The 4th International Online Conference on Crystals

18–20 September 2024 | Online

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Welcome from the Chair

Dear Colleagues,

You are cordially invited to participate in the 4th International Electronic Conference on Crystals (IOCC 2024), sponsored by the MDPI open access journal *Crystals*. This is a new and improved initiative based on the experience from the 1st, 2nd, and 3rd International Electronic Conference on Crystals, (https://iecc_2018.sciforum.net/; https://iocc_2020.sciforum.net/; https://iocc_2022.sciforum.net/) which affords the opportunity for researchers engaged in the study of crystalline materials to present their research and exchange ideas with their colleagues. We take full advantage of the Internet, removing the need to travel and omit participation expenses. This is a virtual conference held at Sciforum.net. Sciforum.net is a platform developed and sponsored by MDPI to organize electronic conferences, and to provide our community with the technical support for hosting our digital conferences.

The fourth conference will be organized around the following topics and related themes:

1. Liquid Crystals
2. Crystal Engineering
3. Inorganic Crystalline Materials
4. Organic Crystalline Materials
5. Hybrid and Composite Crystalline Materials
6. Materials for Energy Applications
7. Crystalline Metals and Alloys

Participants stand a chance to win six highly coveted Best Oral Presentation Awards and Best Poster Awards, with prize money.

Accepted papers will be gathered in the *Proceedings* journal (ISSN: 2504-3900) of the conference for free. Selected extended versions of the papers can be published in the journal *Crystals* with a discount of 20% on the Article Processing Charge (ISSN 2073-4352; Impact Factor: 2.4).

I am looking forward to seeing your participation in these exciting discussions, hearing new ideas and perspectives in the field and welcoming all participants to the online conference.

Prof. Dr. Alessandra Toncelli
Conference Chair
Department of Physics, University of Pisa, Pisa, Italy

crystals
an Open Access Journal by MDPI

Crystals (ISSN 2073-4352) is an **open access** journal that covers all aspects of crystalline material research in different sections: https://www.mdpi.com/journal/crystals/sections. Crystals provides a forum for the advancement of our understanding of the nucleation, growth, processing, and characterization of crystalline and liquid crystalline materials. Their mechanical, chemical, electronic, magnetic, and optical properties, and their diverse applications, are all considered to be of importance. Additionally, we encourage contributors to send articles focused on crystals research (of small and high molecular weight). Their characterization by using modern techniques for crystal growth and high resolution characterization such as synchrotron radiation and modern methods for the growth of crystals for X-ray free electron lasers (XFELS) would also be welcome.

Journal Webpage: https://www.mdpi.com/journal/crystals

Invited Speakers

Dr. M. Ajmal Khan

Riken, Wako, Japan

https://sciprofiles.com/profile/1919852

Prof. Dr. Vladimir Chigrinov

Hong Kong University of Science and Technology, Hongkong, China

Prof. Dr. Danil N. Dybtsev

Nikolaev Institute of Inorganic Chemistry, Novosibirsk, Russia

Dr. Yuri Panarin

Technological University Dublin, Dublin 7, Ireland

Prof. Dr. Silvia Bracco

University of Milano-Bicocca, Department of Materials Science, Milano, Italy

Dr. Nikos Karayiannis

Institute for Optoelectronic Systems and Microtechnology (ISOM) and Escuela Técnica Superior de Ingenieros Industriales (ETSII), Universidad Politécnica de Madrid (UPM), Madrid, Spain

Prof. Dr. Mehmet Senel

Liverpool John Moores University, Liverpool, UK

Program at a Glance

	Morning	Afternoon
Day 1	**Session 1.** Liquid Crystals	**Session 5.** Hybrid and Composite Crystalline Materials **Session 4.** Organic Crystalline Materials
Day 2	**Session 7.** Crystalline Metals and Alloys	**Session 2.** Crystal Engineering
Day 3	**Session 3.** Inorganic Crystalline Materials	**Session 6.** Materials for Energy Applications

IOCC 2024 Program

18th September 2024 (Wednesday)

Session 1. Liquid Crystals

Time: 9:00 (CEST, Basel) | 03:00 (EDT, New York) | 15:00 (CST Asia, Beijing)

CEST Time	Speaker	Title
9:00–9:10	**Prof. Dr. Alessandra Toncelli** Event Chair	*Welcome from the Event Chair*
9:10–9:15	**Prof. Dr. Vladimir Chigrinov** Session Chair	*Welcome from the Session Chair*
9:15–9:40	**Prof. Dr. Vladimir Chigrinov** Invited Speaker	Liquid Crystal Photoalignment by Azodye Nanolalayers: Physics and Applications
9:40–10:05	**Dr. Yuri Panarin** Invited Speaker	Giant Dielectric Permittivity in the Ferroelectric Nematics
10:05–10:20	Omar Aljohani	Thermally Stabilizing and Tuning Photonic Liquid Crystal Phases with Nanoparticles
10:20–10:35	Stanisław Różański	The effect of liquid crystal electrolyte modification on the efficiency of organic photovoltaic cells
10:35–10:50	Ankita Sutar	Exploring Optical Properties of Nematic Liquid Crystals dispersed with Perovskite Quantum Dots
10:50–11:05	Seiji Fukushima	Design method of a variable-focus-length lens employing a liquid-crystal-loaded metasurface
11:05–11:20	Abhilash T K	Integration of Cellulose Nanocrystals Derived from Plants as Pre-Alignment Layers for Ferroelectric Mesogens in Display Technology
11:20–11:35	Chung-Hao Chen	Refilled polymer-stabilised liquid crystals

Session 5. Hybrid and Composite Crystalline Materials
Session 4. Organic Crystalline Materials

Time: 14:00 (CEST, Basel) | 08:00 (EDT, New York) | 20:00 (CST Asia, Beijing)

CEST Time	Speaker	Title
14:00–14:10	**Prof. Dr. Ferdinando Costantino** Session Chair	*Welcome from the Session Chair*
14:10–14:35	**Prof. Dr. Silvia Bracco** Invited Speaker	Dynamics and Luminescent Properties in Nanoporous Crystalline Architectures
14:35–14:50	Sara Illescas	Composite Protein Crystals doped with Metal Nanoparticles as a complete antibacterial system
14:50–15:05	Nadia Anter	Extraction and Modification of Cellulose nanocrystals
15:05–15:20	Marco Sanna Angotzi	The Intricate Magnetic Properties of Co-Mn Ferrite Nanoparticles Studied by Neutron Scattering
15:20–15:35	Dhiman Kalita	Self-Trapped Excitons in Organic Lead Halide Perovskites
15:35–15:40	**Dr. Rodolfo Reda** Session Chair	*Welcome from the Session Chair*
15:40–15:55	Janet Eleojo AL-HASSAN	Exploring the Impact of Edge and Surface Sites on Functionalized Graphene-based Membrane in H2S Adsorption: A Computational Study
15:55–16:10	Jin Maeda	Improved Experimental Yield of Temperature-Cycle-Induced Deracemization (TCID) with Cooling and Crystal Washing: Application of TCID for the Industrial scale
16:10–16:25	Muhammad Asif Hossain	Investigating the crystallization process of medical bio-polymer Poly(3-hydroxybutyrate) using experimental methods and coarse-grained molecular dynamics simulations

19th September 2024 (Thursday)

Session 7. Crystalline Metals and Alloys
Session 2. Crystal Engineering

Time: 9:00 (CEST, Basel) | 03:00 (EDT, New York) | 15:00 (CST Asia, Beijing)

CEST Time	Speaker	Title
09:00–09:10	**Prof. Xuejun (James) Ren** Session Chair	*Welcome from the Session Chair*
09:10–09:35	**Prof. Xuejun (James) Ren** Invited Speaker	Integrated data-led modelling of complex materials at different scales: opportunities, challenges and missing linking
09:35–09:50	Jaime Lazaro Nebreda	Three-dimensional characterization of Fe-rich intermetallics in Al-Si-Mg (A6xxx) aluminium alloy DC cast billets with an increased scrap content by X-ray tomography
9:50–10:05	Mane Sahakyan	Optical and pressure-induced investigations of double perovskite Ba2TiMnO6 from the first principle.
10:05–10:20	Xiaoliang Qing	Data-led modelling and analysis of defects and doping in different carbides
10:20–10:35	Jayant Kumar Sahoo	Mineralogical Studies of Low-Grade Iron Ores from Daitari Iron Ore Deposit, Odisha, India
10:35–12:00	**Break**	
12:00–12:10	**Dr. David B. Cordes** Session Chair	*Welcome from the Session Chair*
12:10–12:35	**Dr. Nikos Karayiannis** Invited Speaker	Molecular Simulation as Tool to Study Crystallization
12:35–12:50	Okba Al Rahal	Structure of the Caffeine-Pyrogallol Complex: Revisiting a Pioneering Structural Analysis of a Model Pharmaceutical Cocrystal
12:50–13:05	Alexander P. Voronin	Polymorphism in riluzole salts and cocrystals with aromatic carboxylic acids
13:05–13:20	Dilyara Mingazhetdinova	Non-covalent structure-forming bonding of 2-aryhydrazone thiazolo[3,2-a]pyrimidines in the crystalline phase

20th September 2024 (Friday)

Session 3. Inorganic Crystalline Materials

Time: 9:00 (CEST, Basel) | 03:00 (EDT, New York) | 15:00 (CST Asia, Beijing)

CEST Time	Speaker	Title
9:00–9:10	**Prof. Dr. Vladimir P. Fedin** Session Chair	*Welcome from the Session Chair*
9:10–9:35	**Dr. M. Ajmal Khan** Invited Speaker	AlGaN-based far-UVC LED for Medical and Agricultural Applications
9:35–10:00	**Prof. Dr. Danil N. Dybtsev** Invited Speaker	Adsorption and separation of light hydrocarbons by a series of porous metal-organic frameworks
10:00–10:15	Driss Akhlidej	Investigation of the structural, microstructural, optical and electrical properties of iron-doped barium titanate ceramics
10:15–10:30	Win Thi Yein	Interfacial Action of Co-Doped MoS2 Nanosheets on the Directional Piezoelectric Catalytic Generation of Reactive Oxygen Species
10:30–10:45	Veronika D. Grigorieva	Sodium polymolybdates grown by low-thermal-gradient Czochralski technique for scintillating applications
10:45–11:00	Julio Corredoira Vázquez	A trans-diacetate dysprosium complex with a flexible hexaazatetramine 18-membered macrocycle
11:00–11:15	Alice Leoncini	Developments, features and perspectives of crystal scintillators of the Cs2MCl6family (M = Hf or Zr) to search for rare processes
11:15–11:30	Ana Rovisco	Influence of the seed-layer material on the direct growth of zinc-tin oxide (ZTO) nanostructures

Session 6. Materials for Energy Applications

Time: 14:00 (CEST, Basel) | 08:00 (EDT, New York) | 20:00 (CST Asia, Beijing)

CEST Time/CST Asia Time	Speaker	Title
14:00–14:10	**Dr. Ioannis Spanopoulos** Session Chair	*Welcome from the Session Chair*
14:10–14:25	Francesca Perra	Sorbents and catalysts based on mesostructured silica for pollutant removal and Carbon Capture and Utilization technologies
14:25–14:40	Fabio Manna	Optimizing the CO_2 uptake performance of an anilato-based ultramicroporous 3D MOF through a New Synthetic Protocol
14:40–14:55	Chaitanya Hirenkumar Jani	Recovery of Precious Metals from the Spent Catalyst
14:55–15:10	Fausto Secci	Highly dispersed ultra-small NiO nanoparticles on mesostructured silica as efficient catalysts for CO2 methanation
15:10–15:25	Fatima Baila	Recovery of mica minerals from granite waste for energy applications
15:25–15:40	Amretashis Sengupta	Lithium adsorption properties of two-dimensional chromium nitride

Session 1. Liquid Crystals

sciforum-094326: Self-Avoiding Rotating Walks as Models of Crystals Made of Freely Rotating Polymers in Two Dimensions

Carlos González-Chamorro Sánchez *, Cédric Loussert, Ismael Alati Benhammou, Javier Benito and Nikos Ch. Karayiannis

Universidad Politécnica de Madrid, Madrid, Spain

The concept of random walk (RW) [1] and its variation in the form of the self-avoiding random walks (SAWs) [2] are important tools in studying complex processes in a wide variety of fields, including, among others, polymer physics. Recent molecular simulations on extremely confined, monolayer films made of athermal semi-flexible polymers have revealed a wealth of structural behavior as a function of surface coverage chain stiffness, in the form of equilibrium bending angle [3]. Inspired by this and to quantify the thermodynamic stability of the two-dimensional polymer crystals, we map them into self-avoiding rotating walks (SARWs), restricted to follow the geometric constraints of the corresponding lattices. For a reference crystal, and by selecting a compatible equilibrium bending angle, we enumerate all possible configurations of single-chain crystals and calculate the corresponding size distribution as a function of the number of steps. SARW enumeration has been performed on honeycomb, square, and triangular lattices, all being characterized by different coordination numbers and lattice connectivity. The scaling of the number of SARWs, as well as their average size, as a function of steps are fitted using exponential-power-law asymptotic expressions and critical amplitudes; the connective constant and the critical exponents are compared against the analogous ones for conventional SAWs, corresponding to freely jointed polymers, under the same conditions [4,5].

[1] R. Bhattacharya, and E. C. Waymire, Random Walk, Brownian Motion and Martingales, Springer-Verlag (2021).
[2] N. Madras, and G. Slade, The Self-Avoiding Walk; Birkhauser: Boston (1996).
[3] D. Martínez-Fernández et al., J. Chem. Phys. (2024, under review).
[4] N. Clisby, Phys. Rev. Lett. 104, 055702 (2010).
[5] Parreño et al., Polymers 12, 799 (2020).

sciforum-093663: Topological Defects and Active Matter in Aqueous Lyotropic Chromonic Liquid Crystals

Sana Rahim * and Ammar Ahmed Khan

Physics Department, SBASSE, LUMS, Pakistan

Aqueous Lyotropic chromonic liquid crystals (LCLC) constitute a class of anisotropic fluids valuable for self-assembly at the microscale. Disodium Cromoglycate (DSCG) (commonly used commercially as an anti-asthmatic drug), is of particular interest to explore the behavior of microscopic biological organisms (such as rod-like bacteria and mammalian cells) in an environment where local rotational symmetry is broken. Fabrication of LCLC-based devices critically depends on the well-controlled molecular orientation/alignment of LCLC assemblies. This, however, has traditionally been difficult compared to more traditional Thermotropic LC phases due to low surface anchoring energy provided by conventional-rubbed alignment layers. Uniform alignment and spatially non-uniform patterned LCLC facilitate emerging applications. In the proposed project, we present planar alignment of DSCG LC by modifying the surface anchoring strength using a UV-cured polymer layer (SU-8) for alignment. Furthermore, we demonstrated the controlled topological defects by patterning the DSCG LC into micro-patterned arrays (prepared via photolithography) using square air pillars. The primary objective of the project is to direct distributions and trajectories of active and passive matter using pre-engineered LCLC director arrangements.The primary objective of the project is to direct distributions and trajectories of active and passive matter using pre-engineered LCLC director arrangements.The primary objective of the project is to direct distributions and trajectories of active and passive matter using pre-engineered LCLC director arrangements.

sciforum-094211: Molecular Simulation Studies of the Isotropic-to-Nematic Transition of Rod-like Polymers in the Bulk and under Confinement

Biao Yan, Daniel Martínez-Fernández, Katerina Foteinopoulou and Nikos Ch. Karayiannis

Universidad Politécnica de Madrid

In this research work, we conduct extensive Monte Carlo simulations to investigate the factors that affect the isotropic-to-nematic transition [1,2] of hard colloidal polymers in bulk and under various conditions of confinement. Polymers are represented as linear chains of tangent hard spheres of uniform length, with the stiffness being controlled by a bending potential leading to rod-like configurations [3]. Confinement is realized through the presence of flat, parallel and impenetrable walls in one, two or three dimensions [4], and periodic boundary conditions are applied in the unconstrained dimensions. All simulations are performed through the Simu-D software, composed of conventional and advanced, chain-connectivity-altering Monte Carlo algorithms [5].

The local and global structure of the computer-generated system configurations are gauged through the Characteristic Crystallographic Element (CCE) norm [6] and the long-range (nematic) order parameter [1]. Distinct factors, including chain length and stiffness, confinement and packing density are found to profoundly affect the isotropic-to-nematic transition at the level of chains, and the establishment of close-packed crystallites at the level of monomers.

[1] D. Andrienko, *J. Mol. Liq.* **267**, 520 (2018).
[2] S. A. Egorov, A. Milchev, and K. Binder, *Polymers* **8**, 296 (2016).
[3] D. Martínez-Fernandez *et al.*, *Polymers* **15**, 551 (2023).
[4] P. Ramos *et al.*, *Polymers* **13**, 1352 (2021).
[5] M. Herranz *et al.*, *Int. J. Mol. Sci.* **22**, 12464 (2021).
[6] P. M. Ramos *et al.*, *Crystals* **10**, 2073 (2020).

sciforum-094210: 8CB-Based Plasmonic Nanomaterials

Karolina Ordon, Olga Kaczmarczyk and Katarzyna Matczyszyn

Wrocław University of Science and Technology

Arranging plasmonic nanomaterials in a certain way can create materials with special optical properties, such as having anisotropy with refractive indices of simultaneously opposite signs for opposite light polarization. This type of material can be based on doping a liquid crystal system with nanoparticles with the indicated properties. Gold nanorods (AuNRs) are rod-shaped nanoparticles with size-dependent optical responses, and because of their plasmonic properties, they are used in imaging and fluorescent enhancement.

In our work, we investigated the influence of gold nanorods on the phase transitions and optical properties of the liquid crystal 8CB, known for its thermotropic behaviour. Gold nanorods were synthesized using a seed-mediated approach to obtain nanoparticles with the desired dimensions (aspect ratios: 5,6; 8,2; 10,8), which were observed and measured using transmission electron microscopy. Different concentrations of AuNRs were added to the 8CB samples, which were then inserted into liquid crystalline cells. All the samples were observed under a polarized light microscope equipped with a heating stage. At each concentration of the AuNRs, different optical structures were observed in both the nematic and smectic phases. The temperatures of the phase transitions also differed depending on the amount of the AuNR dopant in the system. The observed changes obtained by doping 8CB-based systems with nanoparticles may lead to the design of new metamaterials.

sciforum-094102: Design Method of a Variable-Focus-Length Lens Employing a Liquid-Crystal-Loaded Metasurface

Seiji Fukushima [1], Keitatsu Nakamura [2], Tsutomu Nagayama [2], Toshio Watanabe [2] and Hirotsugu Kikuchi [3]

[1] Kagoshima University
[2] Graduate School of Science and Engineering, Kagoshima University
[3] Institute for Materials Chemistry and Engineering, Kyushu University

We have reported light beam steering demonstration by using a liquid-crystal-loaded metasurface (LC-MS), which was based on voltage-controlled refractive index distribution on the metasurface. We can upgrade a beam steering device to a variable-focal-length lens by introducing parabolic refractive index distribution on LC-MS. Moreover, the focal length is controllable by voltage across the liquid crystal. We show the design method of the variable-focal-length lens and their numeric demonstrations in this paper.

The proposed lens model is one-dimensional and has parabolic refractive index distribution. In designing the device, we employed two procedures of theoretical far-field pattern (FFP) calculation and computer-based electromagnetic near-field pattern (NFP) simulation. The FFP calculation was carried out by means of phase calculation on the basis of classic optics. The results indicated the estimation of the lens effect although the preciseness of the focal length was not assured since the number of pixelated LC-MS was too small to evaluate the phases and steering direction of light beams. Then, our next strategy is electromagnetic field (EMF) simulation using the COMSOL simulator that can calculate EMF near the pixelated LC-MS. The simulation results improve by repeating these two processes. As a result, we found that LC-MS functions as a lens and the focal length is variable. The focal length was controllable within approximately 2.2 times, assuming a maximum refractive index change of 0.1, a pixel number of 11, and a wavelength of 600 nm.

To conclude, we established a design method of a variable-focal-length lens that employs LC-MS. The controllability of the focal length and the lens function were numerically demonstrated. This kind of LC-MS device does not require high voltages in general. Experimental demonstrations would be our next study.

sciforum-096451: Design of Neutral and Ionic Copper(I) Metallomesogens with Benzoyl Thiourea Ligands

Muhammed Alkali *, Monica Ilis and Viorel Circu

University of Bucharest

Copper(I) metallomesogens are an intriguing class of materials that combine the self-organizing characteristics of liquid crystals with the unique properties of Cu (I) complexes. These substances have interesting mesomorphic characteristics, which make them an excellent choice for use in display technologies, optoelectronics, and other fields. The study of Cu(I) is not widespread, owing to several challenges, including synthetic complexity, as the synthesis of some Cu(I) metallomesogens can be more complex than simple organic liquid crystals, and factors such as air and moisture sensitivity can add difficulty to the process. However, some copper(I) metallomesogens prepared with various structural components and ligands are known, including ionic and neutral liquid crystals. In this study, we successfully synthesized a new set of luminescent liquid crystals of the smectic A type, based on copper(I) complexes with 6-carbon alkoxy chains on the opposite ends of a benzoyl thiourea(BTU) compound.

The BTU ligand was reacted with $CuBr_2$, $CuCl_2$, and CuI in a 2:1 proportion, respectively, in ethanol to obtain the neutral $Cu(BTU)_2X$ complexes, where X = Cl, Br, or I; meanwhile,the ionic complexes $[Cu(BTU)_4]X^-$ were obtained by reacting the BTU with the Cu(I) precursors $Cu[(CH_3CN)_4]BF_4$ and $Cu[(CH_3CN)_4]PF_4$ in a 4:1 ratio in Toluene by stirring for 2 hours at room temperature. The structures of the prepared compounds were characterized by NMR (^1H, ^{13}C and ^{31}P) and IR studies while the liquid crystalline properties were investigated via a combination study of the use of a polarizing optical microscope (POM) and differential scanning calorimetry (DSC). The compounds prepared in this ongoing study have shown interesting photophysical properties that could make them promising candidates for application in luminescent liquid crystals.

sciforum-096365: Exploring Optical Properties of Nematic Liquid Crystals dispersed with Perovskite Quantum Dots

Ankita Sutar [1,*], Shital Kahane [1] and Swapnil Doke [2]

[1] Department of Physics, Dr. Vishwanath Karad MIT World Peace University, Pune, India
[2] Centre for Materials for Electronics Technology (C-MET), Pune, India

This study demonstrates the enhancement in photoluminescence (PL) of nematic liquid crystals (NLCs) doped with CsPbBr3 (perovskite) quantum dots (QDs). These perovskite QDs significantly boost the PL intensity by improving the anisotropic nature of NLC molecules, thereby reducing light leakage centers and intrinsic defects. Two different sizes of QDs were synthesized using a wet chemical method. X-ray Diffraction (XRD) confirmed the orthorhombic crystallite structure of the QDs, while Transmission Electron Microscopy (TEM) determined their size as 5.5 (±0.98) nm and 10 (±1.8) nm. The optical features of QDs were investigated by recording absorption and emission spectra at room temperature, which revealed unique excitonic peaks at 479 and 513 nm, whereas emission was seen at 503 and 518 nm for two different sizes, respectively. These highly luminescent QDs were further used to enhance the emission of NLC. Initially, liquid crystal (LC) sample cells were fabricated using the conventional polyimide technique, followed by the incorporation of NLC-QD composites via capillary action. The prepared sample cells were then characterized using polarizing optical microscope (POM) images and PL spectra measurements. The intensified dark state and brightened bright state POM images demonstrate improved unidirectional alignment along with a homogeneous texture of the NLC-QD composite. This improvement in molecular alignment, coupled with the reduction in light leakage centres and defects, is reflected in the PL spectra, showing an increased emission intensity of 18 % for the 10 nm sized sample. The enhanced emission of NLCs is attributed to the modified dielectric anisotropy in the presence of QDs. Conversely, 5.5 nm NLC–QD composites led to increased light leakage centres in the POM dark state and a subsequent reduction in PL intensity. The results indicate that these QDs are ideal for fabricating QD-based display devices with enhanced optical contrast, making them a promising choice for next-generation display technologies.

sciforum-096541: Giant Permittivity in Ferroelectric and Superparaelectric LCs

Yuri P. Panarin [1,*], Yadav Nelam [2], Jagdish Vij [2], Wanhe Jiang [3] and Georg Mehl [4]

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[2] Dept of Electronic and Electrical Eng., Trinity College Dublin, Ireland
[3] Dept of Chemistry, University of Hull, UK
[4] Dept of Chemistry, University of Hull, UK

The long-awaited ferroelectric nematic LCs (NF) predicted more than a century ago were finally discovered in 2017, independently in two different materials: RM 734 [1] and DIO [2]. The two common features of these materials are (a) extremely high molecular dipole moment (μ ~10 D) and (b) giant dielectric permittivity ($\varepsilon' \sim 10{,}000$) in the ferroelectric N_F phase (Fig.1(a)). Two new compounds, WJ-16 and WJ-18, based on the chemical structure of DIO, were synthesized for a further enhancement of ferroelectricity by increasing the molecular dipole. As expected, both compounds exhibit extremely high dipole moments (10.6 D and 13.6 D respectively). Surprisingly the increase in dipole moment completely suppresses the ferroelectricity. However, giant permittivity was observed not only in nematic phase, but also in the SmA phases (see Fig.1(b)). After intensive study it is concluded that both samples are paraelectric rather than ferroelectric exhibiting colossal permittivity i.e. they belong to the class of super-paraelectrics (SPE) observed before only in the solid state. This it opens a new range of applications of liquid crystals as the working media for supercapacitors with the potential of using them in energy storage devices.

