2025):

1. *Atomistic insights into halide double perovskite nanocrystals obtained by multistep synthesis and efficient compositional engineering*, N. Dengo, D.F. Macias-Pinilla, P. Anzini, M. Colombo, S. Virga, A. Brambilla, P.A. Zecca, D. Monticelli, F. Giannici, F. Bertolotti, ACS Nano 2025, 19, 30151.
2. *A deep learning approach for quantum dots sizing from wide-angle X-ray scattering data*, L. Allara, F. Bertolotti, A. Guagliardi, npj Computational Materials 2024, 10, 54.
3. *Size- and Temperature-Dependent Lattice Anisotropy and Structural Distortion in CsPbBr3 Quantum Dots by Reciprocal Space X-ray Total Scattering Analysis*, F. Bertolotti, N. Dengo, A. Cervellino, M.I. Bodnarchuk, C. Bernasconi, I. Cherniukh, Y. Berezovska, S.C. Boehme, M.V. Kovalenko, N. Masciocchi, A. Guagliardi, Small Structures 2025, 5, 2300264.
4. *Coupling to octahedral tilts in halide perovskite nanocrystals induces phonon-mediated attractive interactions between excitons*, N. Yazdani, M.I. Bodnarchuk, F. Bertolotti, N. Masciocchi, I. Fureraj, B. Guzelturk, B.L. Cotts, M. Zajac, G. Rainò, M. Jansen, S.C. Boehme, M. Yarema, M.-F. Lin, M. Kozina, A. Reid, X. Shen, S. Weathersby, X. Wang, E. Vauthey, A. Guagliardi, M.V. Kovalenko, V. Wood, A. M. Lindenberg, Nature Physics 2024, 20, 47.
5. *Size segregation and atomic structural coherence in spontaneous assemblies of colloidal cesium lead halide nanocrystals*, F. Bertolotti, A. Vivani, F. Ferri, P. Anzini, A. Cervellino, M. I. Bodnarchuk, G. Nedelcu, C. Bernasconi, M.V. Kovalenko, N. Masciocchi, A. Guagliardi, Chemistry of Materials 2022, 34, 594.
6. *Selective carbon dioxide versus nitrous oxide adsorption in cerium(IV) bithiazole and bipyridyl metal-organic frameworks* M. Pugliesi, M. Cavallo, C. Atzori, B. Garetto, E. Borfecchia, L. Donà, B. Civalleri, G. Tuci, G. Giambastiani, S. Galli, F. Bonino, A. Rossin, Advanced Functional Materials 2024, 2403017.
7. *Investigating the dynamics of a soft crystalline COF during benzene and cyclohexane Adsorption by in situ powder X-ray diffraction*, A. Mauri, R. Vismara, M. Moroni, E. Roldán-Molina, J.A.R. Navarro, S. Galli, Small Science 2024, 4, 2400277.
8. *Mercury clathration-driven phase transition in a luminescent bipyrazolate metal-organic framework: a multi-technique investigation*, M. Moroni, L. Nardo, A. Maspero, G. Vesco, M. Lamperti, L. Scapinello, R. Vismara, J.A.R. Navarro, D. Monticelli, A. Penoni, M. Mella, S. Galli, Chemistry of Materials 2023, 35, 2892-2903.
9. *Impact of pore flexibility in imine-linked covalent organic frameworks on benzene and cyclohexane adsorption*, M. Moroni, E. Roldan-Molina, R. Vismara, S. Galli, J.A.R. Navarro, ACS Applied Materials & Interfaces 2022, 14, 40890.
10. *Temperature-dependent nitrous oxide/carbon dioxide preferential adsorption in a thiazolium-functionalized NU-1000 metal–organic framework*, G. Mercuri, M. Moroni, S. Galli, G. Tuci, G. Giambastiani, T. Yan, D. Liu, A. Rossin, ACS Applied Materials & Interfaces 2021, *13*, 58982.
11. *Solvent Engineering for Scalable and Sustainable Fabrication of Lead-tin Perovskite Solar Cells*, L.J. Chen, F. Tavormina, L. Di Mario, M. Pitaro, G. Portale, N. Masciocchi, A. Guagliardi, M.A. Loi, Advanced Energy Materials *2025*, 15, 202405941.
12. *Modulating Trapping in Low-Dimensional Lead-Tin Halides for Energy-Efficient Neuromorphic Electronics*, L.J. Chen, S. Saleh, F. Tavormina, L. Di Mario, J.X. Li, Z.Q. Xie, N. Masciocchi, C.J. Brabec, B. Koldehofe, M.A. Loi, Advanced Materials *2025*, 37, 2414430.