Acknowledgments: We thank the Irish Research Council for awarding the Government of Ireland PDF 2021, GOIPD/2021/858; and the CSC, China for a PhD scholarship.

[1] R. J. Mandle et al, *Phys. Chem. Chem. Phys*. **19**, 11429 (2017).
[2] H. Nishikawa et al., *Adv. Mater*. **29**, 1702354 (2017).
[3] Neelam Yadav et al, *J. Mol. Liq.,* **378**, 121570 (2023).

sciforum-094280: Improvement in Alignment of Gold Nanorod/Ferroelectric Liquid Crystal Composites by Reduction in Ion Impurities

Anupama Sunil Kadam [1,*], Swapnil Doke [2], Madhushree Bute [3], Prasun Ganguly [4] and Suresh Gosavi [1]

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At present, LCDs have completely replaced conventional cathode ray tube (CRT) displays. LCDs offer the advantage of being significantly thinner and lighter, making them highly portable. With advancements in fabrication technology, LCDs have become cost-effective alternatives to CRTs. Over recent decades, extensive research by various groups has focused on liquid crystal (LC)-based nanoparticle (NP) composite materials, a prominent area in LCD-related studies. Research on LC-NP composites allows the exploration of synergistic combinations of LCs and NPs, each contributing unique characteristics. By doping NPs with LCs, properties such as localized surface plasmon resonance (SPR) of metal nanoparticles (MNPs) like Ag, Au, and Pt can be tailored. LCs play a crucial role in modifying NP assembly, thereby influencing the morphological organization of NPs and their remarkable electro-optical and electronic properties, essential for nanoscale device fabrication. Conversely, NPs can also tune the characteristics of LCs, including their EO properties and alignment in display technologies.

This study explores how adding gold nanorods (GNRs) to ferroelectric liquid crystal (FLC) devices affects their properties. GNR concentrations from 0.025 wt.% to 0.1 wt.% were tested. Adding GNRs at 0.025 wt.% and 0.050 wt.% improved optical contrast, tilt angle, absorbance, and photoluminescence intensity. The alignment of FLC composites with GNRs was better, with fewer light leakage centers. Also, the relative permittivity, dielectric loss, and DC conductivity improved with GNR inclusion. This suggests that GNRs can enhance the performance and efficiency of FLC devices.

sciforum-094144: Integration of Cellulose Nanocrystals Derived from Plants as Pre-Alignment Layers for Ferroelectric Mesogens in Display Technology

Abhilash T K *, Hasna M Abdul Hakkeem, Achu Chandran and Saju Pillai

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The efficacy of liquid crystal display (LCD) devices heavily hinges on the alignment of mesogens. In traditional LCDs, mesogens are oriented within substrates using the rubbed polyamide technique, which introduces undesirable contaminants and static charges, compromising device performance. This study presents a novel approach wherein plant-derived cellulose nanocrystals (CNCs) serve as an alternative alignment layer, obviating the need for the conventional rubbed polyamide technique. CNCs, extracted from banana pseudo-stem fibers via acid hydrolysis, are leveraged for alignment layer formation on ITO substrates using a rubbing-free vertical deposition technique. LC devices with various pre-alignment layers, including conventional rubbed polyamide and CNC layers, were fabricated and systematically compared. Through AFM, SEM, and profilometric analyses, we confirmed the presence of micro-sized channels and spindle-like structures of the CNCs, resulting from their self-assembly during vertical deposition. The device with the CNC layer exhibited robust mesogenic alignment and was sensitive to CNC layer thickness. The CNCs' spindle-like structure and self-assembling properties, coupled with vertical deposition, facilitated microchannel formation on the substrate, ensuring homogeneous alignment. The increased surface energy of CNC layers significantly improved mesogenic alignment, as evidenced by polarized optical microscopy and contact angle measurements. Moreover, the influence of these alignment layers extended to dielectric relaxation and transition temperature. Electro-optical properties, including spontaneous polarization, switching time, photoluminescence emission, and P-E hysteresis, were found to be comparable to conventionally rubbed polyimide, all while maintaining transparency. Additionally, CNC layers exhibited ion-capturing capabilities, leading to a reduction in device conductivity. This study underscores the potential of CNCs as an alignment layer for LCD applications, offering advantages such as enhanced wettability, density distributions, and overall orientation.

sciforum-096382: Investigation of the Phases and the Nature of the Corresponding Phase Transition of a Chiral Ferroelectric Liquid Crystalline Compound

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Liquid crystals offer an excellent platform for studying the nature of phase transitions by providing a rich variety of mesophase orderings [1]. In many cases, they occur in narrow temperature ranges, and the phase transitions between different mesophases can be either continuous or weakly first-order. The most commonly studied mesophases are nematic (N), smectic-A (SmA), smectic-C (SmC), and their chiral analogue,s such as N*, SmA*, and SmC* phases. This work mainly focuses on the characteristics of the N* to SmC* phase transition of a pure ferroelectric liquid crystalline (FLC) compound, namely QVE 8/5 [2,3]. The textures are characteristics of the different phases. For the studied compound, the characteristic textures corresponding to the N* and SmC* phases have been detected. The optical transmission method [4,5] has been used in order to investigate the N* to SmC* phase transition. The temperature variation of the transmitted intensity for the compounds QVE 8/5 have been measured for both planar and homeotropic alignments of the molecules. The critical behaviour of the N* to SmC* phase transition has also been investigated. The extracted critical exponent (α') of the investigated compound was found to be less than 0.5, which implies the second-order nature of the N*-SmC* phase transition corresponding to the studied FLC compound.

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sciforum-094154: Liquid Crystal–Ferrofluid Emulsions

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Dispersing nanoparticles in liquid crystals (LCs) is used to tune liquid crystal properties, to add functionality, or to exploit the self-organization of the liquid crystals to transfer order onto dispersed particles. Dispersing ferrofluid droplets into liquid crystals (LCs) not only adds magnetic functionality to the LCs, but also produces unique systems. Magnetic functionality can be used to measure the anisotropic viscosities of the LCs on a microscopic scale when moving the ferrofluid inclusions through various thermotropic, lyotropic, and colloidal LCs using an external magnetic field. The magnetite nanoparticles of the ferrofluid form a boundary layer at the interface between the LC and the ferrofluid droplets. The viscosities are calculated using Stokes' Law, together with the introduction of the boundary layer at the LC–ferrofluid interface. The viscosities for a variety of different liquid crystalline systems were measured as a function of changing environment, such as temperature, concentration, or pitch.

In nematic LCs, ferrofluid droplet chains are formed due to the topological defects in the LC induced by the dispersed ferrofluid droplets. The movement of these chains can be controlled by the external magnetic field. The velocities of water-based ferrofluid droplet chains in nematic 5CB, while varying factors such as the average size of the droplets, the number of droplets in the chain, and the external magnetic field strength, are reported. Adding a surfactant to the LC–ferrofluid emulsions enables the production of ferrofluid droplet chains encoated with a membrane in the LC. A comparitive study between the behaviour of the LC–ferrofluid emulsion with the addition of the surfactant polysorbate 60 (Tween-60) and uncoated ferrofluid droplet chains is reported. Different surfactants and lipids are used to produce membranes around the ferrofluid droplets to create a synthetic structure which mimics a magnetotactic bacterium.

sciforum-094044: Liquid Lecithin Crystals as Carriers of Biologically Active Substances and Nanoparticles

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Lecithin liquid crystals are promising carriers for transdermal drug delivery. They are able to include both lipophilic and hydrophilic substances, as well as solid particles. In this work, liquid crystals in a system comprising lecithin, avocado oil, tea tree oil, and water, containing biologically active substances and nanoparticles, were studied.

It was shown that in the range of shear rates from 0.01 to 1.0 s^{-1}, the introduction of 1.0 and 3.0 mol/L NaCl aqueous solutions increased the viscosity of liquid crystals, on average, by 4 and 9.1 times in comparison with the control sample. The introduction of potassium chloride glucosamine sulfate solutions with mass concentrations of 50, 100, and 150 g/l increased viscosity by 1.3, 2.2, and 3.3 times, while the introduction of 1 wt.% albumin in a citrate buffer solution into the liquid crystalline sample increased its viscosity by 1.5 times.
The addition of 0.3 wt.% of CuO nanoparticles (92±3 nm) increased the viscosity by 2.0 times, and that of $CuSO_4$ aqueous solution by 2,5 times compared with the control sample. When 0.3 wt.% of CuO microparticles (31,2±3,5 mm) was added, the viscosity decreased by 1.3 times. The kinetics of the release of copper ions from liquid crystals (copper content 2.4 mg/g) by dialysis were studied at T = 37 °C. The release rate of Cu^{2+} for liquid crystals with the $CuSO_4$ solution was $7{,}6 \cdot 10^{-4}$ g/($m^2 \cdot h$); for CuO nanoparticles, it was $5{,}86 \cdot 10^{-4}$ g/($m^2 \cdot h$); and for microparticles, it was $2{,}36 \cdot 10^{-4}$ g/($m^2 \cdot h$). Therefore, a dimensional effect was observed. This difference can be explained by the fact that copper ions in liquid crystals with $CuSO_4$ are already in the solution, but for samples with CuO particles, their dissolution is required.
The results obtained will help in the development of medical products based on lecithin liquid crystals.

sciforum-094412: Local and Global Order in Two-Dimensional Packings of Semi-Flexible Polymers

Daniel Martínez-Fernández *, Clara Pedrosa, Miguel Herranz, Katerina Foteinopoulou, Nikos Ch. Karayiannis and Manuel Laso

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Dense packings of semi-flexible polymer chains are researched through the Monte Carlo suite Simu-D [1] in extremely confined monolayers, effectively corresponding to two-dimensional films [2]. We systematically study the effect of chain stiffness on the packing ability and the emergence of local and global orders of semi-flexible polymers, modelled as linear chains of tangent hard spheres, the chain stiffness of which is tuned by a harmonic bending potential [3]. Thus, the limit of random close packing (RCP) is explored as a function of the equilibrium bending angle, while the local and global order of the emergent structures is quantified by the degree of crystallinity [4] and the nematic and tetratic orientational order parameters [5], respectively. A multi-scale wealth of structural behaviour is observed for the different semi-flexible systems studied, which is inherently absent in packings of athermal individual monomers, and which is surprisingly richer than that in three dimensions under bulk conditions. As a general trend, an isotropic to nematic transition is observed at sufficiently high surface coverages. As surface coverage further increases, the nematic phase is followed by the establishment of a tetratic state, which in turn marks the onset of RCP. For chains with right-angle bonds, the incompatibility of the imposed bending angle with the neighbour geometry of the triangular crystal (the densest structure in two dimensions) leads to a singular intra- and inter-polymer tiling pattern made of squares and triangles. The present study could serve as a step towards the design of hard colloidal polymers with tuneable behaviour for 2D applications.

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sciforum-096355: Micro-Rod Particle Dynamics in the Nematic Phase of Liquid Crystals Under Electric Fields

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Liquid crystals (LCs) have a wide variety of applications, propelling them to the forefront of electro-optics and displays. In many more recent applications, the behaviour of liquid crystals have reliedon particles suspended within them. Yet, particle behaviour and distribution can be significantly influenced by the application of an electric field. As a result, particles dispersed in the liquid crystal experience forces that can induce motion, change their translational direction, and even alter spatial organization [1]. Polarizing microscopy enables the examination of alignment quality and facilitates the identification of the electric field frequency stability regimes where particular particle behaviors are observable [2].

Investigating micro-rods with different aspect ratios leads to a wealth of additional degrees of freedom for motion as compared to the translation observed for spherical particles [3]. Insight into their behaviour is crucial for engineering novel materials and devices with specific features to diverse applications. The significance of aspect ratios in influencing the dynamic behavior of micromaterials in various settings is investigated in this work. Our experiments have unveiled novel modes of motion, encompassing both linear and nonlinear dynamics, for rod-shaped particles in a nematic liquid crystal under the influence of an electric field. The observed behaviors included linear translation, circular motion, and a newly characterized pattern involving rotation around both the long and short axes of the rods, obviously absent for spherical microparticles. Additionally, we identified novel macroscopic modes of motion, such as looping and logarithmic spiral trajectories.

The dynamic behaviour depends on particle size, confining cell gap, viscosity via temperature change, and electric field amplitude and frequency. The molecular boundary conditions produced by various cell gaps can alter how the particle in the liquid crystal reacts to outside stimuli, i.e., electric fields in our case. The results are of importance to fundamentally understand the motion of particles of different shape.

sciforum-094334: Modeling the Kinetics of auto-Oscillations in a Nematic Liquid Crystal Cell with Photoaligning in an azo-dye Layer on a Substrate

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Azo-dye layers have shown great promise due to the possibility of obtaining noncontact photoalignment layers of high quality. In this study, we investigate a structure that consists of a nematic liquid crystal (NLC) cell, in which one of the substrates is covered with a photosensitive azo-dye layer. The NLC has an initial planar director orientation. The linearly polarized light falls normally on the surface of the cell and propagates through the liquid crystal, reaching the azo-dye layer and interacting with it. The interaction of the light with the azo-dye leads to reorientation of the molecules of the azo-dye perpendicular to the light polarization. This changes the boundary condition for the NLC director and can result in its reorientation to a twisted state. Considering the NLC cell parameters that facilitate the Mauguin regime, the same photoalignment mechanism then kicks in in a perpendicular direction, leading to oscillations of the boundary conditions for the director and of the NLC director profile.

The dynamics of the NLC director reorientation is modeled using the free energy formalism, and the reorientation of the azo-dye molecules is modeled within the 2D Brownian orientation diffusion model. It was established that when the incident light intensity reaches a threshold value, the induced photo-alignment of the azo-dye becomes sufficient to start the NLC director reorientation toward a $\pi/2$ twist state. The threshold intensity increases with the Frank elastic constant and decreases with the anchoring energy. An increase in the light intensity and the azo-dye intermolecular interaction coefficient and the decrease in the viscosity of the NLC director lead to faster transitions between states and a lower period of oscillations.

sciforum-094437: Molecular Simulation of the Phase Behaviour of Attractive Rod-like Polymers

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Through a hierarchical modelling scheme, we determine a phase diagram of attractive rod-like polymers in three dimensions, comparing them with their freely jointed polymer counterparts [1,2]. Rod-like polymers are modelled as linear chains of tangent hard spheres whose chain stiffness is governed by a tuneable harmonic potential for the bending angle [3]. Employing the Simu-D suite [4], extensive Monte Carlo simulations provide a surprisingly rich collection of distinct crystal polymorphs, which can be finely tuned according to the range of attraction. These crystal polymorphs, identified by the Characteristic Crystallographic Element (CCE) norm [5], include face-centred cubic, hexagonal close-packed, simple hexagonal, and body-centred cubic structures and their combinations, as well as the establishment of the Frank–Kasper phase for freely jointed chains. Furthermore, employing the concept of cumulative neighbours of ideal crystals, a simple geometric model is proposed as a function of the range of attraction to accurately predict most of the observed structures and the corresponding transitions [2]. A geometrical analysis is provided of the characteristics of the self-assembled polymer clusters and crystals under conditions corresponding to a vacuum. Therefore, the present study demonstrates, at a fundamental level and in a highly idealised model, the capacity to fine-tune a single interaction parameter to employ for the design of polymer crystals with tailored morphologies.

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sciforum-094351: Refilled Polymer-Stabilised Liquid Crystals

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The original purpose of polymer stabilisation of liquid crystals was the exploitation of scattering devices in electronic paper/eBook readers, but advancements in other technologies have replaced their initial purpose. However, novel uses continue to emerge, such as intelligent privacy windows, smart glass, reflective displays, broadband reflective cholesteric devices, uses in lasing or holography, and blue-phase displays. Motivated by the need to enhance the performance of smart windows, polymer-stabilised cholesteric liquid crystals (PSCLCs) are applied in this technology. This study investigated the morphology and spectroscopic characteristics of refilled polymer-stabilised liquid crystals. The polymer network is fabricated by introducing a small amount of bifunction monomer into a nematic or chiral nematic liquid crystal. This is then photo-polymerised to form a network which templates the liquid crystal structure it was formed in. The system formed is a bi-continuous material with a continuous polymer network within a continuous liquid crystal. Washing out the liquid crystal leaves a long-range orientationally ordered network for polymerization in the nematic phase and a helical network for the chiral nematic phase.

The primary aims of this research are the utilisation of different types of polymer networks, refilled with various liquid crystal phases. Different lyotropic or cholesteric liquid crystals with opposite handedness and varying pitch are refilled into a specific polymer network, and the interaction between network and liquid crystal characterized by polarizing microscopy and spectroscopy as well as scattering measurements is observed. We demonstrate significantly enhanced orientation of lyotropic LCs, low pitch limits of helical transfer, and induced twist grain boundary-like structures.

sciforum-093693: The Effect of Liquid Crystal Electrolyte Modification on the Efficiency of Organic Photovoltaic Cells

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In many modern devices used to convert or store electricity, such as dye-sensitized solar cells (DSSCs), fuel cells, lithium-ion batteries or supercapacitors, one of the critical elements is the organic electrolyte, the stability and physicochemical properties of which significantly affect the efficiency of the processes of converting or storing electrical energy. The essence of the concept of using liquid crystals in such devices is that properly ordered structures at the nanometer scale lead to an increase in ionic conductivity in a specific direction and fulfill the role of stabilizing the system mechanically and thermally. Moreover, temperature induction of phase transitions enables switching off functions in a given electrolytic structure.

DSSCs with porous semiconductor titanium dioxide (TiO_2) electrodes were sensitized using ruthenium-based dyes purchased from Solaronix. In this experiment, the following ruthenium dyes were used: cis-diisothiocyanato-bis (2.2'-bipyridil-4.4'-dicarboxylic acid) ruthenium (II), known as N3; cis-diisothiocyanato-bis (2.2'-bipyrida-4, 4'-dicarboxylato) ruthenium (II) bis(tetrabutylammonium), marked as N719; and the amphiphilic ruthenium dye cis-diisothiocyanato-(2.2'-bipyridil-4.4'-dicarboxylic acid)-(2.2'-bipyridil-bipipyridil-4.4'-dinonyl) ruthenium (II), known in the literature as Z907. The electrolyte (AN-50) with a low viscosity contained iodide/tri-iodide as a redox couple, and a redox concentration of 50 mM was used.

The current–voltage (I-U) characteristics were determined for the ruthenium-based dyes mentioned above in order to check the influence of their structure on the efficiency of the DSSC cells. Next, it was checked what effect the addition of a nematic liquid crystal of 4- cyano-4'-pentylbiphenyl (5CB) to the iodide electrolyte had on the I-U characteristics. Modification of the I-U characteristics was found, in particular a change in the values of I_{SC} current and U_{OC} voltage.

sciforum-096441: The Universe in a Liquid Crystalline Droplet

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There is strong evidence that many natural phenomena could be described using geometrical approaches. Consequently, it is of interest to identify experimentally accessible systems in which universality of geometry-based approaches could be tested or/and investigated in detail. Testbed laboratory systems (i.e., analogs) could serve as gateways toward a deeper understanding of phenomena in other ways hardly or even experimentally inaccessible systems that are mathematically related to such analogs.

Diverse liquid crystalline (LC) phases and configurations are ideal candidates for such purposes. These optically anisotropic soft matter representatives combine properties of ordered crystals and liquids, and exhibit rich diversity of different symmetries. Their states could be well described by mesoscopic molecular fields, which could be easily manipulated by diverse external stimuli, and the resulting field-configurations could be probed using relatively simple and inexpensive optical methods (e.g., optical polarizing microscopy).

In our presentation we intend to illustrate how phenomena studied in LCs could be exploited to get insight into open problems of particle physics and cosmology. In particular, we address (i) the Kibble-Zurek mechanism describing coarsening dynamics of the Higgs field in the early universe, (ii) the stabilization and manipulation of skyrmion-family structures (these quasiparticle configurations were originally proposed to describe hadrons and mesons) and (iii) the stabilization and manipulation of fermionic Weyl-type excitations. We also (iv) illustrate analogs of “virtual particles”, and suggest a possible origin of (v) dark matter and (vi) of the asymmetry between “particles” and “antiparticles” in the Universe.

sciforum-094150: Thermally Stabilizing and Tuning Photonic Liquid Crystal Phases with Nanoparticles

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Photonic liquid crystal (LC) phases, such as blue phases (BPs) and the cholesteric phase (ChP), have contributed to a variety of photonic devices due to their three-dimensional and one-dimensional photonic band gaps (PBGs), respectively. These phases exhibit a helical periodic structure, which functions as a PBG that selectively reflects circularly polarized light (CPL). Tuning the PBG by adjusting its pitch length and extending the thermal stability and design applications of these phases have been significant research objectives over the last decade. Recently, a promising approach for thermally stabilizing blue phases and tuning the PBG to fabricate novel devices involve dispersing nanoparticles (NPs) into liquid crystal hosts that exhibit BPs and ChPs. In this study, various nanoparticles, including Al_2O_3, $BaTiO_3$, C60, and cellulose nanocrystals (CNCs), were dispersed into two liquid crystal hosts, a thermochromic mixture (TLC) and mixtures of cholesteryl nonanoate (CN) with nematic MBBA at different concentrations, to investigate their effects on the thermal stability and tunability of the PBG. The results demonstrate clear evidence of the extension of the BPs' thermal stability and the tuning of their PBG pitch. Notably, BPs exhibited greater thermal stability during cooling than during heating, which is an indication of increased supercooling effects. Furthermore, an increased cooling rate proportionally enhanced the thermal stability of the BPs, likely because of supercooling phenomena. Additionally, although BPs do not require alignment, their selective reflection wass enhanced by introducing planar alignment. Moreover, enhanced tuning of the pitch length was observed when NPs were added to the BPs and ChP compared to the pure LC host. The thermal stability improvements and enhanced tuning of the PBG suggest potential for developing more robust photonic devices, particularly for lasing and smart window applications.

sciforum-096017: Thiourea-Based Liquid Crystals: Metallomesogens, Gel Formation, and Luminescence

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Thiourea represents an interesting scaffold used to create new compounds with a wide range of applications, including biology, catalysis, nanotechnology, materials science. While N-H groups can be exploited in designing various H-bonding receptors, the C=S thione group is instrumental in coordination chemistry as it can bind to various metals. When supported by the C=O carbonyl group of an adjacent acyl fragment, the coordination abilities of the N-acylthioureas are enormous, leading to very stable metal complexes. But, despite the exceptional coordination capacities, thiourea-based ligands are not commonly used to create liquid crystals (LCs) or metal complexes with liquid crystalline behavior (metallomesogens). This is due to the limitations imposed by the molecular structure of the resulting complexes. This work will present an investigation of the effect of using ligands containing sulfur (benzoylthiourea-type derivatives—BTU) on the mesomorphic behavior of palladium(II), platinum(II), and copper(I) complexes. The organic ligands may be either simple or functionalized with different types and numbers of mesogenic groups. These products exhibit a combination of liquid crystalline properties and metal-dependant highly intriguing emissive properties. While the BTU organic derivatives can produce physical LC gels with E7, some palladium(II) complexes can display both gel and lyotropic phases in alcohol solvents. Various structural parameters can be adjusted to produce lamellar liquid crystal phases or columnar phases, which are assigned according to commonly used techniques: differential scanning calorimetry (DSC), polarized optical microscopy (POM), and X-ray diffraction (XRD).

Session 2. Crystal Engineering

sciforum-094314: C-H/O Interactions of Aromatic Ligands in Organometallic Compounds—Crystallographic and Density Functional Study

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C-H/O interactions are among the most abundant weak hydrogen bonds due to the omnipresence of C-H groups and oxygen atoms. Previous studies have shown that coordination with metals can cause the strengthening of noncovalent interactions, such as hydrogen bonds, stacking interactions, cation–π, and anion–π interactions. In this work, we studied the influence of transition metal coordination on C-H/O interactions of aromatic ligands in organometallic complexes.

Crystal structures of high quality, deposited in the Cambridge Structural Database (CSD, version 5.43, November 2022), were studied using the ConQuest program (version 2022.3.0) to find C-H/O interactions between the η^6-coordinated benzene and the oxygen atom of a Z_1-O-Z_2 fragment, where Z_1 or Z_2 could be any atom. The contact was accepted as a C-H/O interaction if the O···H distance was shorter than 2.9 Å and the C-H···O angle was bigger than 110°. The density functional theory was employed to calculate the energies of C-H/O interactions.

Our CSD search resulted in 152 C-H/O interactions of coordinated benzene, mostly in organometallic half-sandwich compounds. The analysis of geometrical parameters shows that preferred O···H distances in these interactions are between 2.3 Å and 2.5 Å. These O···H distances are shorter for coordinated than uncoordinated aromatic rings, indicating that coordinated aromatic rings form stronger C-H/O hydrogen bonds than uncoordinated ones. These findings are confirmed by our preliminary B3LYP-D3/aug-cc-pVDZ calculations, which showed that in the organometallic half-sandwich model system $Cr(C_6H_6)(CO)_3\cdots H_2O$ the C-H/O interaction reaches the energy of -3.88 kcal/mol, which is considerably stronger than the C-H/O interaction between (uncoordinated) benzene and water (-1.64 kcal/mol).

Our joint crystallographic and computational study points towards the enhanced ability of coordinated aromatic rings to form substantial C-H/O interactions. This study provides further insights into the strengthening of noncovalent interactions via transition metal coordination.

sciforum-096303: Coordination Polymers as Functional Materials

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The advanced synthesis of coordination polymers is fascinating due to its resulting structural diversity and vast opportunities to design new functional magnetic materials.

The physicochemical properties of coordination polymers result from a combination of synthesis conditions and properties of simple, well-known precursors [1,2,3]. This generates the possibility to model the electrical, magnetic, and optical properties of coordination polymers. These could find application as luminescent materials, catalysts, sensors, ion exchangers, and as magnetic materials. An important research topic in recent years is the luminescent properties of these materials. In comparison with organic compounds that are used, e.g., in the manufacturing of OLED-type diodes, inorganic coordination compounds prevail as they possess a much higher thermal stability, widening the operational temperature range.

Depending on the valence electrons' configuration, the luminescent properties of coordination polymers are governed by MLCT (metal–ligand charge transfer), LMCT (ang. ligand–metal charge transfer), LLCT (ang. ligand–ligand charge transfer), or IL (ang. inter-ligand charge transfer) states.

Herein, we present novel coordination polymers based on copper ions and organic aminocarboxylate ligands. For these compounds, the complexation of copper ions results in the amplification of emissions and an increase in the maximum emission shift.

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sciforum-093772: Crystallization Control Possibilities of Para-Aminobenzoic Acid Using Crystallization Additives

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University of Latvia

Polymorphism in active pharmaceutical ingredients has been the subject of intense investigation in the drug industry due to its influence on the properties of a drug. A better understanding of the formation of different polymorphic forms and control mechanisms may improve crystallization process efficiency and reduce production costs [1-2].

In this study, *para*-aminobenzoic acid (*p*ABA) was used as a model substance to investigate the crystallization control approach using additives. *p*ABA has four polymorphic forms, in which there are different types of hydrogen bonding and aromatic interactions [3].

The polymorphic outcome of crystallization of *p*ABA was explored under different conditions by performing evaporation and cooling crystallization from different solvents and in the presence of different additives. For the cooling crystallization, different cooling rates were used. Solid products obtained in the crystallization were characterized by powder X-ray diffraction. The solubility of different *p*ABA polymorphic forms was determined in water and the presence of selected additive. Additionally, induction time measurements were performed to determine the effect of the selected additive on the crystal nucleation rates.

In most cases, the crystallization results with an additive present were the same as those from the pure solvent. However, polyacrylic acid has shown the potential to form a metastable form by cooling crystallization. In the crystallization using the fastest cooling rate, α or β form or their mixture was obtained, but when using the slower cooling rate pure metastable β form was achieved. The solubility of *p*ABA α and β forms in the presence of polyacrylic acid is lower than in water. Additionally, polyacrylic acid slows down the nucleation of *p*ABA.

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sciforum-094312: Hydrogen bonds between Coordinated Water Molecules: A Crystallographic and Density Functional Study

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Hydrogen bond is the most abundant noncovalent interaction of water molecules. Previous studies have shown that the strength of the water–water hydrogen bond (-5.0 kcal/mol) increases if one of the water molecules coordinates to transition metal (-9.7 kcal/mol). One of the indicators of this strengthening is the shortening of H···O hydrogen bond distances in the crystal structures deposited in the Cambridge Structural Database (CSD).

To study how the coordination of both water molecules influences their hydrogen bonds, we used the ConQuest program to screen high-quality crystal structures deposited in the CSD. The contacts between two aqua ligands in these crystal structures were accepted as hydrogen bonds if the O···O distance was shorter than 4.0 Å and the O-H···O angle was bigger than 110°. The energies of hydrogen bonds were calculated using the B97D/def2-TZVP level of theory.

The majority of the obtained hydrogen bonds have H···O distances between 1.8 Å and 2.0 Å, which is longer than hydrogen bonds between coordinated and free water (1.6 – 1.8 Å). Although this might point towards the weakening of hydrogen bonds by the coordination of both water molecules, the DFT calculations show that the energy of a single hydrogen bond between aqua ligands reaches -11.0 kcal/mol, most likely due to increased dispersion effects. We found that the observed increase in the lengths of hydrogen bonds between aqua ligands is induced by the size of aqua complexes and their tendency to form multiple simultaneous hydrogen bonds. Our DFT calculations show that the supramolecular structures with multiple hydrogen bonds between aqua ligands reach an interaction energy of –70.0 kcal/mol.

This study implies that the coordination of both water molecules further increases the strength of their hydrogen bonds and shows that hydrogen bonds between aqua ligands are significant contributors to the stability of supramolecular systems of metal complexes.

sciforum-096234: Is bridging water in metal complexes the strongest hydrogen bond donor? Crystallographic and DFT insights

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Arguably the most famous type of noncovalent interactions, hydrogen bonds are very important in numerous chemical and biological systems, including the ones with aqua complexes. Metal coordination enhances the strength of hydrogen bonds of water by amplifying the positive charge on interacting hydrogen atoms. In this work, the hydrogen bonding ability of water molecules acting as bridging ligand in metal complexes was studied by the means of crystallographic analysis, as well as density functional calculations.

A survey of crystal structures of high quality from the Cambridge Structural Database (CSD) was performed using the ConQuest program to find hydrogen bonds between bridging water in metal complexes as a hydrogen bond donor and the water molecule as a hydrogen bond acceptor. The energies of hydrogen bonds found in the CSD were calculated in the Gaussian 09 suite of programs using the dispersion-corrected B97D density functional and the def2-TZVP basis set.

A total of 88 hydrogen bonds of bridging water in metal complexes was found. The majority of these hydrogen bonds have short H···O distances, mostly between 1.7 Å and 1.9 Å, with several examples even below 1.6 Å. Additionally, these hydrogen bonds possess a high degree of linearity, with the majority of O-H···O angles between 165° and 175°. These geometrical parameters indicate short and linear, and therefore strong, hydrogen bonds. DFT calculations show that these interactions are indeed very strong. Specifically, neutral complexes containing bridging water form hydrogen bonds with free water that can reach an energy of -15.4 kcal/mol. This is significantly stronger than hydrogen bonds of neutral metal complexes of non-bridging water, which do not surpass -10.0 kcal/mol.

The joined crystallographic and computational study demonstrates the enhanced ability of bridging water in metal complexes to act as hydrogen bond donor.

sciforum-094622: Non-Covalent Structure-Forming Bonding of 2-aryhydrazone thiazolo[3,2-a]pyrimidines in the Crystalline Phase

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Currently, hydrazones are promising building blocks for the creation of various supramolecular architectures, since they can undergo conformational and configuration changes under the influence of external conditions. Thus, from the point of view of supramolecular chemistry, the potential use of compounds containing a hydrazone functional group for the design of molecular switches, as well as for the creation of new materials, has been demonstrated.

This work is devoted to the synthesis and study of 2-arylhydrazone thiazolo[3,2-*a*]pyrimidine derivatives structures in the crystalline phase.

The obtained derivatives are characterized using a complex of physico-chemical (IR-, NMR ^{1}H- and ^{13}C-spectroscopy, ESI-MS spectrometry, and X-ray diffraction) analyses.

It was confirmed that arylhydrazones are in the *Z*-isomer form in the crystalline phase. Additionally, it was established that non-covalent intramolecular and intermolecular interactions play the main role in supramolecular organization in crystals. So, the formation of hydrogen-, chalcogen-, π-π-bonded racemic dimers, and halogen-bonded homochiral chains was shown.

The structure of arylhydrazones containing halogen substituents in aryl fragments has also been studied. The embedding of a sterically inaccessible halogen substituent, blocked for the formation of intermolecular interactions, into one of two aryl fragments that switch off the action of structure-forming halogen bonding in one position and switch on in the second one, together leads to different self-assembly in the crystalline phase.

Thus, the synthesis and study of the supramolecular organization of 2-arylhydrazone thiazolo[3,2-*a*]pyrimidine derivatives in the solid phase were successfully carried out, and the possibility of implementing various supramolecular ensembles was discovered.

sciforum-096554: O-H...O AND O-H...N Hydrogen Bonds as Supramolecular Syntons in the Formation of Chiral Architectures on Thiazolo[3,2-*a*]pyrimidine 2-Arilmethylidene Derivative Frameworks in the Crystalline Phase

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The synthesis of new antitumor drugs is a promising direction in modern science. Nowadays, some thiazolopyrimidine derivatives are already known to exhibit different antitumor activities. Since the biological activities of racemate and pure enantiomers of many biologically active compounds may greatly differ from each other, the question of their separation, i.e., obtaining them in enantiopure form, is a pressing one.

Non-covalent interactions may be important for understanding the mechanism of drug action and can also be used in crystallization to separate racemic mixtures into pure enantiomers. Since a racemic mixture is formed during the synthesis of thiazolo[3,2-*a*]pyrimidine derivatives, the study of these derivatives in the crystalline phase is an essential problem.

This work is devoted to the synthesis and study of the supramolecular organization of new thiazolo[3,2-a]pyrimidine derivatives in the crystalline phase. The structure of all obtained compounds was characterized by IR, NMR ^{1}H and ^{13}C spectroscopy, ESI-MS spectrometry, and SCXRD analysis.

The influence of the synthesized derivatives' structure and the used solvent's nature on the supramolecular motif of their organization in the crystal phase due to the presence of O-H...N and O-H...O type hydrogen bonds was established.

The majority of derivatives containing the *o*-vanillin fragment form racemic dimers. Derivatives containing a 4-hydroxybenzylidene fragment form zigzag homochiral chains. When derivatives containing a 2-hydroxybenzylidene fragment crystallize, bridging hydrogen O-H...N and O-H...O bonds are produced with a solvate molecule. It causes the formation of zigzag homochiral chains in the crystalline phase.

The crystallization of derivatives containing 2-methoxyphenyl with 2-hydroxybenzylidene and phenyl with 2-hydroxy-3-methoxybenzylidene moieties, respectively, from ethanol resulted in the formation of conglomerates.

sciforum-094361: Polymorphism in Riluzole Salts and Cocrystals with Aromatic Carboxylic Acids

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In this work, we investigated the influence of positional isomerism on the packing arrangements and the hydrogen bond network in multicomponent crystals of the drug riluzole with hydroxybenzoic acids. A combined theoretical/experimental study, including virtual screening, X-ray diffraction, IR/Raman spectroscopy, thermal analysis and periodic DFT computations, was conducted to isolate and identify the novel crystal forms. By surveying multicomponent crystals of riluzole deposited in the Cambridge Structural Database, we found that salicylic acid derivatives with pKa 3.8 form salts with riluzole, while benzoic acid derivatives without ortho-hydroxyl groups form cocrystals. New multicomponent crystals of riluzole with salicylic, 4-hydroxybenzoic, 2,3-, 2,4- and 2,6-dihydroxybenzoic acid were obtained and structurally characterized. Varying the experimental conditions allowed us to isolate samples of metastable polymorphs of salts with salicylic, 2,4- and 2,6-dihydroxybenzoic acids. For Form II of the riluzole + 2,6-dihydroxybenzoic acid salt, the crystal structure was determined based on data on powder diffraction of high-energy synchrotron radiation. The hydrogen bond network was found to be identical in riluzole 2,6-dihydroxybenzoate Form I and Form II, and the difference was limited to the mutual orientation of hydrogen-bonded layers, which is a rare example of packing polymorphism. The metastable form was found to undergo an irreversible phase transition at about 120°C, visible as an exothermal event on the thermogram. For riluzole salicylate, two polymorphic modifications were discovered in addition to the already reported form, and the stability relationship between them was studied based on DSC, HSM and dissolution studies. In addition, solvated salt forms were found in the systems with 2,4- and 2,6-dihydroxybenzoic acids during slurry experiments in water, dioxane and DMSO. For the newly obtained phases and pure components, their solubility was determined in aqueous buffer solutions at different pHs and organic solvents, and salt formation thermodynamic functions were obtained from the thermodynamic cycle.

sciforum-092996: Screening Conditions for the Synthesis of Crystalline Spherical Clusters using 5-Hydroxynicotinic Acid

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Crystallization is used for product separation and purification in production sectors such as food, agriculture, electronics, and pharmaceuticals.[1] However, a considerable lack of understanding about the molecular mechanisms behind the formation of crystals remains. Systematic solubility and crystallization studies on families of compounds are useful to understand how slight changes in molecular structure can impact the crystallization outcome. Building upon previous studies on the hydroxynicotinic acid family,[2] in this work, novel insights into the optimization of synthetic procedures to obtain crystalline spherical clusters of 5-hydroxynicotinic acid (5HNA) are presented. It meticulously explores and identifies the most favourable conditions for producing spherical clusters of 5HNA. The systematic screening of various synthetic conditions has led to the successful formation of these clusters. This work opens up new avenues for the potential applications of 5HNA spherical crystalline clusters. Such clusters have diverse diameters depending on the solvent and the synthesis conditions. The clusters were characterized by optical microscopy, scanning electron microscopy (SEM) and powder X-ray diffraction (PXRD). Possibly the clusters were formed by a self-assembly process driven by hydrogen bonding and π-π interactions between the 5HNA molecules. The solvents ought to play a relevant role in such self-assembly process. The clusters exhibit different crystallinity depending on the solvent. Such clusters could be used as building blocks for nanomaterials with potential applications in a multitude of fields.

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sciforum-096589: Structure of the Caffeine-Pyrogallol Complex: Revisiting a Pioneering Structural Analysis of a Model Pharmaceutical Cocrystal

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Introduction

The 1967 attempt of structural analysis of the solid-state complex of caffeine (**caf**) and pyrogallol (**pyg**) was a pioneering structural investigation in supramolecular chemistry of caffeine. While this might be one of the earliest attempts, if not the earliest, to report structural properties for a molecular cocrystal of caffeine, the heavily used molecule in crystal engineering, the reported structural model showed multiple structural issues such as distortion of aromatic rings of caffeine and pyrogallol from planarity and the non-optimised molecular geometry. Our aim therefor was to revisit this structural model demonstrating this long-overlooked complex is most likely a tetrahydrate with a different structure and composition than initially proposed and provide the crystal structure of the anhydrous cocrystal.

Methods

Computational techniques such as density functional theory, structure determination from powder X-ray diffraction data (PXRD) and Rietveld refinement techniques were employed. In addition, mechanochemical and solution crystallisation methods were used for sample preparation. Multiple instrumentations such as single crystal XRD, variable-temperature (VT-PXRD), thermal analysis, dynamic vapor sorption (DVS) and Fourier-transform infrared attenuated total reflectance (FTIR-ATR) spectroscopy were used for structural, physicochemical characterisation and phase behaviour study.

Results

The crystal structure of the solid-state complex was found to be a channel hydrate with a tetrahydrate (**caf**·**pyg**·$4H_2O$) composition. The water molecules arrange into columns extending along the crystallographic *c*-axis, exhibiting edge-fused hydrogen-bonded pentagons and heptagons. The newly discovered anhydrous structure (**caf**·**pyg**) is monoclinic and consists of tetrameric (**caf**)$_2$(**pyg**)$_2$ units. Reversible hydration/dehydration behaviour is demonstrated through DVS and VT-PXRD studies.

Conclusion

In conclusion, we re-investigated caffeine-pyrogallol solid state complex, showing that the complex is a tetrahydrate rather than pentahydrate as initially reported. We also reported an anhydrous form of this historically important system and studied their phase behaviour.

Session 3. Inoganic Crystalline Materials

sciforum-096466: Developments, Features and Perspectives of Crystal Scintillators of the Cs_2MCl_6family (M = Hf or Zr) to Search for Rare Processes

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Recently, there has been considerable interest in the development of crystal scintillators of the Cs_2MCl_6 family of metal hexachlorides (M = Hf or Zr) due to their exceptional properties: high light yield (up to 40000 photons/ MeV), good linearity in the energy response, excellent energy resolution (3.5% at 662 keV in the best configuration) and excellent ability to discriminate between pulse shapes (PSD) of $\beta(\gamma)$ and α particles. One Cs_2HfCl_6 (CHC) crystal scintillator was measured, over 2848 h of data taking, deep underground in the STELLA laboratory at the Gran Sasso National Laboratory of the INFN, Italy. Its residual radioactive contaminants were studied and are presented here. The total α activity of the detector was at the level of 7.8(3) mBq/kg. A measurement using two Cs_2ZrCl_6 (CZC) crystal scintillators (11 g and 24 g) was performed in the DAMA/CRYS low-background setup deep underground at LNGS. Chemical purity, residual radioactive contaminants, scintillation, and PSD performance are discussed in this paper. The low-background measurements over 456.5 days demonstrated the crystals' high radiopurity, showing a counting rate of 0.17(kg·keV·y)$^{-1}$ at the $Q_{2\beta}$ = 3.35 MeV of ^{96}Zr. Another measurement was subsequently carried out using three new CZC crystals and one CHC crystal in optimized geometry. The crystal growth technique, raw material purification, and post-growth material treatment are discussed here. Moreover, the three CZC crystals were grown using starting materials with different purities to study their resulting characteristics and were encapsulated using a silicone-based sealant. The results obtained are presented in this paper.

sciforum-096222: Impact of TiO2 on Glass–Ceramic Photocatalysis

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Glass ceramics, formed through the meticulous control of glass crystallization, have become indispensable in modern life owing to their multifaceted utility. Their shape and size adaptability, exceptional stability across various conditions, ease of fabrication, and consistent performance render them pivotal in addressing pressing environmental concerns. These qualities position them as potential solutions to urgent challenges.

Phosphate glasses, widely utilized, offer fertile ground for exploration in photocatalysis with the integration of TiO2. In our study, glasses with varying TiO2 concentrations (0%, 2.5%, 5%, 7.5%, and 10%) were melted at 1200°C. This process induces the transition from an amorphous state into a glass ceramic state within a temperature span encompassing both melting and crystallization. Analysis of thermal, structural, and morphological attributes reveals that augmenting TiO2 content in phosphate glass amplifies its photocatalytic efficacy, resulting in the accelerated degradation of organic pollutants under light exposure. These findings underscore the pivotal role of TiO2 in enhancing the environmental performance of glass, thus paving the way for sustainable and innovative advancements.

In summary, the evolution of glass ceramics from controlled crystallization techniques heralds a new era in addressing environmental challenges. Incorporating TiO2 into phosphate glasses is promising for advancing photocatalytic applications, offering a pathway to mitigate environmental degradation. As research progresses, these materials are poised to play a pivotal role in fostering sustainability and innovation.

sciforum-096497: Spectroscopic Properties of Nd^{3+}-Doped Sr_2LaF_7 Nanoparticles

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Lanthanide-doped nanocrystals are widely known systems thanks to their emission characteristics, such as their exceptional thermomechanical properties, chemical stability, large effective Stokes shifts, narrow emission spectra, and long lifetimes. Alkali-earth lanthanide nanophosphors (M_2LnF_7, where M represents Ca, Sr, Ba, etc., and Ln^{3+} stands for Y, La, Gd, Lu, etc.) have been proposed as good host materials. They possess elevated upconversion (UC) luminescence properties and can be grown in dimensions suitable for biomedical imaging applications.

Neodymium (Nd) ions possess intense emissions across various infrared regions, at wavelengths around 900 nm, 1064 nm, and 1300 nm. These emissions originate from transitions between the $^4F_{3/2}$ state and the lower-lying $^4I_{9/2}$, $^4I_{11/2}$, and $^4I_{13/2}$ energy states, respectively.

In this work, we present a thorough investigation of the spectroscopic properties of Sr_2LaF_7 phosphors with different Nd^{3+} ion concentrations (x=1, 2, 3, and 5 mol%). The samples were synthesized using the hydrothermal method and structurally and morphologically characterized. Powder X-ray diffraction analysis confirmed that the materials crystallize in a cubic crystal structure while transmission electron microscopy shows nanoparticles with an average particle size of ~ 40 nm.

All the Nd^{3+} ion concentrations that we studied present a slightly sublinear trend in the emission spectra as a function of the pump power. This indicates the presence of some loss in the energy transfer processes. Moreover, we studied the emission trend as a function of the concentration at a fixed pump power. This study suggests that the optimum concentration for the maximum emission intensity is 3% Nd. The trend shows a decrease in intensity at higher concentrations.

We will present both the emission trends and the lifetime of the $^4F_{3/2}$ level as a function of the sample temperature, which will range from -190 °C to 600 °C, with insights into the possible energy transfer processes.

sciforum-093646: The temperature-dependent luminescence efficiency of a hygroscopic cerium-doped lanthanum bromide ($LaBr_3$:Ce) single-crystal scintillator

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Background

Scintillators are used in a variety of applications, including modalities in environmental conditions of extreme temperature or radiation flux. Thus, knowledge of their luminescence performance under the influence of temperature or radiation flux is of paramount importance. In this framework, the aim of this study was to examine the influence of temperature on the luminescence efficiency of a hygroscopic cerium-doped lanthanum bromide ($LaBr_3$:Ce) single-crystal scintillator. The crystal output was compared with a cerium-doped lanthanum chloride ($LaCl_3$:Ce) crystal scintillator of equal dimensions, in similar experimental conditions.

Materials and Methods

The experimental setup comprised a CPI series CMP 200 DR medical X-ray source set to a fixed high voltage (90kVp) to expose the sample to X-ray radiation under temperature conditions in the range of 23–154 °C. $LaBr_3$:Ce is an extremely efficient crystal, with a high light yield of 63,000 photons/MeV and a fast decay time (25ns). The crystal was removed from the protective aluminum encapsulation (thickness 0.7 mm). Heating was performed using a Perel 3700-9 2000W heating gun. The temperature on the crystal surface was monitored using an Agilent Technologies U1253A digital multimeter, coupled to a U1185A thermocouple (J-Type) with a temperature probe adapter.