13. *Crystal Orientation, Strain, and Microstrain of Perovskite Films in a Complex Compositional Parameter Space*, F. Tavormina, E. Quadrivi, P. Biagini, R. Po, R, Marrazzo, M.A. Loi, L. Barba, N. Masciocchi, A. Guagliardi, Chemistry of Materials 2024, 36, 8880.

Available instrumentation

	**A) Powder X-ray Diffractometer.** The instrument is capable of measuring X-ray diffraction patterns from polycrystalline powder samples (minimum amount 10^{-3}, maximum 1 cm^3) under ambient conditions, in the 2–100° 2θ range. It is equipped with a six-position autosampler and a fast PSD detector, and is typically used for qualitative phase analysis to identify chemical nature, purity, and crystallinity of reaction products and intermediates, as well as for quantitative phase analysis. Typical acquisition times range from 10 minutes to 12 hours, depending on sample type. It is also used for mineralogical or forensic samples, for the characterization of historical artefacts and industrial materials.
	**B) High-resolution Powder X-ray Diffractometer.** The instrument is capable of measuring high-resolution X-ray diffraction patterns from polycrystalline powder samples (minimum amount 10^{-3}, maximum 1 cm^3), bulk materials, and thin films under ambient conditions, at variable temperature (from room temperature up to ~450 °C) or under inert atmosphere, in the 3–145° 2θ range. It is equipped with a fast PSD detector and alternative sample stages, and is typically used for structural and microstructural analysis, as well as for quantification of amorphous phases. Typical acquisition times range from 10 minutes to 12 hours depending on sample type. It is also used for pharmaceutical samples, for energy and environmental materials, and in industrial applications.
	**C) Optical imaging.** Several optical and interferometric microscopes are available, with digital image acquisition, enabling micrometric and nanometric visualization of liquid or solid samples and thin films under ambient conditions. The collected images can be analyzed using dedicated software to determine Mail angle, surface roughness, and profilometry. These instruments are also commonly used for botanical and environmental samples, as well as for the characterization of materials and devices for the photovoltaic industry.

	**D) Sample treatment and conditioning.** Several modules are available (dryers, glove boxes, ovens, muffle furnace, incubator, freeze-dryer, ball mill, centrifuge, solvothermal reactors, and inert-atmosphere Schlenk-type setups) for the synthesis, treatment, and storage of samples under controlled conditions. These systems allow maintaining samples under controlled atmosphere and temperature, simulating ageing processes (shelf-life), removing residual solvents, and inducing phase transitions via solid-state reactions, among other applications. They are routinely used for pharmaceutical and environmental samples, as well as for organic and inorganic synthesis products and intermediates, including those of industrial relevance.
	**E) X-ray fluorescence spectrometer (XRF).** The instrument is capable of measuring the X-ray emission spectrum of liquid and solid samples (minimum amount 10^{-3}, maximum 1 cm^3) under ambient conditions, in the 2–18 keV range. It is equipped with a twelve-position autosampler and a fast energy-dispersive detector, and is typically used for qualitative elemental analysis and subsequent quantitative determination. Typical acquisition times range from 1 to 30 minutes, depending on sample type. In addition to its routine use for materials within the facility, it can also be applied to mineralogical, forensic, industrial samples, or for the characterization of historical artefacts and cultural heritage materials.
	**F) Thin film deposition systems.** Several systems with digital control of deposition parameters are available, including two spin coating units and one blade coating system, the latter equipped with a heating plate (up to 150 °C). Typical deposition times range from 30 seconds to 5 minutes, depending on sample type. These systems are commonly used for application-oriented materials such as perovskites for photovoltaics, organic semiconductor films for optoelectronics, and coatings of inks and pigments.
	**G) Software and structural databases.** Several software packages are available for structural analysis, including single crystal, powder, and thin film diffraction, as well as for different experimental configurations (including SAXS, GIWAXS, neutron and electron diffraction). A variety of electronic databases are also available for phase identification, diffraction pattern indexing, quantitative analysis, thermal analysis, visualization of molecular and crystalline structures, calculation of strain effects (chemically or thermally induced), bibliographic research in scientific and patent literature, and related applications.