Results

The luminescence efficiency of $LaBr_3$:Ce decreases with increasing temperature, from 69.58 EU at 23.0°C to 18.27 EU at 154°C (EU is the S.I. equivalent $\mu Wm^{-2}/(mGy/s)$. The corresponding values for $LaCl_3$:Ce were 33.14 to 17.96 EU in the temperature range from 29 to 162 °C. The room-temperature absolute efficiency of $LaBr_3$:Ce, with the protective aluminum encapsulation, was 50.02 EU.

Conclusion

$LaBr_3$:Ce is an extremely efficient crystal scintillator and knowledge of its performance in various temperatures could be useful for various applications, from medical imaging to detectors for extreme environments.

sciforum-094230: A *trans*-diacetate dysprosium complex with a flexible hexaazatetramine 18-membered macrocycle

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Introduction

Hexadentate N_6 macrocycles could be adequate for obtaining lanthanoid complexes with coordination number 8 and axial hexagonal bipyramidal geometry. However, achieving this is not straightforward, as the geometry of these complexes is strongly influenced not only by the flexibility of the macrocycle but also by the features of the selected ancillary donors, as indicated by some prior findings using chloride and nitrate as auxiliary ligands in macrocyclic lanthanoid complexes.

Synthesis and methods

With the intention of delving deeper into this issue, we present here the result of the synthesis and crystallographic characterization of the dysprosium complex $[DyL(OAc)_2]OAc{\cdot}7H_2O$, arisen from the interaction of dysprosium acetate tetrahydrate and a macrocyclic hexaazatetramine ligand, derived from diacetylpyridine (L = 3,6,10,13-tetraaza-1,8(2,6)-dipyridinacyclotetradecaphane) in a 1:1 molar ratio in chloroform. Its crystal structure was solved using standard methods of single-crystal X-ray diffraction.

Results

Despite the desired *trans* disposition of the acetate anions, with the macrocycle L in a rather plane disposition, the dysprosium atom is deca-coordinate, as both acetate complexes behave as bidentate chelating donors, forming a mutual angle of 72.6 °. The spatial arrangement of the ligand leads to a bicapped square antiprism calculated geometry, but with a significant distortion to a sphenocorona.

Conclusion

Despite achieving a desired *trans* disposition for the ancillary ligands, the substitution of acetate as an auxiliary donor, instead chloride or nitrate, has not allowed us to obtain an axial octacoordinate Dy^{3+} complex, but a decacoordinate one.

sciforum-096584: As ^{V} AND As^{III} Removal from Water by Different Iron Oxyhydroxides Nanosorbents

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Introduction

Arsenic pollution in surface water and groundwater is a worldwide problem originated by dissolution of arsenic from soil, mainly due to anthropogenic activities. Due to the possibility to form inner-sphere complexes, the high surface-to-volume ratio and, therefore, the high density of active sites (-OH groups), nanopowders of iron oxides and oxyhydroxides show a high affinity for arsenate and arsenite species in wide pH ranges and pollutant concentrations.

Methods

Akaganeite (β-FeOOH), ferrihydrite ($Fe_5HO_8{\cdot}4H_2O$), and feroxyhyte (δ-FeOOH) were synthesized by simple precipitation methods and tested for the removal of arsenic from water by changing different parameters (initial concentration, contact time, ionic strength, presence of competing ions and solid to liquid ratio). The same experimental conditions for the batch tests allowed a direct comparison between the adsorbents. All sorbents were characterized by XRD, TEM and HRTEM, N_2-physisorption, ELS, TGA,ATR-FTIR.

Results

Thanks to its high and positive surface charge, akaganeite is found to be the most promising sorbent in the whole pH range for As(V) (adsorption capacity equal to 99% for C_{As} = 100 mg/L); it also shows good adsorption capacity for As(III) (81% and 83% for pH 3 and pH 8 respectively at 100 mg/L,). The best sorbent for As(III) is, however, ferrihydrite (98% at 100 mg/L for both pH 3 and pH 8), due to its high surface area. Preliminary results on feroxyhyte prove its suitability as a sorbent for As(V) (92% at 100 mg/L for pH 3).

Conclusions

Akaganeite is the most promising sorbent in the whole pH range for As(V), while ferrihydrite is the best sorbent for As(III). Results on feroxyhyte proved its suitability as a sorbent for As(V) as a promising alternative to akageneite, due to its straightforward and quick synthesis process.

sciforum-094294: Bite angle assessment of coordination geometry of zinc(II) 2, 2'-bypiridine crystal

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Literature reports of zinc(II) 2,2'-bipyridine crystal in chemistry journals by different researchers call for urgent attention because of its significance in catalysis, drug delivery, electrochemistry, materials chemistry, nanomedicine, and nanotechnology. Here, different coordination geometries reported include distorted tetrahedral, distorted octahedral, tetrahedral, octahedral, and square pyramidal geometries. Outside other forms of characterization, there are techniques of bite angle, such as computational chemistry and nuclear magnetic resonance (NMR); this study considered the concept of bite angle determined experimentally from X-ray crystallography. This led to the following research question: "how does the bite angle assess the different coordination geometries of zinc (II) 2,2'crystal reported in the literature of Chemistry journals?". In response to this question, qualitative research was used as the methodological approach to explore how the ligand field theory (LFT) supports the bite angle's assessment of the coordination geometry of zinc(II) 2, 2'crystal using X-ray crystallography from recently reported literature in top-rated chemistry journals. Results showed how bite angles of similar zinc(II) 2,2'crystal compared with LFT to validate the reported coordination geometry of zinc(II) 2,2'-bipyridine crystal. The implication of this study is to enhance the relevance and importance of bite angle in zinc(II) 2, 2'crystal.

sciforum-095405: Breathing layered metal–organic frameworks based on 1,3-bis(imidazolyl)propane

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Metal–organic frameworks are a class of porous materials that are widely used in various fields of science, such as gas sorption and separation, sensing, catalysis, and others.

Currently, most MOFs are created on the basis of hard aromatic carboxylic acids or N-donor ligands. However, ligands with flexible aliphatic bridges that provide conformational mobility to the ligand are promising. This mobility can be transferred to the MOF, or at least the flexibility of such a ligand can lead to its variability and atypical structure. Such structures may exhibit unusual gas adsorption properties.

Layered MOFs have a special feature—their layers are not bound by rigid ligands, so they can "breathe", that is, they can move relative to each other. In the initial state, a MOF may be a low-porosity or non-porous compound, but at gas pressure, it begins to show a "gate-opening" effect, which can lead to the selective adsorption of gases.

Our work is devoted to the study of layered MOFs based on 1,3-bis(imidazolyl)propane (*bip*) containing a -C3H6-alkyl group. Due to its conformational mobility, *bip* acts as a bridging ligand that connects two metal atoms into one secondary building block (*SBU*). Secondary building blocks M $(bip)_2^{2+}$ (M = Cd, Cu) form a layered mobile structure with the help of functionalized terephthalic acids (bdc-NO_2).

The sorption characteristics of these compounds are of great interest to the research community. As part of our work, we investigated the adsorption of industrially important hydrocarbons such as methane, ethane, ethylene, acetylene, propane, and propylene at different temperatures. Using the example of C_3-hydrocarbons, we show an anomalous dependence of the amount of adsorbed gas on temperature. Usually, as the temperature increases, the volume of sorbed gas decreases. In the case of the studied compounds, an inverse, more complex dependence is observed.

sciforum-096597: Chemical Equitable Partitions of Inorganic Lattices

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Introduction

Graph-theoretical approaches in the study of materials can shed new light on their structure--property relationships. Here, a novel concept termed Chemical Equitable Partition (CEP) [1,2] was used as a means to look at crystal symmetries and classify atoms accordingly.

Methods

The study focused on inorganic perovskites and oxides, without partial or mixed occupancies. Atom pairs were marked as adjacent when the sum of the atoms' radii exceeded the pair distance, respecting unit-cell periodicity. Atom radii proposed by Alvarez [3] were used (occasionally rescaled to reproduce coordination numbers). The atoms' connectivity profiles were processed as described by Michos and Raptis [1] to derive Chemical Equitable Partitions. Electrostatic lattice site potentials were calculated using VESTA's [4] built-in functionality. CEP cells were compared to the atom groups defined by Wyckoff positions, on the one hand, and site potentials, on the other.

Results

Highly symmetric cells featured identical partitions, according to CEP, Wyckoff positions, and Madelung potentials, whereas CEP in systems with lower symmetry was a refinement of the partitions with respect to electrostatic potentials and Wyckoff positions.

Conclusions

CEP provides an alternative perspective on crystal structure and symmetry. Forthcoming research will specify how CEP seamlessly incorporates organic moieties, as found in hybrid organic/inorganic crystals, within a unifying framework.

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sciforum-093661: Cone Beam Computed Tomography: Preliminary studies on novel detector schemes

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Background: Cone beam computed tomography (CBCT) offers a comfortable breast examination accompanied by 3D breast representation, at the same or lower dose levels in comparison to classical mammography and its derivative tomosynthesis. In the case of dense breast, it provides specialists a reliable anatomical representation towards an accurate diagnosis of breast pathologies. CBCT system detector configuration usually is based on a CsI:Tl scintillator.

Materials and Methods: The purpose of this study was to instigate novel detector schemes applied to a simulated micro-CBCT system, with a view to designing future experimental setups. The energy spectrum of the CBCT system X-ray source ranged from 10 to 40 keV. The system relied on a 360° rotating table. Different detector materials, of the same size and shape, were simulated and investigated: LSO:Ce, LYSO:Ce, LuAG:Ce, GAGG:Ce, $LaBr_3$:Ce, $LaCl_3$:Ce, and CZT. A bone tissue capillary was used in order to investigate possible differences in the system's spatial resolution. Further, a breast phantom was simulated in order to evaluate image quality, as it is derived from contrast-to noise ratios (CNRs) of specific ROIs (regions-of-interest). System simulation was based on GATE software. Images were reconstructed with FBP and OSEM. The evaluation was performed in conjunction to the standard CsI:Tl detector setup. All schemes were simulated with the same front-end electronic configuration.

Results: Image quality assessment depicted a dependence on detector material. LYSO:Ce, LuAG:Ce, GAGG:Ce, $LaBr_3$:Ce, and $LaCl_3$:Ce presented high CNRs for materials of different composition. CZT is a promising semiconductor energy converter in the case of a low-density bone tissue. Spatial resolution depends only on the reconstruction algorithm.

Conclusion: The aforementioned examined materials with increased CNRs could be an efficient alternative in a future CBCT system that will overcome further dense breast imaging limitations.

sciforum-093329: Disorder effects in magnetic properties and electronic structure of orthorhombic Mn_2TiGe

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Heusler alloys attract much attention due to their potential application in spintronic, magneto-optical and magnetocaloric devices [1-3]. In this work, we theoretically studied disorder effects in the electronic structure and magnetic properties of full Heusler Mn_2TiGe alloy, crystallized in the orthorhombic *Ima2* structure within density functional theory (DFT). We calculated that Mn_2TiGe without defects exhibits metallic properties with a total magnetic value of 4.6 μ_B/f.u. and with partial magnetic moments of 3.2 μ_B/Mn, 1.3 μ_B/Ti and 0.1 μ_B/Ge. This value is higher than the value of 1.99 μ_B/f.u., reported recently from theoretical calculations for the $L2_1$ phase of Mn_2TiGe [4]. In our additional calculations for Mn2TiGe with the antisite defects Mn-Ge, the total magnetic moment was decreased to 1.3 μ_B/f.u. with 0.9 μ_B/Ti and a negligible Ge moment. An almost identically low value of the total moment 1.1 μ_B/f.u. was found in Mn_2TiGe with the antisite defects Mn-Ti; in this case, the partial moments gradually decreased. The largest effect on the magnetic moment is exhibited by the antisite change between Ti and Ge, because it provides further suppression of the Mn and Ti moments, causing the total magnetic moment to be equal to 0.6 μ_B/f.u. Also, in all cases, the Mn electronic states shift to lower energies, forming two peaks of states in the valence band in the electronic structure. Thus, we demonstrated that the investigated antisite disorder types result in a significant (by several times) reduction in the magnetic moment of the novel orthorhombic Mn_2TiGe alloy. This research was supported by the Russian Science Foundation, grant number RSF 22-42-02021.

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sciforum-093360: Effect of extract concentration and temperature on microstructural properties of biological ZnO nanoparticles

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Due to their diverse properties, zinc oxide nanoparticles (ZnONPs) have shown great potential in various applications. These nanoparticles exhibit unique characteristics, including antimicrobial, anti-inflammatory, wound healing, catalytic, magnetic, optical, and electronic properties, making them useful in various fields. The size and crystalline structure of the material are crucial factors affecting these properties. In recent years, using plant extracts to synthesize nanoparticles has emerged as a technique that allows for the control of the size, shape, and properties of these materials. The main objective of this work is to study the influence of extract concentration and temperature on the synthesis of ZnONPs using Flourensia cernua extract. Zinc nitrate hexahydrate was used as a precursor, and we tried different extract–solvent ratios, such as 0.5:10 and 1:10 w/v. The ZnNPs were synthesized at varying temperatures ranging from 300 to 500 °C. ZnONPs were characterized using X-ray diffraction (XRD), transmission electron microscopy (TEM), and Fourier transform infrared spectrometry (FTIR). The XRD patterns showed a wurtzite hexagonal phase of ZnO. According to TEM characterization, crystalline particles with a semi-spherical morphology were obtained in a size range between 10 and 22 nm. Interestingly, increasing the amount of extract led to a decrease in the particle size. On the other hand, an increase in the calcination temperature caused the growth of the nanoparticles. This method showed that extract concentration and temperature greatly influence the size of the ZnONPs. The application of these particles in the photodegradation of organic dyes is being studied. Using plant extracts as a green synthesis method for ZnONPs can provide a sustainable and eco-friendly approach to developing customized nanoparticles for various applications.

sciforum-093657: Effective luminescence efficiency and spectral matching of a cerium fluoride crystal scintillator with various optical sensors

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Introduction. The aim of this study was to examine the effective luminescence efficiency (ELE) and the spectral matching of a 10×10×10 mm^3 cerium fluoride (CeF_3) single-crystal scintillator with various optical sensors. Numerous investigations have shown that CeF_3 crystals have a non-proportional response to gamma rays, and they have already been successfully used in high-rate calorimetry, including the Large Hadron Collider's high-luminosity phase experiments. However, the scintillation response of CeF_3 has not been systematically examined in the energy range covering medical imaging applications.

Methods. Measurements were performed with a CPI Inc. CMP 200 DR X-ray generator and the X-ray tube IAE SpA model RTM90HS in the range of 60–150 kVp and 63 mAs. Twenty mm of Al was added in addition to the inner filter of the X-ray tube to simulate attenuation from a human chest. The effective luminescence efficiency (ELE) and the spectral matching (SMF) of the scintillator wwere examined with various optical sensors.

Results. The effective luminescence efficiency increases continuously in the examined energy range (60-150 kVp), with the maximum value (0.812 efficiency units (EU) is the S.I. equivalent $\mu Wm^{-2}/(mGy/s)$) at 150 kVp. With an emission maximum at 314 nm, the optimum effective efficiency was found for a multialkali photocathode (0.81 EU) and the flat-panel position-sensitive photomultiplier (PS-PMT) H8500D-03 (0.808). The corresponding spectral matching (SMF) values were equal to 0.97 for both the multialkali photocathode and the PS-PMT H8500D-03.

Conclusion. Within the examined energy range, the resulting values are considered low compared to those for typical materials used as X-ray radiation-t-light converters; thus, CeF3 could not be used in radiological applications covering this energy range. It is possibly worth studying CeF_3 crystals at higher energies considering that the luminescence efficiency did not reach the maximum value at 150 kVp (the maximum energy of the medical X-ray tube).

sciforum-095011: Formation of a semiconductor state in oxysulfostibnite $RSbS_2O$ with R = Gd, Dy, Ho, and Er

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The features of the semiconducting state formation in oxysulfostibnites of the rare earth metals $GdSbS_2O$, $DySbS_2O$, $HoSbS_2O$, and $ErSbS_2O$ have been investigated. Our theoretical calculations were performed in the framework of the GGA+U method accounting for strong electron correlations in the 4f shell of rare earth metals and they showed that these compounds, $GdSbS_2O$ [1], $DySbS_2O$, $HoSbS_2O$, and $ErSbS_2O$ [2], are semiconductors with a small direct gap at high-symmetry point X. For the first time, it was found that for the band gap formation in the rare-earth-metal oxysulfostibnites, it is important both to optimize the crystal structure and to take into account the spin--orbit coupling. The rare-earth-metal oxysulfostibnites, along with their layered structural analogues oxysulfides, due to their distinctive properties, can be widely used in biomedicine, photoluminescence, and other fields. Our calculations were performed on the Uran supercomputer at the Institute of Mathematics and Mechanics of the Ural Branch of the Russian Academy of Sciences. This research was carried out within the framework of the state assignment of the Ministry of Education and Science of Russia, theme “Electron”, No. 122021000039-4.

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sciforum-094273: Generative Modelling and Novelty Detection in the Search for Functional Characteristic Interceptions in the Physicochemical Space

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Identifying the physics and chemistry of processes that determine material properties is the acknowledged aim of multidisciplinary science. The collective atomic vibrations are the phenomena in common for many diverse functional characteristics of materials. In this study, generative modelling and novelty detection are involved in the analysis of functional characteristics, which are rare in most of the known classes of materials and, in some cases, are revealed simultaneously.

In this study, we demonstrate the capabilities of novelty detection and generative modelling approaches for the investigation of microwave dielectric ceramic materials with close-to-zero thermal expansion characteristics. The known examples of compounds with these characteristic interceptions are considered as the desired targets of this search comprising two basic steps: (i) novelty detection methods aimed to reveal the compounds with this desired functionality and (ii) generative modelling, which is intended to suggest candidates with the same properties. This search was extended to the different structural types of ceramic oxide materials with the parallel consideration of microwave dielectric characteristics as the main functional property and close-to-zero thermal expansion as the target one. The descriptors responsible for both properties are analysed. The impact of the synthesis of the functional characteristics is discussed.

sciforum-093965: Green Synthesis of Zinc Oxide Nanoparticles Using Itsit (*Trianthema portulacastrum*) Extract and Their Catalytic Activity

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Green synthesis of nanoparticles is more promising versus chemical and physical methods as it is environmentally friendly, cost-effective, and non-toxic. Considering environmental sustainability, this study was designed to explore Itsit (*Trianthema portulacastrum*) efficacy for green synthesis of nanoparticles. The main objective of this study was to investigate the potential of zinc oxide (ZnO) nanoparticles developed from Itsit extract, through green methods for the treatment of textile dyes. This investigation reports that using the plant extract of Itsit, synthesis of nanoparticles of zinc oxide occurs in which zinc oxide is used as a precursor. In the green method, the plant extract that includes the biomolecules is used to reduce the zinc ions into zinc atoms like ZnO nanoparticles. Flavonoids, phenolic compounds, terpenoids, alkaloids, and flavone are all plant metabolites, the potential reducing agents used for ZnO nanoparticle preparation. The zinc oxide nanoparticles were prepared and characterized through UV--visible, FT-IR, and Zetasizer. The application of nanoparticles developed for their photocatalytic potential was investigated for the decolorization of a synthetic dye, phenol red. The ZnO nanoparticles prepared from Itsit showed 38% decolorization of phenol red, showing its promising catalytic potential under sunlight. Based on these findings, it can be concluded that Itsit demonstrated promising photocatalytic potential for the remediation of textile dye and could be employed for the treatment of textile wastewater.

sciforum-093888: Influence of the seed-layer material on the direct growth of zinc-tin oxide (ZTO) nanostructures

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Recently, metal oxide nanostructures have seen significant advancements in synthesis and device integration. Considering the sustainability of materials and processes, as well as multifunctionality, zinc-tin oxide nanostructures are among the most promising oxide nanostructures being researched. Their ternary oxide nature allows for impressive multifunctionality, with applications including catalysis, electronics, sensors, and energy harvesting. To synthesize these materials, the use of seed layers can be beneficial since it can influence the growth of nanostructures and is advantageous for applications where nanostructures on film are desired, such as photocatalysis and sensors.

In this work, several seed layers (namely Cu, stainless steel, Cr, Ni, etc.) were tested for the synthesis of ZTO nanostructures. It was generally observed that the structures grown on the seed layers differed from those obtained with the seed-layer-free hydrothermal method (under similar synthesis conditions [1-3]), demonstrating the effectiveness of seed layers in influencing growth. Various types of structures were obtained, such as $ZnSnO_3$ nanowires and Zn_2SnO_4 nanoparticles, octahedrons, and nanowires. The results suggest a correlation between the phase of the employed seed layer and the resultant phase of the nanostructures. Furthermore, it was generally seen that while shorter times favored the production of nanostructures, longer times resulted in thin films with a nanostructured surface when employing the seed layers [4]. This emphasizes the influence of seed layers on nanostructure growth, not only by inducing the phase but also by accelerating the growth process.

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sciforum-094076: Interfacial Action of Co-Doped MoS_2 Nanosheets on the Directional Piezoelectric Catalytic Generation of Reactive Oxygen Species

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Molybdenum disulfide (MoS_2) with single- and odd-numbered layers is a novel piezocatalyst, and its piezocatalytic molecular oxygen activation, which produces reactive oxygen species (ROS), has been considered a promising and low-cost strategy for environmental remediation. However, its performance is still far from satisfactory, and the limited knowledge regarding its molecular oxygen activation process significantly impedes its further development. Herein, several numbered layers of Co-doped MoS_2 ultrathin nanosheets (UNs) with a thickness of 3.2 nm were successfully fabricated via hydrothermal synthesis. The single Co atom-doped odd-numbered layers of MoS_2 nanosheets strongly interacted with adsorbed oxygen molecules for a highly efficient generation of ROS in the piezocatalytic degradation process. The dopant-induced enhanced carrier density (electron density) of Co-doped MoS_2 was 7.7 × 10^{18} $cm^{-3,}$ compared with 2.9 × 10^{16} cm^{-3} for bare MoS_2. Moreover, the interfacial action of Co-doped MoS_2 nanosheets on directional molecular oxygen activation properties were predicted by DFT calculation and monitored by generated reactive oxygen species (ROS) evolution. Co-doped MoS_2 decomposed tetracycline (an antibiotic) by 99.8% in 15 min through shaking vibration in the dark. It was found that Co active sites can facilitate the one-electron reduction of molecular oxygen activation by introducing a Co^{2+}/Co^{3+} redox couple. In addition, a tentative mechanism was proposed to explain the origin of the piezocatalytic enhancement in Co-doped MoS_2. Thus, in order to meet the requirements in the field of wastewater pollutant remediation, the current research effort may provide guidelines for constructing 2D TMDCs piezoelectric catalysts and comprehending the mechanisms of the directional piezoelectric catalytic generation of reactive oxygen species through the doping route.

sciforum-096522: Investigation of the structural, microstructural, optical and electrical properties of iron-doped barium titanate ceramics

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The structural, microstructural, optical, and electrical properties of nanoceramic $BaTi_{1-x}Fe_xO_{3-\delta}$ synthesized by sol--gel have been investigated. The X-ray diffraction analysis demonstrates that samples have a single-phase tetragonal structure with P4mm symmetry. This result was confirmed by the Rietveld method. Infrared spectroscopic analysis (FTIR) shows the presence of two bands at 490 Cm^{-1} and 2358 Cm^{-1} corresponding to T-O and C=O, respectively. On the other hand, scanning electron microscopy (SEM) results show that nanoceramics sintered at 1250°C have a spherical grain morphology. Grain size is small at X=0.02 and increases progressively thereafter. The UV--vis absorption spectrum confirms the influence of Fe concentration on the direct optical band gap of $BaTi_{1-x}Fe_xO_{3-\delta}$ ceramics. The optical band gap shifts from 2.63 eV to 2.35 eV. Making this material a good candidate for solar photo-catalytic. There is an increase in Urbach energy as the Fe concentration increases from 0 to 0.4. On the other hand, the AC conductivity of the materials is subject to Joncher's law. The effect of Fe substitution concerns the decrease in conductivity at x=0.02 and then increases. The Cole--Cole complex impedance diagram was studied for the prepared samples. The compounds showed non-Debye-type dielectric relaxation, with a poor grain radius as Fe-doping increased.

sciforum-092883: Low-cost ceramic membrane from marble waste: Characterization and optimization using experimental design.

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In the field of wastewater treatment, ceramic membranes have emerged as a promising technology due to their high filtration efficiency and durability. Unlike traditional polymer membranes, ceramic membranes are made from inorganic materials such as alumina, silica or other ceramic materials. They can withstand extreme operating conditions, such as high temperatures.and can be produced through compaction processes, sol-gel methods, extrusion, and hydrothermal synthesis techniques. Among these, compaction is the most frequently used method for fabricating.

Clay minerals are major raw materials for ceramic production that undergo a number of characteristic reactions, Clay is more durable and requires lower firing temperatures, as highlighted by several studies on the development of low-cost porous ceramics based primarily on clay as the main raw material.

To produce a membrane with high porosity and acceptable mechanical strength with the minimum of experimentation, we opted for optimized the preparation conditions by adjusting the sintering temperature, time and as well as the rate of marble waste addition.In this study, the Response Surface Methodology (RSM), based on the Doehl-type experimental design,In order to determine the optimal conditions of the preparation, the Doehlert design and Desirability function were applied.

Various analytical techniques, including X-ray diffraction (XRD), X-ray fluorescence (XRF), thermogravimetric analysis (TDA-TG), scanning electron microscopy (SEM), and Archimedes principal testing, were used to investigate the properties of these ceramic membranes.

sciforum-096515: New quaternary chalcogenides $Ag_{11}D^{IV}C^{III}_3S_{12}$

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Ternary and quaternary silver chalcogenides are promising semiconductor materials for practical use that possess various valuable physical properties such as optical, electric, ferroelectric, ionic conductivity. Antimony chalcogenides are of interest to the research for thermoelectric properties and optical absorption suitable for thin-film solar cells. Our investigation combined these two directions in the quasi-ternary systems Ag_2S–$C^{III}_2S_3$–$D^{IV}S_2$ (C^{III}–Sb, As; D^{IV}–Ge, Sn) where three new quaternary sulfide compounds were found, $Ag_{11}GeSb_3S_{12}$, $Ag_{11}SnSb_3S_{12}$, and $Ag_{11}SnAs_3S_{12}$.

Alloys of the systems were synthesized by co-melting the elements at up to 1220 K, slow cooling to 500 K, annealing for 500 hrs followed by quenching. $Ag_{11}GeSb_3S_{12}$ forms at the intersection of $AgSbS_2$–Ag_8GeS_6 and Ag_3SbS_3–Ag_2GeS_3; $Ag_{11}SnSb_3S_{12}$ forms at the intersection of $AgSbS_2$–Ag_8SnS_6 and Ag_3SbS_3–Ag_2SnS_3; and $Ag_{11}SnAs_3S_{12}$ forms at the intersection of $AgAsS_2$–Ag_8SnS_6 and Ag_3AsS_3–Ag_2SnS_3. In all cases, the component ratio is 3:1. X-ray phase analysis and microstructure studies show that each compound has a modest homogeneity region of up to 5 mol.%.

The crystal structure of $Ag_{11}GeSb_3S_{12}$ was investigated by X-ray structural analysis. The diffraction dataset was recorded at a DROM 4-13 powder diffractometer, CuKα radiation, angle range $10° \le 2\theta \le 100°$, scan step 0.02°, 10 s exposure in each point. The diffraction pattern of $Ag_{11}GeSb_3S_{12}$ was indexed in the cubic symmetry, space group *I3m*, lattice parameter a=0.54127(2) nm. Sulfur atoms form three-layer closest packing, the statistical mixture of Ag and Ge atoms occupies one half of the octahedral voids, and Sb atoms occupy one quarter of the tetrahedral voids.

Further investigation of the crystal structure of two other compounds as well as the study of optical absorption and electrophysical properties to quantify the prospects of these compounds as materials is pending.

sciforum-090811: Nickel phosphate crystal material: Synthesis and characterization

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Phosphate materials have a wide range of applications such as fluorescent materials where fluorescent lanthanide orthophosphate was used and showed fluorescent properties during its internalization into human umbilical vein endothelial cells. In addition, they have been considered as ceramic materials with high magnetic and electrochemical properties [1].

Since the utilization of calcium phosphate nanoparticles in biological, therapeutic, and bio-medicinal fields, such as the treatment of cancers, carries inhibitions, researchers resort to the use of other metals and the modification of phosphate materials, for example, cobalt phosphate nanoparticles, modified by Nickel, and Zirconium phosphate nanoparticles, which are used as electro-catalysts for water treatment, dye removal and the treatment of cancers [2]. Several methods are used to synthesize phosphate materials, such as precipitation, co-precipitation, impregnation, deposition, and hydrothermal rout. This last method can lead to different shapes and structures, which can affect their activity and crystallite nature.

In this study, we prepared Nickel phosphate material (NiP) using hydrothermal rout. During preparation, several conditions were used, modifying the urea amount and acid volume. So, different structures were achieved. The material was characterized using SEM, EDX, UV–Vis, and XRD. The material was used as a catalyst for the synthesis of several heterocyclic structures. The catalyst was reused with high activity and stability.

[1] M. Moustafa, M. Sanad and M. Hassaan, Journal of Alloys and Compounds, 845 (2020) 156338.
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sciforum-096282: Preliminary structural characterization of ceria–titania polymorphic mixtures achieved by high-energy ball milling

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High-energy ball milling is a simple and eco-friendly technique that has gained increasing popularity in recent years. This one-pot method of synthesis allows for the preparation of solid materials from a green perspective, avoiding multiple and complex steps, the use of solvents and the extreme pressure and temperature conditions commonly employed. Due to its multiple advantages, high-energy ball milling can make structural and surface modifications within the solid matrix according to the physicochemical properties needed, such as defect accumulation, polymorphic transformations, grain boundaries, amorphization, particle refinement and increases in specific surface area and ion mobility. In this regard, ceria–titania mixtures were obtained using several high-energy ball milling conditions (varying the metal oxide concentration, ball-to-powder ratio, time and rotational speed). The crystal structures created by the milling process were studied by means of X-ray Powder Diffraction (XRPD), including cerianite, anatase, rutile and high-pressure TiO_2 (II) formation. Moreover, the crystallite sizes and the specific surface area (S_{BET}) values were estimated using the Scherrer equation and N_2 physisorption (BET method), respectively. According to this preliminary study, the materials generated through this sustainable, cost-effective and easy-to-scale technique could be useful as catalyst supports for different metal nanoparticles or could act as catalysts in a variety of applications, e.g., oxidation and photocatalytic reactions in both the liquid and gas phases.

sciforum-096606: Sodium polymolybdates grown by low-thermal-gradient Czochralski technique for scintillating applications

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Presented work is dedicated to the search of new perspective scintillating materials for rare events physics, particularly neutrinoless double beta-decay projects. Such implementations imposes strict requirements on scintillator quality and radioactive background. Most bivalent cations have radioactive isotopes, thus, light alkali cations are better fitted for this purpose. Moreover, due to their small ionic radii Li and Na are less substituted by U and Th.

Another issue with obtaining crystals for scintillation purposes is the minimal working size of the element – 40*40 mm^3 while maintaining uniformity in entire bulk volume. We propose the low-thermal-gradient Czochralski technique (LTG Cz) developed at NIIC SB RAS as a unique technology for obtaining bulk oxide crystals of high optical quality. Temperature gradients in LTG Cz compared to the conventional Czochralski technique are two orders of magnitude lower, less than 1 deg/cm.

In literature several versions of Na_2O-MoO_3 phase diagrams are presented, stating stable compounds Na_2MoO_4, $Na_2Mo_2O_7$, Na2Mo4O13 (impossible for obtaining because of polymorphic phase transition) and in different works $Na_4Mo_9O_{29}$, $Na_6Mo_{10}O_{33}$, $Na_6Mo_{11}O_{36}$. Space group of the compound $Na_6Mo_{11}O_{36}$ was determined on powder samples as triclinic. In presented work, $Na_xMo_yO_z$ crystals were grown by LTG Cz technique. Space group of $Na_6Mo_{11}O_{36}$ crystal sample was determined as monoclinic.

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sciforum-096919: Study of synthesized molecular chiral lactam structures for volatile compound profile enrichment using gas chromatography–mass spectrometry (GC-MS) technique

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In a study of the chiral enantiomer structure of cyclic trilactams possessing C3 symmetry, the dimer structure was established through the formation of three NH···O type complementary H-bonds at three amides which were applied as agents for volatile compound profile extraction in a sample via the liquid phase extraction technique.

The extraction efficiency of cyclic trilactam materials for analytes found in perfume samples was assessed using HS-SPME-GC-MS. The experimental arrangement of perfume solution was combined with the materials in EtOH solvent in an open vial, while the perfume in EtOH (without the materials) served as the control. Following overnight evaporation at room temperature, the remaining liquid was collected for HS-SPME-GC-MS analysis. Extraction took place overnight to explore the materials' extraction efficiency and facilitate re-crystallization. The materials underwent re-crystallization, with the collected crystals revealing a similar shape to the observed dimers. This suggests a robust hydrogen bonding interaction within the dimer and the volatile compounds interacting. A list of identified compounds during extraction was compiled for each material and the control. The enrichment peak areas in the chromatogram results were determined as the analyte peak area in the sample containing the materials to the area of the same analyte in the control. This indicated the extraction performance of volatile analytes in the sample containing the materials compared with the control sample, such as Linalylformate $(5.1\pm0.015)\times10^7$, Citronellol $(5.1\pm4.2)\times10^6$, Carvone $(4.2\pm3.5)\times10^5$, Linalylacetate $(2.5\pm2.2)\times10^7$ and α-Terpinylacetate $(2.3\pm1.7)\times10^5$ of the main potential compounds. Higher enrichment signifies stronger interactions between the analytes and these materials.

The solubility between the compounds in less polar solvents can be attributed to their structural features and the nature of the solvent. Specifically, the solubility of each compound is influenced by factors such as polarity, hydrogen bonding capability, and the molecular size and shape of the compounds can influence their interactions with the solvent molecules, further impacting solubility differences between compounds in less polar solvents.

sciforum-093393: Study of the percolation effect in the luminescent structure of ZnS:Cu,Br phosphors on improving their radioluminescence

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Solid-phase synthesis of ZnS-based luminescent material enclosing the associative luminescence centres formed by the dopant atoms of copper and bromine Cu'Zn-BrS● is discussed. Annealing the powder mix of ZnS, CuCl, and NH4Br in reducing atmosphere provides the diffusion and volume distribution of Cu+ and Br- ions in the two-phase ZnS matrix.

It was stated experimentally in five series of the synthesized phosphors that ZnS:Cu,Br forms the combined sphalerite--wurtzite crystal structure and the intensity of radioluminescence given by the Cu'Zn-BrS● associates sharply increases at a certain content of the wurtzite phase in ZnS structure 1.

A description of this phenomenon can be provided by the percolation theory instruments. The formation of the long interphase boundary between sphalerite and wurtzite phases in the phosphor grain of ZnS matrix as a percolation infinite cluster analogue results in the grain boundary diffusion rate increasing and an improvement in the luminescence centres' forming ability on the intercrystalline borders. Associated defects migrating through the volume of the crystal to its surface provide the surface luminescence centres and improve tritium radioluminescence.

Computer modelling of the diffusion process in the discussed system was conducted and a descriptive model of structure defect migration through the two-phase phosphor structure was developed. The application of this approach in solid-state physical chemistry provides an additional tool for controlling the structure and properties of functional materials.

sciforum-096414: Synthesis and characterization of Metal-Organic Framework based on N,N'-dioxide for selective adsorption of iodine anions

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Introduction

This study presents the synthesis and characterization of a new metal-organic framework (MOF) incorporating cobalt(II) and 1,4-diazabicyclo[2.2.2]octane N,N′-dioxide (odabco), namely $[Co_2(H_2O)(NO_3)(odabco)_5](NO_3)_3$. The anion-substitution reaction in the framework has been studied, and the adsorption selectivity and reversibility of iodide ions by compound have been investigated.

Methods

Synthesis: A mixture of $Co(NO_3)_2{\cdot}6H_2O$ (0.10 mmol) and odabco$\cdot 3H_2O_2$ (0.30 mmol) was prepared in a glass vial. The mixture was dispersed in a solution of DMF (5.0 ml), water (0.4 ml) and nitric acid (25 µl, 62%). The mixture was kept at 70°C for 72 hours. The crystal structure of the compound was confirmed using powder X-ray diffraction (PXRD) analysis. The chemical purity of the sample was verified using CHN-analysis, infrared (IR) spectroscopy, and thermogravimetric analysis (TGA).

Ion exchange was studied using capillary zone electrophoresis (CZE). Iodide positions were within the porous adsorbent were determined by single crystal XRD. The structural integrity of the samples was verified using XRD and other methods.

Results

The cationic coordination network was found to exhibit a high affinity for iodide, the degree of substitution of guest nitrates by iodides was 75%. Iodide positions were directly determined by single crystal XRD method within anion-exchanged adduct $[Co_2(H_2O)(NO_3)(odabco)_5]I_2(NO_3){\cdot}1.85H_2O$. Adsorption of iodide is selective and reversible. Iodide anions occupying specific positions within the network, stabilized by the aliphatic core of the odabco ligands. Incorporation of iodide into the pore structure stabilizes it and has the potential to effectively remove iodide from solutions.

Conclusions

This study emphasizes the significance of MOFs for addressing challenges related to selective ion sorption and has potential applications in environmental management and health protection. Further research into similar systems and modifications may lead to the development of improved adsorbent materials for removing ions from solutions.

sciforum-092846: The influence of an ultra-small amount of heterovalent Y^{3+} activator ions in aqueous solution on the defect formation of different growth sectors of α-$Ni^{2+}SO_4·6H_2O$ crystals

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Materials based on α-$NiSO_4·6H_2O$ (NSH) (sp. gr. $P4_12_12$, Z = 4) are used for lithium-ion batteries and UV filters for the solar-blind range. Their performance characteristics can be varied by introducing activator ions M. The behaviour of M in NSH depends on differences in crystallochemical characteristics of M^{n+} and Ni^{2+} ions, the way of introducing M ions into the solution, and the growth sectors of the crystals. The goal of this work is to establish the distribution of Y^{3+} ions over the growth sectors of NSH:Y crystals when they are introduced into a solution in extremely small quantities (c = 10 mM).

Two crystals were grown on NSH (001) plates: NSH:Y-1—perpendicular to 001> (32 g; growth duration 144 h); NSH:Y-2—parallel to 001> (269 g; growth duration 336 h). The habit (*mmm*) was found for NSH:Y-1, faceted by {001}, {101}, {011}, {012}, and {110} with face areas ($S_{face(hkl)}$) {101}>{011}>{012}>{001}>{110}. In the habit (*mm2*) of NSH:Y-2 crystals, new faces ((102), $(1\bar{1}2)$, and $(1\bar{1}\bar{1})$) with $S_{face(hkl)}$ (101)>(012)>(102)>(011)>(001)>$(1\bar{1}2)$>$(1\bar{1}\bar{1})$>(110) also appeared. The NSH:Y-2 crystal, by its $(00\bar{1})$ face, was at the bottom of the crystallizer during growth (uneven supply of the solution).

The c, Å tetragonal crystal parameter (X-ray diffraction of powdered crystals) decreased with the decrease in Y^{3+} content ($c_м$, ppm—mass spectrometry), c{101}>c{102}>c{001}, consistent with crystal morphology. Defect formation can be described by the quasi-chemical reaction $0 \rightarrow V_{Ni}^{n'}+Y_i^{m\cdot}$ and the composition $(Ni^{2+}_{1-x}[])(Y^{3+}_{i(x)})SO_4]$. In the {101}–{102}–{001} series, a decrease in Y^{3+} content is accompanied by a decrease in the Y^{3+} interstitials ($Y_i^{m\cdot}$) and vacancies in the Ni^{2+} site ($V_{Ni}^{n'}$).

The compositions of the NSH:Y growth sectors, on which the functional properties depend, are important for the application of the material in the form of plates.

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sciforum-096261: The influence of the counterion in the behavior of a *trans*-diacetate dysprosium complex with a semirigid macrocycle

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Introduction. After studying the magnetic properties of $[Dy(L)(OAc)_2]NO_3{\cdot}2H_2O$ (L = 2*E*,6*E*,9*E*,13*E*-3,6,10,13-tetraaza-1,8(2,6)-dipyridinacyclotetradecaphane-2,6,9,13-tetraene), its single-molecule magnet behavior under an optimal field of 2000 Oe was revealed. Furthermore, luminescence measurements indicated that the ratio between the integrated intensity of the macrocyclic Schiff base and that of the Dy^{3+} $^4F_{9/2} \rightarrow {}^6H_{13/2}$ transition can define a secondary luminescent thermometer, with a maximum relative thermal sensitivity value of 2.3% K^{-1}. In view of these interesting properties, we changed the counterion from nitrate to tetraphenylborate to see its influence.

Synthesis and methods. Here, we present the result of the synthesis and characterization of the dysprosium complex $[DyL(OAc)_2]BPh_4$. It was obtained by a template synthesis of 2,6-pyridinedicarboxaldehyde, dysprosium acetate tetrahydrate and ethylenediamine, and a subsequent reaction with sodium tetraphenylborate. Single crystals of the compound were obtained via the recrystallization of the solid in dichloromethane with an Et_2O layer in the fridge. Then, it was characterized by elemental analysis, IR spectroscopy and single X-ray diffraction techniques.

Results. Two slightly different moieties of $[DyL(OAc)_2]^+$ are present in the unit cell, alongside tetraphenylborate anions, but no other species are present. Thus, the crystal packing lacks classic H bonds, whereas many C-H···O and C-H···π interactions are present in the crystal packing scheme. This cationic complex shows a decacoordinate metal center, almost forming a distorted tetradecahedron. The characterization of this Dy^{III} complex allows us to compare its properties with those of other closely related species.

Conclusion. The presence of such a hydrophobic counterion strongly influences the crystal packing of this species, but is does not have such an intense impact on other features, mostly related to the $[DyL(OAc)_2]^+$ cation.

sciforum-096232: The influence of the substitution in cation and anion sublattice on the HT-Pb_2GeS_4 structure

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The HT- Pb_2GeS_4 (SG *I*-43*d*) is a prospective material for investigation. The structure of HT-Pb_2GeS_4 crystallizes in cubic symmetry. The positions 24*d*, 16*c*, and 48*e* can be modified through the substitution of atoms Pb and S. We investigated the crystalline structure of four compositions, $Pb_{1.9}Sn_{0.1}GeS_{3.52}Se_{0.48}$, $Pb_{1.86}Sn_{0.14}GeS_{3.32}Se_{0.68}$, $Pb_{1.82}Sn_{0.18}GeS_{3.16}Se_{0.84}$, and $Pb_{1.58}Sn_{0.42}GeS_{3.64}Se_{0.36}$, changing the cation and anion sublattice simultaneously.

Samples with the nominal compositions of $Pb_{2-x}Sn_xGeS_{4-y}Se_y$ (x = 0.1, 0.14, 0.18, and 0.42; y = 0.36, 0.48, 0.68, and 0.84) were prepared by melting high-purity Pb (shot, 99.99 %), Sn (shot, 99.99 %), Ge (shot, 99.999 %), S (shot, 99.99 %), and Se (shot, 99.99 %) in quartz containers evacuated to a residual pressure of 10^{-2} Pa. The total mass of every sample was 1 g. The ampules with the stoichiometric mixtures of elements were heated up to 1423 K at a rate of 12 K/h; kept at this temperature for 4 h; cooled down to 773 K at a rate of 12 K/h; annealed at this temperature for 500 h; and quenched in cold water without breaking the containers.

The substitution in cation and anion sublattice on the Pb_2GeS_4 crystal structure leads to the increase in the volume of the lattice from 2794.9 Å to 2852.2 Å due to the change of *y*. The lattice parameter *a* changes from 14.086 Å to 14.1816 Å. A distortion of the cation sublattice is also observed.

Hence, such peculiarities of the crystal structure may improve some thermoelectric and optical properties.

sciforum-094168: The peculiarities of the crystal structure of the monoclinic modification of aragonite

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The crystallization and precipitation of calcium carbonate minerals is the subject of intensive research due to the existence of its polymorphic and morphological varieties in geological and biological systems, as well as due to its application both in industrial fields, in particular, in the production of plastics, rubbers, and paper production, and for the creation of biomedical implants and drug delivery systems.

The existence of a new polymorphic modification of calcium carbonate, monoclinic aragonite $CaCO_3$, has been experimentally discovered [1]. Its crystal structure has been solved and its crystal structure has been discussed. It was found that, unlike the previously known modification, orthorhombic aragonite with cell parameters a = 4.961 Å, b = 7.967 Å, and c = 5.740 Å, the new polymorph belongs to monoclinic symmetry, crystallizes in the space group $P2_1/c$, and has cell parameters a = 12.732 Å, b = 5.740 Å, c = 9.378 Å, and b =96.91°.

The crystal cell of the new polymorph is formed by three Ca^{2+} cations and three carbonate anions occupying general positions. In the structure, carbonate anions form stacks along the b axis, in which they are arranged in a mutually overlapping manner. The stacks are surrounded by Ca^{2+} cations coordinated by nine oxygen ions. The new monoclinic polymorph has pseudohexagonal symmetry, and this effect is observed only along the b direction of the cell and is absent in the direction of other axes. As in the case of vaterite, the existence of a supercell can be assumed in the structure of the new aragonite, resulting in the high R-factor.

A three-dimensional set of diffraction reflections was obtained for a single crystal at room temperature using a Rigaku OD XtaLAB Synergy-S single-crystal diffractometer on MoK_α radiation (λ = 0.71073 Å). The experimental data were processed using the CrysAlisPro v. 1.171.39.46 software package. The crystal structure was determined based on direct methods using the SHELX [2] software package.

sciforum-096581: Use of boron-doped nanocrystalline diamond microelectrodes for amperometric determination of serotonin release in human platelets

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Introduction

Boron-doped nanocrystalline diamond (BDD) is an outstanding structure, and one of the best materials for high-sensitivity amperometric measurements. Nanocrystalline diamond structures show a high concentration of electrical charge carriers.

Amperometry is a widely used technique for studying the exocytosis of biological amines (dopamine, serotonin, noradrenaline, adrenaline, and histamine), and multielectrode array (MEA) systems have increased the efficiency and speed of amperometric studies.

In human, platelets are the most accessible cells to study the exocytosis of serotonin.

Methods

BDD-MEA fabrication utilizes several processes typical of microelectronics, here including chemical vapor deposition (CVD), optical lithography, metal evaporation, and reactive ion etching (RIE).

We detected amperometric recordings from the quantum release of serotonin from human platelets with boron-doped nanocrystalline diamond on MEA systems (BDD-MEA) of 16 microelectrodes. Our studies were carried out with devices on silicone matrices (BDD-on-silicon MEA)[1] and quartz substrates (BDD-on-quartz MEA)[2].

Results

Typical amperometric signals were obtained from the release and subsequent oxidation of serotonin molecules stored in platelet vesicles. We carried out and compared the release measurements both under basal conditions and after loading the platelets with 10 μM serotonin for 2 h. In this communication, we show different types of peaks registered in these studies and we present kinetics parameters obtained with both types of MEA systems (maximum oxidation current, spike width at half maximum, spike net charge, and ascending slope of spike).[1,2]

Conclusions

BDD MEA devices have proven to be effective and biologically compatible in amperometric studies with live platelets. Here, we demonstrate their usefulness in studies of serotonin exocytosis from human platelets.

[1] González Brito, R; Montenegro, P; Méndez, A; Carabelli, V; Tomagra, G; Shabgahi, R.E.; Pasquarelli, A.; Borges, R. *Biosensors***2023**, *13*, 86.
[2] González Brito, R; Montenegro, P; Méndez, A; Shabgahi, R.E.; Pasquarelli, A.; Borges, R. *Biosensors***2024**, *14*, 75.

Session 4. Organic Crystalline Materials

sciforum-096593: Exploring the Impact of Edge and Surface Sites on Functionalized Graphene-based Membrane in H_2S Adsorption: A Computational Study

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In our modern world, environmental concerns have become paramount, with a particular focus on mitigating the release of harmful gases into the atmosphere. One such gas of significant concern is hydrogen sulfide (H_2S), known for its noxious odor and detrimental effects on both human health and the environment. This study delves into the crucial importance of removing H_2S from effluent gases before their release into the environment. We bridge existing knowledge gaps by investigating the adsorption of hydrogen sulfide on graphene sheets, utilizing advanced computational tools. Through detailed simulations, we explore various adsorption sites on the graphene surface, including top (T), bridge (B), and hollow (H) sites, to determine the most effective removal mechanisms. Most importantly, we carefully explore the impact of the adsorption sites present at the edge and center regions of the graphene surface. Our study reveals that there are significant differences in the adsorption strength of hydrogen sulfide across the sites present at the edge and surface regions of the graphene sheets, confirming that edge sites are more effective for hydrogen sulfide adsorption. The findings derived from our study not only contribute to a deeper understanding of hydrogen sulfide adsorption but also highlight the promising role of carboxylate-function-decorated graphene (via its edge and surface sites and functional group assessment) in environmentally friendly gas removal technologies.

sciforum-096183: New Quantitative Visible (VIS) Spectrophotometric Analysis of pure Oxacillin in a Pharmaceutical: A Statistical Study of Linear Regression

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Oxacillin is a penicillinase-resistant, narrow-spectrum beta-lactam crystalline antibiotic of the penicillin class, resistant to beta-lactamases. The main purpose of this paper was to develop and apply a new spectrophotometric method in the visible (VIS) field for the analysis of pure Oxacillin from various pharmaceutical samples. Oxacillin reacted completely with 1.10 Phenanthroline 0.2% alcoholic solution in the presence of an aqueous solution of ferric chloride ($FeCl_3$, 6%), which led to the quantitative formation of a intense bright yellow complex with a faint orange tint, after heating the solutions for 20 minutes at 70 °C constant temperature. The intense bright yellow colored synthetized complex was then spectrophotometrically determined at λ = 420 nm corresponding to its absorption maximum, in relation to double-distilled water as a blank. One solid pharmaceutical capsule officially contained 500 mg pure Oxacillin, as reference value. As a result of the experiment, 491.308 mg of pure Oxacillin/solid capsule was obtained. This amount corresponded to a percentage content of 98.262 % determined by pure sodium Oxacillin and calculated per solid capsule of pharmaceutical product. The obtained result was very close to the reference value which was 500 mg of pure Oxacillin. The relative percentage deviation (relative percentage procedural error) was only E = 1.738 % to the official value and it fit perfectly within the official normal limits of values indicated by the Romanian Pharmacopoeia, 10th Edition, and by the European Pharmacopoeia Rules (± 5 %). Statistical analysis revealed a very good linearity of the visible spectrophotometric method for pure standard analyzed solutions in a large concentration range, from 1,20 µg/mL to 36,00 µg/mL. The linear regression coefficient R^2 was 0,999504 and the correlation coefficient R was 0,999752; as $R^2 \geq 0.9990$ and $R > 0.9990$, they were found to be within the normal official range of values.

sciforum-093340: Structural and thermal properties of 3-substituted quinazoline Schiff base conjugates

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Quinazoline Schiff base conjugates have recently attracted considerable attention from the scientific community due to their potential application as anti-cancer drugs and promising multidentate ligands. Unfortunately, reports dealing with the structural characterization of these compounds are incomprehensibly scarce. To contribute and explore the supramolecular features of these perspective compounds, we have prepared and crystalized four quinazoline Schiff base conjugates (**SB1**= 3-{(*E*)-[(2,4-dihydroxyphenyl)methylidene]amino}-2-methylquinazolin-4(3*H*)-one, **SB4**= 3-{(*E*)-[(2-chlorophenyl)methylidene]amino}-2-methylquinazolin-4(3*H*)-one, **SB8**= 3-{(*E*)-[(2,3-dihydroxyphenyl)methylidene]amino}-2-methylquinazolin-4(3*H*)-one, and **SB21**= 3-[(*E*)-benzylideneamino]-2-methylquinazolin-4(3*H*)-one). Single crystals were obtained by recrystallization of the crude products from different solvents, and crystal structures were determined by a single crystal X-ray diffraction. The prepared compounds can be described as Schiff bases composed of 2-methyl-quinazoline-4-one moiety and differently substituted benzene moieties connected by the imine bond. Considering their molecular structure, these compounds are similar, with the most pronounced differences being in the dihedral angle between aromatic systems. In the crystal, compounds with OH groups on the benzene ring (**SB1** and **SB8**) are primarily connected by strong O-H···N hydrogen bonds, and unsubstituted (**SB21**) and Cl-substituted (**SB4**) compounds via N-H···O hydrogen bonds and $\pi\cdots\pi$ interactions. Thermal analysis results have shown that the highest melting point compound is 2,4-OH-substituted **SB1** (226 °C), followed by 2,3-OH-substituted **SB8** (201 °C), unsubstituted **SB21** (192 °C); the lowest melting was found with Cl-substituted **SB4** (159 °C). Additional Hirshfeld surface analysis and intermolecular energy calculations indicate that the electrostatic interactions (hydrogen bonds) have the largest impact on thermal stability, and that the dispersive interactions are important for stability but can be sterically hindered by bulky substituents on aromatic systems.

sciforum-094224: Arrays of Lander molecules stabilized by multiple interactions on surfaces

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Molecular assemblies driven by non-covalent interactions have sparked enormous interest in the last decade, due to their high versatility, flexibility, and recoverability. To figure out the interplay of the non-covalent interactions, such as hydrogen bonding (HB), electrostatic interaction, stacking, metal–organic coordination, van der Waals (vdW) forces, etc., intensive attention has been focused on the sophisticated systems composed of multiple components that are balanced by multiple non-covalent interactions.

Theoretical investigations have been carried out with an extended semiempirical atom superposition and electron delocalization (ASED+, Atom Superposition, and Electron Delocalization), based on the extended Hückel molecular orbital theory. Calculated STM images were obtained within the EHMO-ESQC method (Extended Hückel Molecular Orbital–Elastic-Scattering Quantum Chemistry), which describes the electronic scattering between the substrate and the tip by modeling the chemical structure of the tunnel gap (substrate, molecule, tip apex, and tip substrate).

Molecular Landers are a distinctive family of molecules, with bulky functional groups acting as the legs to lift up the aromatic molecular board. When the compounds are adsorbed on surfaces, only the legs are in contact with the surface, while the molecular board is decoupled from the substrate. To align these Landers into extended and well-ordered arrangements, different routes have been employed. In our previous work, we have demonstrated that one-dimensional (1D) and two-dimensional (2D) well-ordered assemblies of Landers can be observed not only between the same compounds, but also between hetero-Landers. However, all these interactions occurred when the molecular boards have an identical or comparable height, while the possibility of bonding between Landers and legless molecules remains unknown. Moreover, besides the two routes mentioned above, guest–host chemistry has been recognized as another fascinating way to align molecules on surfaces.

sciforum-093608: Biological activities investigations of new sulfanilamide derivative: single crystal X-ray diffraction analysis, in-silico ADME and molecular docking studies.

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Introduction–Sulfanilamide's were the first chemical drugs used as preventive and therapeutic agents against various infection diseases [1]. They generally act as structural analogues of *para*-aminobenzoic acid and therefore inhibit dihydropteroate synthase [2]. After the discovery of Penicillin [3], their use decreased significantly. Nevertheless, in recent years, their synergistic activity has gradually attracted the attention of researchers [4-5]. In this work, we report synthesis, crystal structure, ADME prediction, molecular docking, antibacterial and toxic activities of new sulfanilamide derived Schiff base (SB), i.e. 2-(2-hydroxyphenyl)quinoline-6-sulfonamide (HPQS).

Experimental - HPQS is synthesized through a two-step process, *viz*, reflux and solvothermal methods. In the first step, condensation reactions similar to those reported for similar SB were carried out [6]. The second step involved using a Teflon-lined autoclave [*7*]. GOLD software [8] was used to conduct docking investigations. ADME parameters and drug-likeness were estimated using SwissADME [9].

Results and Discussion - Single crystal X-ray diffraction indicates that the HPQS crystallize in $P2_1/c$ space group, with two molecules in the asymmetric unit (A and B). The crystal structure features N—H···O, C—H···O and C—H···π hydrogen bonds and π–π stacking interactions. Additionally, Drug-likeness and pharmacokinetics parameters revealed that the compound exhibited favorable ADME properties. Finally, molecular docking study was carried out to investigate the possible binding mode of the sulfanilamide derivative. Molecular docking studies and biological screening of HPQS explored its diverse potential application as antibiotic agent. It showed high negative binding scores due to the presence of different hydrogen bonding types. Therefore, docking studies revealed strong interactions and high binding potencies and affinities against the tested macromolecular receptors.

Conclusions - In this study, we have reported the synthesis and caracterisation of new SB derived from sulfanilamide (HPQS). Considering the findings of the study, it has been proven that this new compound constitutes a promising therapeutic agent capable of managing bacterial infections.

sciforum-096601: Crystal structure determination and Hirshfeld surface analysis of $C_{17}H_{11}N_3O$ azo compound

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Introduction

Azo compounds are one of the most frequently used compounds in organic chemistry, mainly because of their relatively simple preparation methods. They were, therefore, widely used, especially as dyes for textiles, printing inks, printing cosmetics, and food additives. In addition to their use as dyes, they have attracted much attention from chemists as their potential applications are important.

Methods

The X-ray diffraction of our structure established by Bruker APEXII diffractometer achieves not only the size of the mesh but also the nature of chemical bonds and form molecules. All this information is of fundamental importance for the study of material properties that depend either on their atomic structure or defects of this structure.

Results

The crystal structure shows a dimer that crystallizes in space group P-1 of triclinic system. There are two molecules (A and B) in the asymmetric unit. The crystal structure features three types of intermolecular N-H···O, C-H···O, and C-H···N hydrogen bonds. The C-H..A bind molecules in the crystal and form ribbons along [110]. These ribbons are linked via π-stacking interactions involving the benzene and naphthalene rings of inversion-related A and inversion-related B molecules, thus forming a three-dimensional structure.

The contributions to crystal stacking were studied using Hirshfeld surface analysis.

Conclusion

In this work, we have demonstrated not only the structure of (E)-1-[2-(2-Cyanophenyl)diazen-2-ium-1-yl]naphthalen-2-olate but also the Hirshfeld surface analysis; the azo dyes herein synthesized are good candidates for further study.

sciforum-094293: Improved Experimental Yield of Temperature-Cycle-Induced Deracemization (TCID) with Cooling and Crystal Washing: Application of TCID for the Industrial scale

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TCID is a method used for obtaining enantiopure solids from racemic mixtures in the crystalline phase, while fast racemization occurs in solution, with solubility affected by temperature swings. Although TCID theoretically doubles the yield compared to chiral separation methods due to the conversion of the counter enantiomer, the experimental yield remains unproven. One setback is the extraction of the dissolved solute while maintaining chiral purity. Furthermore, due to the slow induction time and the stochasticity of deracemization, an initial suspension with 20% c.e.e. (crystal enantiomeric excess) is commonly imposed to bias the deracemization, but this investment may be undesirable for industrial applications.

Herein, we applied TCID to (1-(4-chlorophenyl)-4,4-dimethyl-2-(1H-1,2,4-triazol-1-yl) pentan-3-one), employing a cooling step at the end of the process to overcome the issue of yield, and a washing step to further improve the c.e.e. This adjustment produced a mass yield of 92% with 99.9% c.e.e. within 24 hours on an 8.6 g scale. The final cooling step removes the majority of dissolved solute, enhancing the yield without significantly prolonging the process, and the washing step improves the enantiopurity.

Additionally, we investigate the stochasticity of deracemization during the initial stages, focusing on the development of c.e.e. from low initial values (1-5% c.e.e.) at a 2.5-gram scale. By assessing the kinetics, we determine that an initial c.e.e. of 2% for this system is adequate without significant risk of chiral flipping and to avoid the induction time. Our findings show the suitability of TCID to be performed on the industrial scale, with reduced initial c.e.e. to direct and overcome the induction time and a simple method to optimize the final yield and purity.

sciforum-094153: Investigating the crystallization process of medical bio-polymer Poly(3-hydroxybutyrate) using experimental methods and coarse-grained molecular dynamics simulations

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Poly(3-hydroxybutyrate) (PHB) is a storage compound synthesized by the bacteria *Azotobacter chroococcum*. This semi-crystalline polymer is both biodegradable and biocompatible, making it an ideal compound for tissue engineering materials. The key determining factor of the physical and mechanical properties of materials based on PHB is the distribution of amorphous and crystalline phases. Our research aims to further the understanding of how these phases arise and how they interact with each other. Five PHB samples with molecular masses ranging from 384 kdA to 1095 kdA were used for the current study. Raman spectroscopy and surface-free energy calculations were carried out. From our experiments, it was found that samples had similar surface-free energies. Three different boxes of molecular dynamics simulations representing three different hypotheses were set up: a box according to a classical theory of nucleation, a box with shear flow, and a box with heightened hydrophobic interactions. Our simulations show that a box according to the classical theory of nucleation shows the smallest amount of self-organization while the heightened hydrophobic interactions give rise to configurations that resemble reality the most. From our results, we can conclude that for semi-crystalline biological polymers such as PHB, hydrophobic interactions play a significant role in self-organization during the crystallization process.

sciforum-093808: Nucleation, nuclei stability, and crystal growth in supercooled organic melts of benzocaine and tolbutamide

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The investigation of crystallization kinetics in supercooled melts has spanned more than a hundred years and is relevant to many areas of science and technology. Conventional techniques, however, limit the range of systems where this study is possible due to relatively slow crystallizers. As such, the nucleation kinetics in supercooled melt was accessed only for a few organic compounds.

Fast scanning calorimetry (FSC) allows us to greatly increase the range of molecules that can be supercooled by providing a cooling rate of thousands of degrees per second and beyond. FSC was extensively used to study nucleation and crystallization kinetics in polymers, but rather few applications of the method to small organic molecules are reported. Using the FSC technique, we have studied the nucleation and crystallization of benzocaine, a rapidly crystallizing molecule, from supercooled melt. The nucleation of benzocaine was observed at –70 °C (supercooling of about 160 degrees), which is more than 50 degrees below the glass transition of the compound. The crystallization half-times greatly depend on temperature and cover nearly five orders of magnitude.

Nucleation and crystal growth in the supercooled melt were also studied in tolbutamide. Compared to benzocaine, tolbutamide has lower critical cooling and heating rates, permitting the application of the two-stage nuclei development method based on FSC. In tolbutamide, the isothermal nucleation and crystallization kinetics were studied. A modified two-stage nuclei development technique was used to probe the nuclei stability and obtain an estimate of the lateral growth rate of the nuclei, providing a unique insight into the properties of crystal nuclei. The interplay between the nucleation, crystallization, and polymorphism of tolbutamide was also accessed.

The results of the measurements are discussed in the framework of the Classical Nucleation Theory.

sciforum-096469: Organic menthol crystals: An overview of innovation based on relevant patents

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Organic menthol crystals, derived from mint essential oils, are natural, waxy, clear, or white crystalline substances that are solid at room temperature, melting slightly above. Menthol, a cyclic monoterpene alcohol, is synthesized from natural or synthetic precursors and has a significant demand globally, with various protocols available for its synthesis. It is commonly used in perfumery, cosmetics, and medicinal products for its cooling effect and minty scent. Menthol's safety profile and anticancer properties have been extensively studied, showing promising results in inhibiting different cancer cells through multiple pathways like apoptosis induction, cell cycle arrest, and the disruption of tubulin polymerization. Additionally, menthol's impact on respiratory health and digestive issues, and its potential to exacerbate allergic rhinitis have been explored, highlighting both its beneficial and potentially harmful effects on human health.

In this study, we provide an in-depth overview of innovation based on relevant patents related to menthol crystals and its derivatives and their applications. By analyzing these patents, we aim to present the current state of the art and identify emerging trends in the field of plant-derived menthol.

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sciforum-090883: Structural insights into the Polymorphic toxin–Immunity pair system of *Bacillus subtilis*

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Polymorphic toxins are weapons of bacterial warfare which are being used to restrict competitors, aid kin selection and shape bacterial communities. Polymorphic toxin systems (PTSs) are well studied in Gram-negative bacteria; however, there are limited studies in Gram-positive bacteria. In *Bacillus subtilis*, several members of toxin–immunity protein pairs including YeeF-YezG, YobL-Y, and obK YxiD-YxxD, have been reported. There are few studies describing structural/mechanistic details of these toxin–immunity pairs. This toxin requires a Type VII secretion system. We have shown that the C-terminal domain of YeeF (YeeF-CT) harbours the toxin with DNase activity. The expression of YeeF-CT causes growth defect and leads to morphological changes in *Escherichia coli,* while the co-expression of the toxin–immunity pair restores normal bacterial growth. Here, we report the crystal structure of $YeeF^{-CT}$ bound to its cognate antitoxin YezG at 2.1 Å resolution. The crystal structure reveals that the toxin (YeeF-CT) undergoes major conformational changes upon binding its cognate immunity protein (YezG). Comparative structural analysis reveals that six β-sheets of the toxin, required for nuclease activity, are ripped apart into two sub-domains upon binding the immunity protein. This mechanism is unlike other Type II toxin–antitoxin systems, where an intrinsically disordered region of the antitoxin binds at the active site of the toxin, hence sterically occluding the binding of its substrate. We are currently working on the structure-guided detailed characterization of this toxin–immunity protein pair.

sciforum-094274: Synthesis and crystal structure analysis of monochloroacetic acid 2,4-dinitrophenylhydrazide

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Our main goal was to form various compounds of the chloroacetylation product of p-methoxyphenol (4-methoxyphenyl 2-chloroacetate) with various amines using the Menshutkin reaction. This article presents a part of our research, namely, the reaction process with 2,4-dinitrophenyl hydrazine and its analysis. The process was carried out in different solvents. The expected product of the reaction was 2-(2,4-dinitrophenyl)-1-(2-(4-methoxyphenoxy)-2-oxoethyl)hydrazin-1-ium chloride. Due to regrouping, another product was formed. As a result of our research, 2,4-dinitrophenylhydrazide of monochloroacetic acid (2-chloro-N'-(2,4-dinitrophenyl)acetohydrazide) was formed. Crystal structure analysis was performed. This is of interest because of its potential applications in various fields, including pharmaceuticals and materials science. The synthesis of the compound was achieved by a direct synthetic route and confirmed by spectroscopic methods such as IR, NMR, and elemental analysis. Single-crystal X-ray diffraction analysis provided detailed structural information, revealing the molecular arrangement within the crystal lattice. Crystallographic data revealed a monoclinic crystal system with the space group P21/n, which revealed the molecular conformation, intermolecular interactions, and crystal packing motifs. This comprehensive structural characterization enhances our understanding of the compound's properties and provides valuable insights for further exploration of its potential applications. As a result, a compound with a confirmed crystal structure was entered into the reference of Structures The Cambridge Crystallographic Data Centre (CCDC).

sciforum-094270: Synthesis, crystal structure, and Hirshfeld surface analysis of isomeric ((1-(4-nitrophenyl)-1H-1,2,3-triazol-4(5)-yl)methoxy)benzaldehyde compounds

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Among nitrogen-containing heterocyclic compounds, triazoles have high pharmacological properties and are therefore of interest for structural and physico-chemical studies. Structurally, triazoles can be divided into two different subsets: 1,2,3-triazole and 1,2,4-triazole. Due to their structural characteristics, 1,2,3- and 1,2,4-triazoles can accommodate a wide range of substituents (electrophiles and nucleophiles) around their core structures, opening the way for the synthesis of various new bioactive substances [1]. Although it has been more than 120 years since the initial discovery of the method for the synthesis of 1,2,3-triazoles by cross-alkynes and azides, the interest in this chemical class of molecules has been increasing rapidly in the last 20 years. The reason for this is the introduction of catalytic methods for cyclization reactions, which made the generation of 1,2,3-triazole derivatives widely accessible for pharmacological applications. With the advancement of click chemistry, scientific work on these five-member heterocyclic compounds is growing rapidly [2]. Here, we report the synthesis and structural characterization of 2-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methoxy)benzaldehyde **(1)** and 3-((1-(4-nitrophenyl)-1H-1,2,3-triazol-4-yl)methoxy)benzaldehyde **(2)** using X-ray crystallography. The structures of compounds **1** and **2** were established by single-crystal X-ray diffraction, and the identified conformations were described in the context of their stabilizing intra- and inter-molecular interactions, particularly highlighting the significant hydrogen bonds of the crystals. For molecular crystals, Hirshfeld surface analyses can provide crucial insight into the intermolecular interactions. These analyses were performed to determine intermolecular interactions in **1** and **2**. According to our results, the molecules are associated by intra- and intermolecular hydrogen bonds, C—H···π, and N—O···π stacking interactions. The three-dimensional Hirshfeld surface analysis and two-dimensional fingerprint plots revealed that the structures are dominated by H···H, H···C/C···H and H···O/O···H contacts.

Session 5. Hybrid and Composite Crystalline Materials

sciforum-093761: The Intricate Magnetic Properties of Co-Mn Ferrite Nanoparticles Studied by Neutron Scattering

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Cobalt-substituted mixed spinel ferrites, used in various applications, have adjustable magnetic properties influenced by cation type and structural features. The theoretical framework for these materials assumes homogeneously magnetized, single-domain, non-interacting particles. However, recent studies reveal that nanoparticle systems are more complex, even with highly crystalline, monodisperse, non-interacting ensembles. Factors like spin disorder and dipolar interactions can significantly affect the material's magnetic properties. In this study, we delve into the evolution of magnetic and structural properties within a series of oleate-capped manganese-substituted cobalt ferrites (denoted as $Mn_xCo_{1-x}Fe_2O_4$) with varying Co/Mn molar ratios. The results can be interpreted solely based on their actual composition, independent of other parameters, thanks to the single-phase nanoparticles with similar crystallite and particle sizes (about 10 nm), size dispersity (14%), and weight percentage of capping oleate molecules (17%). The temperature and magnetic field dependences of the magnetization revealed magnetic anisotropy to be the key parameter affecting the magnetic parameters, including T_{max}, T_{diff}, T_b, H_c, H_K, and M_r/M_s, caused by different cobalt contents. Deviations from the ideal scenario of non-interacting NPs become evident in all samples when employing IRM-DCD protocols, showing negative ΔM peaks in Mn-rich samples (with a correlation between cobalt content and magnetic anisotropy), while positive ΔM is observed in the Co-enriched sample, possibly due to strong dipole–dipole interactions or surface spin phenomena. Small-Angle Polarized Neutron Scattering (SANSPOL) was then employed to study the quantitative distribution of magnetization within NPs, to reveal the presence of surface spin disorder, to access the surface anisotropy constant, and therefore to isolate the magnetocrystalline anisotropy and correlate it with the Mn content.

sciforum-083151: TiO_2 nanotubes decorated with Ag spheres for electrochemical sensing applications

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The detection of organic and inorganic compounds using electrochemical sensors has garnered attention due to their low-cost fabrication and excellent sensitivity. To enhance the sensitivity of the sensor using metal oxides as active materials, defect states such as oxygen vacancies have been studied. These defects operate as donor levels near the conduction band of the metal oxide. In this study, we present the synthesis TiO2 nanotubes decorated with Ag spheres, along with an investigation into their chemical, structural, and optical properties for electrochemical sensing applications. TiO2 nanotubes were synthesized through a three-step anodization process, while the Ag spheres were deposited using electrochemical deposition. The electrolyte solution for TiO2 nanotubes growth consisted of ammonium fluoride and ethylene glycol, while silver nitrate and citric acid were employed as the electrolyte solution for Ag sphere deposition. FE-SEM analysis revealed the successful deposition of Ag spheres with a spherical morphology over TiO2 nanotubes, with the morphology significantly influenced by the concentration of organic acid in the electrolyte solution. Stoichiometry analysis was performed on both the TiO2 nanotubes film and that film decorated with Ag spheres. Additionally, the band gap energy was calculated from the diffuse reflectance spectroscopy (DRS) spectrum. According to Photoluminescence analysis, a larger area associated with oxygen vacancies in TiO2 nanotubes decorated with Ag spheres was identified. The presence of localized energy levels within band gap resulting from oxygen vacancies and Ag spheres led to a reduction in the band gap energy of the semiconductor. This phenomenon is particularly relevant for creating more active sites suitable for the adsorption of compounds in electrochemical sensing applications.[1,2]

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sciforum-096418: Composite Protein Crystals doped with Metal Nanoparticles as a complete antibacterial system

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The increasing prevalence of antimicrobial resistance is challenging the global healthcare system (1). The overuse and inappropriate use of antibiotics have resulted in pathogens with multi-drug resistance, leading the world to a pre-antibiotic era (2,3).

Therefore, the objective of this work is to develop an innovative drug delivery vehicle capable of addressing multidrug-resistant bacterial infections by converting them into an active support. To do this, we have encapsulated silver or gold metallic nanoparticles (MNP) in cross-linked lysozyme crystals. These crystals-composites of proteins and MNPs will behave as release vehicles capable of dealing with infections thanks to their dual composition and the control of the release rate by the degree of cross-linking of the crystals. We anticipate that this synergistic antimicrobial material may be an excellent strategy to combat biofilm formation.

To obtain this material, we followed a bottom-up protocol in which MNPs were firstly obtained in a peptide hydrogel of Fmoc-MF, which contains specific interaction sites with the MNPs to increase their stability during crystallization step. These metallogels were subsequently used as crystallization media to obtain lysozyme (Lzm) crystals. Composite Lzm@MNP crystals were later cross-linked at different degrees to control their dissolution rate.

Herein, we present a proof of concept of a novel active compounds' delivery vehicle, in which the vehicle and itscargo have an active and remedial role.

sciforum-091833: Effect of porosity on the crystallization kinetics of porous polymeric constructs

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Over the years, the crystallization behaviour of various polymeric constructs has been studied in various confined and non-confined morphologies. However, an interesting class of polymers which has gained a significant amount of attention in the past few decades has been the least studied for its crystallization behaviour. Porous polymers have been used for various applications like catalysis, absorption, drug delivery, tissue engineering, and so on. For these various applications, the crystallization behaviour of a material plays a crucial role affecting the material properties. Therefore, polymeric constructs with varying levels of porosity were fabricated by utilizing emulsion templating. The extent of porosity was controlled by changing the dispersed phase volume percentage of the emulsions. The crystallization behaviour of these polymeric constructs was investigated under non-isothermal conditions due to their relevance during real-time application. Various models explaining the crystallization behaviour of substrates under non-isothermal conditions were utilized. It was observed that the inclusion of porosity diminished the crystallization kinetics, illustrating the effect of chain mobility on the crystallization behaviour of a construct. This change in the crystallization kinetics of the material was further prominent in materials with a higher extent of porosity. Additionally, the changes in crystal structure of various polymer materials was observed using an X-ray diffractometer, explaining the crystallization behaviour of the porous constructs.

sciforum-096561: Elucidating the Role of The *O*-Methoxy Group at the Lower Rim-Appended Salicylideneamine Substituents of Calix[4]arene Ligands on the Molecular and Electronic Structure of Dinuclear Fe(Iii)-Based "Diamond Core" Complexes

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New materials capable of storing and processing information at the level of a single molecule (atom) will contribute to the development of digital technologies. This type of molecules has to possess the property of bistability—the ability of molecules to exist in two stable spin states, for example, spin-crossover. In recent decades, there has been a growing interest in control over spin states of coordinative compounds based on Fe(III) cations because of their potential application in fields like molecular spintronics, memory and electronic devices, switches, and sensors [1].

The rational design of molecular building blocks allows researchers to manage the coordination sphere of the metal, and hence magnetic properties can be controlled [2]. Due to the possibility of wide functionalization, calix[4]arenes are extremely attractive for the design of pre-organized ligands. Moreover, the modification of calix[4]arene makes it possible to tune the structure of the complexes as well as to control their size and geometry. Disubstituted derivatives of calix[4]arenes allow the fine-tuning of the metal environment by varying the length of the alkyl spacer and the nature of the substituent in the coordinating fragment. It is particularly attractive to obtain salen-type ligands possessing *N,O*-coordinating chelate fragments.

In this work, we report on the synthesis of new Fe(III)-complexes based on polydentate lower rim disubstituted calix[4]arenes ligands, displaying a salen-type coordination pocket. The structures of prepared coordination compounds were studied by means of X-ray diffraction analysis, IR and 57Fe Mössbauer spectroscopy, and HR-ESI mass spectrometry. The structure–property correlation is also discussed.

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sciforum-084799: Extraction and Modification of Cellulose nanocrystals

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Depending on the source, cellulose microfibrils produced during biosynthesis can range in size from 2 to 20 nanometers in diameter and up to several micrometers in length. Crystalline domains are scattered throughout each microfibril, which also contains amorphous and disordered regions. Chemical hydrolysis is used to break down amorphous chains and liberate crystalline domains from cellulose fibers in order to create cellulose nanocrystals. Sulfuric acid hydrolysis has been used more frequently for the synthesis of cellulose nanocrystals (CNCs) due to its excellent efficiency, as reported in the majority of studies. When sulfuric acid is used as the hydrolyzing agent, disordered or paracrystalline portions of cellulose fibers are preferentially hydrolyzed, while crystalline parts with a higher resistance to acid attack are left intact. It should be noted that sulfuric acid can react with the hydroxyl groups of cellulose during hydrolysis, producing charged sulfate esters on the surface of nanocrystals and facilitating the dispersion of nanoparticles in water . The modification of CNCs is intended to lower the surface energy and increase the degree of dispersion by converting the polar hydroxyl groups on the surface of nanocrystals into moieties that can improve the interactions with non-polar polymers. The main challenge in the surface modification of CNCs is to select a reagent and reaction medium that will allow for modification in a way that preserves the original morphology of the nanocrystals while only changing the surface. The synthesis of glycosilicones from cellulose nanocrystals generally involves several reaction steps: catalysts capable of catalyzing the allylation reaction of cellulose combine cellulose with allyl bromide, followed by a hydrosilylation reaction, are then catalyzed by Karstedt based on platine (0) to combine the hydrophilic allylated cellulose and hydride-terminated hydrophobic silicone. The final polymers were characterized by FTIR, 1H NMR, and solid-state SEM. The glycosilicones were insoluble in water, but swelled in organic solvents.

sciforum-092715: New antimicrobial systems based on zeolites with *RE* = La, Gd functional ions

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Antibiotic resistance necessitates the transition to fundamentally new drugs, in particular *RE*$(NO_3)_3\times$ *x*H_2O salts [1]. To reduce the active substance (*RE* ion) content in drugs while maintaining their functionality, *RE*/MFI and *RE*/BEA systems based on MFI and BEA zeolites are offered.

Composites with MFI ($(H_x)[(Fe^{3+}_xSi^{4+}_{12-x})O_{24}]$ with Si/Fe=25,68: MFI(Fe25), MFI(Fe68); $[(Ti^{4+}_xSi^{4+}_{12-x})O_{24}]$ with Si/Ti=47,60: MFI(Ti47), (MFI(Ti60)); and BEA ($(H_x)[(Al^{3+}_xSi^{4+}_{12-x})O_{24}]$ with Si/Al=12,150: BEA(Al12), BEA(Al150)) and *RE*$(NO_3)_3\times6H_2O$ (*RE*=La,Gd) salts were obtained using the cold impregnation method, with solid-phase mixing of the components (1:1.2), grinding (~4 minutes), and annealing (250°C, 1 hour).

The compositions of *RE*/BEA include amorphous components. Moreover, the samples differ in their particle/associate sizes (*N*, μm), which are greater with MFI (*N*=12.5-35 μm) than with BEA (*N*=7.5-8 μm), except for *RE*/MFI(Ti60).

The growth inhibition zones (*D*,mm) of the bacteria *S.aureus, E.coli, P.aeruginosa, A.baumannii*, and *K.Pneumonia* and the fungi *C.albicans, C.glabrata,* and *C.parapsilosis* on the salts change from *D*=28 to *D*=50 mm with D_{max} for *S.aureus* on Gd; from *D*=45 to *D*=56 mm with D_{max} for *C.albicans* on La, which is a record for these microorganisms; and *D*=0 mm for zeolites. The microorganisms showed high sensitivity to the composites—*A.baumannii* and *P.aeruginosa* with D_{max}=38 mm on Gd/MFI(Ti60) and Gd/MFI(Fe68); and *C.parapsilosis* with D_{max}= 45 mm on Gd/MFI(Fe68)—but less compared to that seen for the salts, while maintaining their excellent biocidal properties. All the new systems demonstrated antimicrobial activity higher than that of the antibiotic penicillin, which makes them promising for biomedical purposes.

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sciforum-094175: Phase Behavior of Athermal Colloidal Mixtures of Chains and Monomers

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Through extensive Monte Carlo simulations, we study the phase behavior of systems composed of freely jointed, hard-sphere polymers and monomers at different number fractions. This work is inspired by the fact that, despite their similarities in crystallization, the melting point of hard-sphere chains [1] is higher than that of their monomeric counterparts [2].

System configurations are generated, equilibrated, and successively analyzed through the Simu-D software [3]. The equilibration part is primarily based on chain-connectivity-altering [4] and identity-exchange Monte Carlo algorithms, especially designed for mixtures of chains and monomers of the same chemical constitution. The structural identification of the computer-generated system configurations is performed through the characteristic crystallographic element (CCE) norm descriptor [5].

We systematically study how both the packing density and the relative number fraction affect the ability of the systems to crystallize. We further identify the entropic origins of the phase transition and the difference in the local environment between spheres belonging to chains and individual ones. Depending on the simulation conditions, different morphologies are established ranging from predominantly amorphous packings to crystal morphologies of mixed hexagonal close-packed (HCP) and face-centered cubic (FCC) character. Extensions of the present work include the molecular simulation of athermal mixtures based on semi-flexible polymers.

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sciforum-094272: Photoluminescence Behavior Combined with Multiple Electrical and Optical Properties in Organic-Inorganic Hybrid Manganese (II) Halide Perovskite

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Organic-inorganic hybrid materials have emerged as a potential candidate due to their fascinating properties for several optoelectronic applications. In this study, lead-free organic-inorganic hybrid perovskite single crystals $[N(CH_3)_4]MnCl_3$ were synthesized through a slow evaporation method using tetramethylammonium as the organic ligand. Systematic characterizations were carried out to reveal the crystal structure and other optoelectrical properties. A series of systematic characterizations were carried out in order to reveal the crystal structure as well as other optoelectrical features. Phase purity and morphology were confirmed by powder x-ray diffraction and scanning electron microscopy respectively. The crystal has a P 63/m space group which belongs to the hexagonal crystal system. The optical band gap was found to be 2.15 eV, and under the excitation of a suitable UV light source, it can emit 635 nm bright red lights with a full width at half maximum of 78 nm at room temperature. Thermal study indicates that the compound is stable up to 300 °C. The compound's electrical properties were studied using Impedance spectroscopy as a function of frequency from 20 Hz to 4 MHz at different temperatures. Finally, the successful achievement of luminescent printing was made possible by harnessing the exceptional photophysical properties of the material. The printed images demonstrated remarkable clarity even after undergoing multiple cycles and remained visible for a prolonged period of 15 days in an air environment, affirming the stability of the printed images. The information stored on the paper can be easily read using a UV lamp. Therefore, these findings highlight the material's outstanding photoluminescence and optoelectrical properties, suggesting its potential for promising applications in optoelectronics, including light-emitting diodes.

sciforum-094244: Self-Trapped Excitons in Organic Lead Halide Perovskites

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Introduction

Broadband emissions related to self-trapped excitons in the sub-bandgap region in organic lead halide perovskite (OLHP) have drawn attention in recent times due to their potential in optoelectronic applications. In this study, we have provided a systematic multi-technique approach to the formation of broad-band emission in OLHPs. We have observed that broad-band emission is closely related to the lattice fluctuation in OLHPs.

Methods

Single crystals of methylammonium lead chloride ($MAPbCl_3$), methylammonium lead bromide ($MAPbBr_3$), and formamidinium lead bromide ($FAPbBr_3$) were grown using solvent evaporation at room temperature method. Temperature-dependent photoluminescence measurements were performed in Edinburg FLS920 spectrometer, synchrotron X-ray powder diffraction measurements were carried out at the P-02.1 beamline at PETRA III, DESY, and temperature-dependent Raman measurements were carried out in a micro-Raman spectrometer (in Via, Renishaw, UK).

Results

Temperature-dependent photoluminescence study shows broad-band emission in $MAPbCl_3$ and $MAPbBr_3$ in the sub-bandgap region, which is missing in $FAPbBr_3$. Synchrotron X-ray powder diffraction analysis suggests cubic phase till 172, 235, and 265 K for $MAPbCl_3$, $MAPbBr_3$, and $FAPbBr_3$, respectively. The tetragonal phase transforms to an orthogonal phase at 167, 148, and 150 K, respectively. Interestingly, below 165 K in $MAPbCl_3$, conventional single *Pnma* symmetry cannot be fitted with low values of reliability parameters, suggesting the presence of another phase. Temperature-dependent Raman study shows stronger N-H---X hydrogen bonding between MA^+ cation and PbX_6 octahedra in the orthorhombic phase of $MAPbCl_3$ and $MAPbBr_3$ than $FAPbBr_3$. The study suggests more tilting of the octahedral framework in both the MA-based compounds.

Conclusions

In summary, our study suggests the emergence of broad-band emission in the two MA-based compounds is due to the transient lattice distortion due to the stronger N-H---X bonding. However, at the lower temperature of $MAPbCl_3$, the presence of double unit cells stabilizes the transient lattice deformation.

sciforum-096260: Separation of benzene and cyclohexane on a metal–organic framework with an alicyclic ligand

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In industry, cyclohexane is obtained exclusively through the hydrogenation of benzene, but the subsequent complete separation of these liquids is very difficult, since they have similar boiling points and form an azeotrope. Their selective adsorptive separation using metal–organic frameworks (MOFs) is one of the promising approaches. Two- and three-dimensional MOFs contain cavities, the size, geometry and chemical nature of which enable the isolation of the desired component from a difficult-to-separate mixture. Combining various organic ligands and metal ions provides almost unlimited design possibilities for MOFs.

The present study considers the sorption of benzene and cyclohexane for five previously reported MOFs based on *trans*-1,4-cyclohexanedicarboxylic acid acting as an example of a ligand with a saturated carbon skeleton: $[Ga(OH)(C_8H_{10}O_4)]$ (**1**), $[Ca(H_2O)_2(C_8H_{10}O_4)]\cdot H_2O$ (**2**), $[Zr_6O_4(OH)_4(C_8H_{10}O_4)_6]$ (**3**) [1], $[Cu_2(C_8H_{10}O_4)_2]$ (**4**) [2], $[Al(OH)(C_8H_{10}O_4)]\cdot H_2O$ (**5**). The adsorption of individual compounds from the liquid and gas phase and competitive adsorption from mixtures were investigated.

For MOFs **3** and **4**, the high selectivity of benzene sorption over cyclohexane was determined, with volume-by-volume selectivity up to ~13. Further, benzene/cyclohexane adsorption selectivities were calculated from the adsorption data using two methods. According to the Henry method, the C_6H_6/C_6H_{12} Henry constant ratios at low pressures were 7105 for $[Zr_6O_4(OH)_4(chdc)_6]$ and 3.63 for $[Cu_2(chdc)_2]$. According to the ideal adsorbed solution theory (IAST) for near-atmosphere pressures, the corresponding selectivity coefficients were 23.6 for $[Zr_6O_4(OH)_4(chdc)_6]$ and 1.23 for $[Cu_2(chdc)_2]$.

These results indicate the promising potential of using metal–organic frameworks **3** and **4** with an alicyclic ligand as highly effective sorbents for the separation of the industrial mixtures of benzene and cyclohexane.

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sciforum-093946: Study of structure and filler crystallinity index of polymer composite with silica nanofibrous filler

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Introduction: In this study the technique of obtaining a composite material based on polyimide track membranes prepared by the deposition of TEOS (tetraethoxysilane) hydrolysis products in medium with acidic catalyst will be considered further. The obtained material sample microstructure and effect of the presence of crystalline forms of silicon dioxide on the overall crystallinity index (CI) of the silica filler will be studied.

Methods: The microstructure of the composite material surface was studied using scanning electron microscopy (SEM TESCAN MIRA 3). The effect of the presence of crystalline forms of silicon dioxide on the overall CI of the silica filler was studied using XRD (ARL X'TRA). For the purpose of this study, the CI was defined as the ratio of the area of the peaks of the crystalline phase in the diffraction pattern to the total area under it. A series of experiments were carried out with a model samples with different wt. % contents of crystalline silica powder and a correlation curve of the crystallinity of the sample and the crystallinity from the diffraction pattern was plotted.

Results: From the surface examination of the samples, it was found that the silica filler deposited in the pores of the polyimide track membrane has a nanofibrous structure. When crystalline powders were added in the amount of 30% wt. of the planned reaction yield, the CI did not exceed ≈32%, which indicates the absence of the formation of a new crystalline phase in the reaction volume.

Conclusion: According to the conducted study advantages of using an acidic catalyst of TEOS, the hydrolysis reaction can be regarded as the most successful, since its use leads to the formation of nanofibrous structures in the pores of the polyimide track membrane. The addition of crystalline forms of silicon oxide studied in this paper did not result in a significant change in the CI of silica filler.

sciforum-094347: Tailoring Magnetite Nanocrystal Morphology via Solvothermal Method for Enhanced Heavy Metal and Fluoride Adsorption

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Contamination by heavy metals is a pressing issue due to its numerous hazardous effects on human health. One of the main challenges associated with this type of contamination is the resistance of heavy metals to degradation and their accumulation in living organisms. However, a wide variety of methods, including ion exchange, membrane filtration, flotation, electrolytic methods, and adsorption, can be employed to eliminate heavy metals from water. To achieve the efficient removal of heavy metals from water, a high-surface-area absorbent is necessary. This enhances contact and interaction with heavy metal ions, and the use of nanoparticles significantly improves this aspect. This study investigates the preparation of Fe_3O_4 nanoparticles using a solvothermal method. This method allows to produce ultrafine magnetite powders with homogeneous particles, a narrow size distribution, and consistent morphology, free from other crystalline phases that could hinder heavy metal ion absorption. The experiments involved varying temperatures (180-220 °C) and reaction times (4-12 h) and utilized $FeCl_3$ as the iron ion precursor. Following the solvothermal treatments, the precipitated particles were magnetically separated from the hydrothermal solution. The magnetic particles were then analyzed using XRD, SEM, and FTIR. Structural characterization via SEM confirmed that the obtained particles were magnetite in the form of homogeneous spherical particles with an average size of 450 nm, composed of smaller agglomerated nanoparticles with an average size of 8.4 nm. Microstructural characterization using the XRD and FTIR techniques also confirmed the magnetite structure, exhibiting defined reflections without any secondary crystalline phases. Kinetic and isotherm data from a preliminary study fit well with established models, indicating efficient fluoride capture. Additionally, the maximum adsorption capacity reached 39.44 mg/g F^- within 30 minutes, remaining stable thereafter. These findings suggest that the synthesized magnetite nanoparticles are ideal candidates for heavy metal and fluoride removal from water.

sciforum-096345: Tb(III) and Eu(III) complexes based on 1,4-diazabicyclo[2.2.2]octane-N,N'-dioxide with different dimensionality

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Lanthanide-based MOFs are promising candidates for the creation of luminescent materials, since REE(III) ions possess predictable, multicolored, narrow-band luminescence with long excited state lifetimes and high quantum yields.

In this research, the structure and properties of coordination compounds of various dimensions based on 1,4-diazabicyclo[2.2.2]octane-N,N'-dioxide (odabco) and Ln^{3+} (Ln^{3+} = Tb^{3+} and Eu^{3+}) cations are studied. Their formulas are: $[Ln(odabco)_3](NO_3)_3 \cdot 4.5H_2O$ (**1**$_{Tb}$; **1**$_{Eu}$); $(Hodabco)_3[Ln(H_2O)_2(NO_3)_4](NO_3)_2$ (**2**$_{Tb}$; **2**$_{Eu}$); $[Ln(odabco)_3]_2[Ln(NO_3)_6](NO_3)_3 \cdot 3H_2O$ (**3**$_{Tb}$; **3**$_{Eu}$).

1$_{Ln}$ contain a three-dimensional porous cell $[Ln(odabco)_3]^{3+}$ with a mononuclear octahedral metal center and disordered nitrate anions in the pores. **2**$_{Ln}$ contain polymeric organic cations $(Hodabco)^+$ interconnected by hydrogen bonds into chains. Aquanitrate complexes and free nitrates are located in the interchain space as counterions. **3**$_{Ln}$ contain a coordination framework close to **2**$_{Ln}$, but they also contain large hexanitrate complexes of lanthanides in their voids. The crystal structures of all compounds were determined by single crystal XRD analysis, and their phase purity and stability were confirmed by PXRD, CHNS analysis, thermogravimetric analysis and IR spectroscopy.

Excitation and emission spectra and kinetic decay curves of luminescence were studied for the all samples. Sensing properties were revealed for **3**$_{Eu}$ – quenching the luminescence of a suspension in ethanol solutions of chromate or dichromate. For the last, LOD was $2.4 \cdot 10^{-6}$ M for 270 nm excitation wavelength and $2.1 \cdot 10^{-7}$ M for 395 nm excitation wavelengths. **3**$_{Tb}$ also show quenching the luminescence for ethanol solution of chromate and dichromate. LODs were $6.6 \cdot 10^{-7}$ M and $1.1 \cdot 10^{-5}$ M respectively. The luminescence response at micromolar concentration range was also found to be fast, with an equilibrium time no longer than 20 min. Therefore, porous MOFs **3**$_{Ln}$ with cationic polymeric structure were found to be the effective luminescent sensors for the toxic Cr(VI) anions.

sciforum-094219: The diastereoselective [2+2]-photodimerization of 2-cyclopenten-1-one within a metal–organic framework

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Selective dimerization of 2-cyclopenten-1-one, which proceeds through the [2+2]-cycloaddition mechanism, was successfully carried out under soft UV irradiation with a reagent trapped within the pores of a metal–organic framework. Such an approach allowed us to achieve very high (up to 98%) selectivity in the formation of the head-to-tail anti-dimer, among other possible diastereomeric dimers, while a similar selectivity rarely exceeds 60% using other known approaches [Photochem. Photobiol. Sci., 2002, **1**, 991] The metal–organic framework used, $[Eu_2(DMF)_4(ttdc)_3]$ (DMF = N,N-dimethylformamide; H_2ttdc – *trans*-thienothiophene-2,5-dicarboxylic acid), containing regular nano-sized pores, acted as a matrix—a “reaction vessel”—which adsorbed the reagent molecules. The highly ordered arrangement of 2-cyclopenten-1-one molecules in the MOF pores, facilitated by the host–guest hydrogen bonds, predetermined the geometry of its dimer at the molecular level and subsequently the extremely high selectivity of its formation, as confirmed by ^{1}H NMR spectroscopy. The stability and geometric rigidity of the porous coordination network structure exclude the formation of other possible product isomers in the reaction. The crystal structure o the inclusion compound of the target product with the MOF was determined by single-crystal X-ray diffraction analysis, providing unambiguous confirmation of the reaction occurring distinctively within the voids of the coordination framework and additional insights into the reaction selectivity in terms of the host–guest interactions. Similar results were obtained for 2-methyl-2-cyclopenten-1-one, while for the 3-methylated derivative, its diastereoselective [2+2] dimerization was found to be impeded due to the different guest orientation in the MOF pores, which did not facilitate a specific product-like pre-organization of the reagent molecules [Chem. Commun., 2023, **59**, 9380].

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Session 6. Materials for Energy Applications

sciforum-096390: Highly dispersed ultra-small NiO nanoparticles on mesostructured silica as efficient catalysts for CO_2 methanation

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Introduction

Due to the attention toward global warming, the current research is focusing on green fuels obtained by the reduction of captured CO_2 (e-fuels). A prominent example of these e-fuels is methane. Ni-based catalysts are among the most investigated systems for CO_2 methanation. Ni is often paired with a promoter, like CeO_2. In this work, composite catalysts consisting of a NiO and NiO/CeO_2 active phase dispersed on mesostructured silica (SBA-15) are presented, which, using a support, should allow us to reach a high activity with a reduced amount of the active phase.

Methods

To obtain NiO- and NiO/CeO_2-based nanocomposites, two different impregnation approaches were used: two-solvent (TS) impregnation and impregnation based on a self-combustion (SC) reaction. The NiO-based catalysts were obtained with a loading of 4.5%; the NiO/CeO_2-based catalysts were obtained using a 1:1 Ni:Ce molar ratio. To determine their structural and morphological properties, the catalysts were characterized with small-angle (SA-) and wide-angle (WA-) XRD (X-ray diffraction), TEM (transmission electron microscopy), and nitrogen physisorption and tested for CO_2 methanation.

Results and discussion

WA-XRD shows that the composites obtained with SC do not feature a diffraction peak, suggesting that NiO and CeO_2 are deposited into the mesopores as ultra-small nanoparticles. On the other hand, the composites obtained with TS impregnation show broad but visible crystal reflections attributed to both NiO and CeO_2, indicating that the active phase has crystallized, forming larger nanoparticles. This finding is also confirmed by the TEM micrographs, which for the SC composites do not show the presence of any visible particles outside the mesopores; the TS systems, conversely, show visibly darker nanoparticles dispersed over the support. The catalytic tests show a positive effect of CeO_2 on performance; furthermore, the catalysts obtained with SC impregnation show a higher CO_2 conversion, presumably due to the higher dispersion of the active phase obtained with this approach.

sciforum-093816: Nano-enhanced phase change materials doped with carbon allotropes for thermal energy storage: a patent landscape analysis

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Nano-enhanced phase change materials (NePCMs) are composites made of an organic or inorganic PCM and nanoparticles (metal, metal oxide, carbon nanotube, graphite, graphene) capable of increasing their thermal capacity or conductivity.

PCMs are classified into three categories, namely organic, inorganic, and eutectic [1,2].

This study focuses on the patent analysis of organic NePCMs doped with carbon allotropes for thermal energy storage.

Patent searches were carried out using two databases (Espacenet, provided free of charge by the European Patent Office, and Orbit, a paid-for system provided by Questel) using precise and controlled keywords in the title/abstract/claims search fields with Boolean and proximity operators and classification codes.

Classification symbols were retrieved by means of the Espacenet classification search tool and the WIPO IPCCAT system.

China is the country with the highest number of patent applications filed for NePCMs with carbon allotropes, followed by the United States, Europe, and South Korea.

The number of patent applications filed increased from 2016 to 2022.

However, it should be noted that the figures for later years are not reliable, as applications are kept secret for the first 18 months after filing.

Graphene and its derivatives are the most frequently claimed compounds in applications and granted patents, followed by carbon nanotubes.

Fullerenes are rarely claimed (1.4% compared to graphene and derivatives), with an even smaller percentage claimed for other nanosized carbon materials (such as nano-onions, nanoscrolls, nanohorns, nanocones, nanowalls, and nanocoils).

Approximately 30% of the applications have either expired or been revoked or withdrawn.

Of the active patents, between 35% (for nanotubes) and 40% (for graphene) remain under examination.

The most commonly used PCMs in combination with carbon allotropes are paraffin, stearic and lauryl acids, and lauryl alcohol.

sciforum-096387: A structural comparison between Co^{II} and Cu^{II} anilato-based ultramicroporous 3DMOFs

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Introduction

Metal–Organic Frameworks (MOFs), porous materials self-assembled by metal ions and organic ligands, are attracting ever-growing interest in material chemistry. Their high porosity, tunable pore size and large surface area make MOFs promising candidates to separate CO_2. Ultramicroporosity (pore size 0,7 nm) and the presence of nitrogen atoms are crucial requirements in the design of MOFs for CO_2 uptake.. Based on this, by combining 3 6-*N*-ditriazolyl-2,5-dihydroxy-1,4-benzoquinone (trz_2An), as the organic linker, with Co^{II} or Cu^{II}, two new ultramicroporous MOFs, formulated as $[Co(trz_2An)]n{\cdot}3H_2O$ (**1**) and$[Cu(trz_2An)]{\cdot}(H_2O)_{2.5}$(**2**), have been obtained.

Material and Methods

MOFs **1** and **2** were synthesized by optimizing the synthetic procedure reported in literature. A solution of $CoCl_2{\cdot}6H_2O$ or $CuCl_2{\cdot}2H_2O$ was slowly added to a mixture of trz_2An, NaOH and water and heated in autoclave at 130 °C for 48 hours. The rectangular crystals, suitable for a single X-ray diffraction study, were washed three times using an acid aqueous solution in order to solubilize and remove the $Co(OH)_2$ and $Cu(OH)_2$ obtained during the reaction.

Results

In **1,** Co^{II} ions are equatorially coordinated to four oxygen atoms of two bis(bidentate) trz_2An ligands. The distorted octahedral coordination sphere of Co^{II} ions is completed with two nitrogen atoms from the N4 atoms of the 1,2,4-triazole substituted pendant rings of trz_2An ligands. Two voids of 90.4 $Å^3$ were found in the unit cell of the crystals, giving a void volume of 23.5%. MOF **2** is characterized by cubic cavities with a volume void of 28 % due to the coordination to the N atom at the 4-position of the triazole ring, which induces an alternate orientation of Cu-anilate chains.

Conclusions

The same trz_2An linker has been employed to obtain, in combination with Co^{II} and Cu^{II}, two robust, isomorphous and ultramicroporous MOFs, suitable for CO_2uptake and separation.

sciforum-094286: Electronic structures of Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals using first-principles calculations

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Electronic structures of all inorganic rare-earth element, such as gadolinium (Gd) and neodymium (Nd), double perovskite crystals (Cs_3GdCl_6 and Cs_3NdCl_6) were characterized for application of photovoltaic devices with photovoltaic performance. The band structure, density of state, electron density distribution, and the real and imaginary parts of the dielectric function of Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals were approximated using first-principles calculations, with GGA-PBE approximation. The Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals had a narrow band dispersion with direct band gaps of 1.0 eV and 0.7 eV. The band structure of the Cs_3GdCl_6 crystal consisted of 5d and 4f orbitals of Gd ions near the valence band (VB) state,the 5d orbital of Gd ions ,and the 6s orbital of Cs ions near the conduction band (CB) state. The band structure of the Cs_3NdCl_6 crystal consisted of the 5p orbital of Cl ions near the VB state, and the 5d orbital of Nd ions near the CB state. The charge transfer and carrier generation related to electron mobility will be caused by the overlap of the 5d orbital of Gd and Nd ions and the 6s orbital of Cs ions near the CB state. The real and imaginary parts of the dielectric function in both cases were obtained in the range of 0 – 1 eV. The photon energies correspond to transition between the energy levels of the split 5d and 4f orbitals of Gd andNd ions coordinated with Cl ions as ligands in the crystal field with charge distribution. The Cs_3GdCl_6 and Cs_3NdCl_6 double perovskite crystals have high potential for the application of photovoltaic devices with photovoltaic performance.

sciforum-092497: Lithium adsorption properties of two-dimensional chromium nitride

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Two-dimensional (2D) materials promise improved performance and energy storage capacities in next-generation Li-ion batteries due to their large surface area, enhanced specific capacity, and quick ion diffusion coupled with light weight and flexibility. Two-dimensional CrN is a recently proposed novel 2D material showing interesting properties regarding ferromagnetism, optical transparency, and good elastic properties, as well as catalytic and gas sensing properties, in free-standing or heterostructure form combined with other 2D materials. This study examines the lithiation characteristics of 2D CrN sheets with density functional theory (DFT) calculations. Using Perdew–Burke–Ernzerhoff (PBE) DFT calculations with the Generalized Gradient Approximation (GGA), we computed the various parameters for Li adsorption on 2D CrN. We carried out structural optimization calculations with the Broyden–Fletcher–Goldfarb–Shanno (BFGS) algorithm for the adsorption studies, and performed a climbing image nudged elastic band calculation to evaluate the diffusion barriers. In all calculations, the van der Waals forces were taken into consideration, with Grimme's DFT-D3 correction scheme. In our studies, 2D CrN demonstrated an excellent theoretical specific capacity up to 1322.73mAhg-1, a small electrode potential of about 0.2V, and a diffusion barrier of 0.17eV. According to the calculations, 2D CrN might be used as a substitute anode material in Li-ion storage.

sciforum-094277: Magnetocaloric $GdMn_{1-x}Ru_xSi$ compounds with x = 0 - 1 for gas liquefaction

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Ternary intermetallic compounds based on rare-earth metals are characterized by high values of the magnetocaloric effect (MCE) and magnetoresistance, making them suitable materials for a variety of innovative, environmentally friendly and efficient applications. Magnetic refrigeration, for example, is a potential candidate for environmentally friendly gas liquefaction and for preventing gas from evaporating during storage. As an example, liquid nitrogen is often used as a final refrigerant for liquefied natural gas at 111 K. Novel intermetallics $GdMn_{1-x}Ru_xSi$ with a tetragonal CeFeSi-type structure (P4/nmm), were synthesized, with x = 0, 0.2, 0.5, 0.8 and 1 [1]. Their Curie temperature T_C changes from 78.3 to 320 K with a change in manganese content. The electronic structure and magnetic moments of $GdMn_{1-x}Ru_xSi$ intermetallic compounds were calculated using the theoretical DFT+U method. The calculated total magnetic moments of $GdMn_{1-x}Ru_xSi$ also show reduced values for intermediate Ru concentrations. In the $GdMn_{1-x}Ru_xSi$ system, MCE occurs during a second-order phase transition and in a wide temperature range from 78.3 (which is near the boiling point of liquid nitrogen at 77.4 K) to 320 K. The $GdMn_{1-x}Ru_xSi$ system, with x = 0 - 1, is of practical interest for the liquefaction of gases, including nitrogen. A cassette can be made from compounds within this range with slightly varying chemical compositions. Due to their properties, the intermetallic $GdMn_{1-x}Ru_xSi$ compounds are novel, more efficient magnetocaloric materials suitable for the liquefaction of nitrogen and other gases.

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sciforum-096391: Optimizing the CO_2 uptake performance of an anilato-based ultramicroporous 3D MOF through a New Synthetic Protocol

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Introduction

Capturing CO_2 from the atmosphere represents a key challenge, since CO_2 has been recognized as the primary anthropogenic greenhouse contributor to the increase of earth's average temperature. Metal- Organic Frameworks (MOFs) given their porosity and versatility are considered excellent candidates for gas adsorptive separation process. We reported herein a new synthetic protocol to obtain an improvement of the BET surface area of the $[Co(trz_2An)]n{\cdot}3H_2O$ MOF, where the ultra-microporosity and the presence of a ligand bearing two triazole pendant arms are fundamental in the CO_2 uptake.

Material and Methods

$[Co(trz_2An)]n{\cdot}3H_2O$ **(Co_MOF')** has been synthesized optimizing the synthetic procedure reported in the literature for **Co_MOF**[1]**.** A mixture of $CoCl_2{\cdot}6H_2O$ and trz_2Anhilate ligand in a 1:1 stoichiometric ratio, via a hydrothermal reaction, was heated at 130°C for 48 hours. The dark brown rectangular crystals, suitable for a single X-ray diffraction study, were washed three times by using an aqueous aqueous solution (pH=5) in order to solubilize and remove the $Co(OH)_2$ obtained during the reaction. FT-IR and BET (Brunauer–Emmett–Teller) measurements were performed to compare the surface area values of **Co_MOF and Co_MOF'**.

Results

The BET surface area of Co_MOF, determined with a high-pressure gravimetric analyzer employing CO_2, showed a value of 431 m^2/g. Advanced characterization of Co_MOF via FT-IR spectroscopy revealed a peak at 3632 cm^{-1}, which could be assigned to the presence of $Co(OH)_2$. The new synthetic protocol allowed us to remove the $Co(OH)_2$, leading to the presence of Co_MOF', which exhibited a BET value of 616 m^2/g (almost 30% of the pristine value).

Conclusions

The optimized synthetic protocol represents a challenging strategy to obtain novel MOFs with different M^{II} eco-friendly transition metal ions with different improved sorption properties and selectivities toward CO_2.

sciforum-095964: Recovery of mica minerals from granite waste for energy applications

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Biotite mica mineral is a common rock-forming mineral that is generally found in metamorphic rocks, but also in igneous rocks. In addition to their high tensile strength, high thermal stability, layered form, and high resistance to chemical and environmental degradation, mica materials also have high electrical resistance. They possess interesting dielectric properties that make them ideal for a number of applications, particularly as a low-cost substitute material for energy storage systems, due to their exceptional insulating characteristics that allow for the transmission of electrical force without conduction. The aim of this article is to investigate the possibility of recovering biotite from granite waste, as part of a circular economy approach, by using a less polluting technique—that of high-intensity dry magnetic separation. Particle size analysis, inductively coupled plasma spectrometry, and X-ray diffraction were used for physicochemical and structural characterization. The findings of this study reveal promising results in terms of content and yield, underlining the effectiveness of this method for biotite recovery compared with other conventional techniques that are used to obtain a high degree of mica biotite purity, as is required in the field of energy storage. This technique is also useful in terms ofgetting rid of waste that represents a heavy environmental burden and has no economic value.

sciforum-096427: Recovery of Precious Metals from the Spent Catalyst

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Catalysts are indispensable in accelerating chemical reactions, and numerous chemical industries rely on heterogeneous catalysts to efficiently transform raw materials into final products. The petroleum, petrochemical, and chemical industries employ a range of heterogeneous catalysts to optimize the conversion of raw materials into products, achieving this with minimal energy expenditure and reduced processing time. Resource scarcity and disposal issues with low-activity catalysts pose major global challenges. Fresh catalysts incur high costs, and the Earth's supply of essential metals is limited. Landfilling of spent catalysts, which contain valuable and expensive metals, is harmful to human health and the environment. Recycling catalytic minerals reduces the need for new resources, aiding in resource conservation.

Conventional recovery methods employed at the commercial level, namely pyrometallurgy and hydrometallurgy, are effective but exhibit considerable drawbacks, including high energy demands and notable environmental impacts. Despite the availability of numerous environmentally friendly techniques for metal recovery, their implementation remains inconsistent. Organic acids are considered more environmentally friendly and cost-effective compared to inorganic acids for the extraction of precious metals. Crude spent catalysts contain trace amounts of valuable metals, such as 0.21 wt.% platinum and 0.25 wt.% rhenium, and the primary objective is the recovery of these metals using organic acids. A 1M solution of tartaric acid achieved over 90% platinum extraction from spent catalysts within 24 hours at 80°C. In comparison, organic acid-based hydrometallurgy exhibits significant potential for the recovery of precious metals from spent catalysts.

sciforum-097085: Sorbents and catalysts based on mesostructured silica for pollutant removal and Carbon Capture and Utilization technologies

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In recent years, concerns about heavy metal pollution and rising CO_2 levels contributing to global warming have intensified. This study focuses on synthesizing and functionalizing mesostructured silicas (MCM-41, MCM-48) to develop amine–silica sorbents for potential applications in removing Cd^{2+} from aqueous solutions and in Carbon Capture and Utilization (CCU) technologies. Due to their ordered mesoporous structure, nitrogen's lone pairs donating to Cd^{2+}, and the high affinity of amines for CO_2, amine–silica sorbents are suitable for these applications. Additionally, mesostructured silica-based composites were developed by impregnating MCM-41 with copper, zinc, and zirconium oxidic phases (CZZ) for potential use in the catalytic hydrogenation of CO_2 to methanol.
Mesostructured silica was synthesized using the sol–gel technique with a templating agent, a siliceous alkoxide precursor, and two distinct solvent systems—water (MCM-41) and water/ethanol (MCM-48). Amine–silica sorbents were obtained through post-synthesis grafting with aminopropyltriethoxysilane, and were tested for Cd^{2+} removal and CO_2 capture. To reduce the environmental impact of the grafting process, an eco-friendly solvent (butanol instead of toluene) was used. The CZZ@MCM-41 composites were prepared through auto-combustion. For developing Cd^{2+}-removal sorbents and CZZ catalysts, mesostructured silica was also synthesized from industrial waste (hexafluorosilicic acid, FSA). All sorbents were characterized using XRD, TEM-EDX, TEM, N_2-physisorption, thermogravimetric analysis, and ATR-FTIR.
MCM-48 was obtained by adding ethanol as a co-solvent, maintaining other experimental conditions equal to MCM-41 synthesis. MCM-41 from both FSA and TEOS exhibited similar textural properties. The amino groups' concentration was similar (~2 mmol/g) for MCM-41 functionalized with either toluene or butanol; however, the use butanol instead of toluene resulted in a lower CO_2 adsorption performance (968 µmol CO_2/g sorbent vs. 480 µmol CO_2/g sorbent). Amine–silica sorbents showed a Cd^{2+} removal efficiency of 98-99% and an adsorbed cadmium amount (q_e) of ~40-45 mgCd(II)/g sorbent for MCM-41 from both TEOS and FSA.

sciforum-093396: Surface plasma oscillations in a conducting layer for a symmetric magnetic field configuration

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In this work, a theoretical model of the surface plasma oscillations' propagation in a conductive layer is constructed. We assume that the layer is located between two insulating layers with the same dielectric constants. We suppose that the surface wave frequency is much lower than the plasma resonance frequency. The case of specular reflection of charge carriers from the semiconductor layer boundaries is considered. Analytical expressions for the propagation coefficients, longitudinal, and transverse attenuation parameters are derived. An analysis of the dependencies of the surface wave parameters on the semiconductor layer thickness, surface wave frequency, and the dielectric constant of insulating layers was carried out. We established that at low frequencies (about ten THz), we observe a linear frequency dependence of the surface wave propagation coefficient. The longitudinal attenuation is practically absent, which may be due to the absence of excess charge at the layer boundaries. At a certain frequency, the longitudinal attenuation coefficient becomes non-zero, and it grows sharply with increasing frequency. The appearance of non-zero longitudinal attenuation is accompanied by a deviation of the frequency propagation coefficient dependence from the linear law. With a further increasing frequency, the propagation and attenuation parameters grow, reach a maximum, and then reduce. It follows from the above that when a non-monochromatic wave arrives at the conductive layer, a redistribution of harmonics across amplitudes occurs during surface wave propagation. This effect can be used to create plasmonic waveguides that filter frequencies corresponding to the minimum longitudinal attenuation coefficient (plasmonic filters). We established that with rising semiconductor layer thickness and dielectric constant of insulating layers, the propagation and attenuation parameter maxima shift towards lower frequencies. Thus, by varying the thickness and selecting the material of the insulating layers with the desired optical characteristics, it is possible to change plasmonic filter pass frequency.

sciforum-096585: Using Cutting-Edge Architectural Technologies and Creative Materials to Support Smart Building Design Paradigm

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Because of its benefits and digitization, smart materials technologies are becoming increasingly popular worldwide, and smart building construction is becoming a new development trend. These technologies are essential for achieving a competitive edge in the construction sector in the twenty-first century. It is anticipated that smart materials will dramatically improve functionality in the development of materials technology by acting like living systems and becoming a component of a structural system that is sensing its surroundings. This study examines the advantages of implementing smart materials technology in the building sector, even if there is less interest in this trend overall, especially in developing nations, than in traditional buildings. This paper also examines the increasingly apparent conventional division between materials science and architecture. It offers a critical examination of smart materials, shedding light on cutting-edge approaches and strategies that will influence architectural design and underscoring the close relationship between the two disciplines. The benefits of smart materials technologies are highlighted in this study, and they include safer, more secure operations, cost-effective maintenance, efficient energy use, employment creation, healthcare management, and real-time monitoring. As such, emerging economies must fully comprehend these advantages. This study emphasizes the advantages of smart materials technology for developing nations and makes the case for the necessity of a collaborative framework between academics and industry professionals in the building industry to advance understanding and successful implementation of this technology.

Session 7. Crystalline Metals and Alloys

sciforum-096587: Data-led analysis and feature-based modelling of critical phases in the dissimilar welding of duplex stainless steel

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Duplex stainless steel (DSS) with a mixed ferrite–austenite structure is an advanced stainless-steel group with mechanical properties and corrosion resistance superior to those of single-phased steels. The dissimilar welding of DSS, between different grades of DSSs and with other material groups, is an active research area with huge importance for DSS applications. However, the complex composition of the alloying system may naturally lead to complicated phase structures, either in isolated form or as connected zones. This directly affects the structure integrity, weldability, corrosion resistance, and aesthetic appearance of stainless steels. The phase structure could also cause complex issues for developing microstructure-based models for different material groups. This work critically reviews and analyses recent developments and data on the dissimilar welding of DSSs, including welding between different groups, such as DSS, Super DSS, and Lean DSS, as well as welding of DSSs with carbon steels, high-strength steels, single-phased stainless steels, and other nonferrous alloys with/without filler alloys. Feature analysis is conducted on the key welding zones, and the main phases, including precipitation phases and intermetallic, primary, and secondary boundaries, are identified. Data analysis is conducted to classify the phase zones formed in the welding of different materials. A microstructural map of the location of intermetallic and secondary phases/zones in different weldments is presented and used to develop feature-based parametric finite element models. The effect of some key features of the phase zones/boundaries (e.g., martensite and intermetallic) on the structural integrity of the weldments is discussed.

sciforum-093966: Data-led modelling and analysis of defects and doping in different carbides

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Point and complex defects and doping play important roles in the mechanical, physical properties and functionality of crystalline materials such as carbides. First-principle calculations of defects/doping based on density functional theory have been widely used as an effective tool for studying the influence of defect and doping elements, which is important for understanding the evolution of precipitated carbides and the development of high-performance carbides. In this study, first principle method is adapted to establish data for two typical carbides - Ni4C and Mo2C in 2D and 3D structures. A systematic approach has been developed for studying and analyzing the effects of a range of doping elements and different types of defects on the mechanical, electronic and magnetic properties.

Calculations show that there is an enhancement in magnetism of Mo2C structure when dopped with Co and Mn, which may be due to the doping elements of changing the electronic structure of Mo2C, introducing local magnetic moments. Data with Co and Mn doping in Ni4C also indicates an increase of the magnetic moment and enhancement of the magnetic performance. In addition, change of magnetic data of Mo2C is observed with some types of vacancy defects and asymmetric structure. The comparative analysis of data for 2D and 3D structures of Mo2C show that the 2D structure has different characteristics from the 3d structure when doped. These results further contribute to the understanding of effects of defects and doping elements on the mechanical and physical properties in particular magnetism of carbides. The potential link between the data to the understanding of carbide formation and their use in new emerging areas is analysed. The issues and use of the data in integrated approaches combining modelling, experimental and data analysis is discussed.

sciforum-094359: Energy distribution in iron nano-spheres with cubic magneto-crystalline anisotropy

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Magnetic memory systems are one of the recently strongly investigated topics in the research area of spintronics. Amongst the different data storage systems, magnetic nanoparticles are of high interest since they can often store large amounts of data on small scales. Such magnetic nanoparticles, however, pose new challenges, such as oxidation and agglomeration. Here, we show micromagnetic simulations using MagPar, which solves the Landau–Lifshitz–Gilbert equation using finite elements, to analyze the energy density of iron nano-spheres. For spheres of 10 nm or 25 nm and different oxide shell thicknesses, 3D energy maps were calculated. Interestingly, the cubic magneto-crystalline anisotropy led to a non-uniform energy distribution of the magnetic nano-spheres, with the number of extrema decreasing for larger oxide layer thicknesses. In the case of the agglomeration of four nano-spheres, the distances between the nano-spheres strongly modified the system's magnetic properties, where an oxide shell enabled bringing the nano-spheres closer together before they start influencing each other, which was evaluated by comparing the magnetic properties of these agglomerates with the single nano-spheres. For the oxide coated system, the maximum packing density could be increased by about 12%, as compared to the non-coated system, indicating that a higher data density can be reached by preparing a matrix of magnetic nano-spheres with oxide shells.

sciforum-093932: Experimental and Computational Methods for Determining the Composition of Commercial Titanium and Aluminum Alloys

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Commercial alloys of **Al-1** (wt.%) (**91.9 -94.6Al, 4.8-5.8Mg**, 0.5 Si =Fe, 0.1Cu, 0.05-0.08Mn, 0.005Be), **Al-2 (90.8-94.7Al**, 1.2-1.8Mg, 0.5Si = Fe, **3.8-4.9Cu**, 0.3-0.9Mn, 0.1Ni), and **Ti (94.2-96.9Ti**, **1.0-2.5Al**, 0.15Si, 0.3Fe, 0.3Zr, **0.7-2.0Mn**, 0.15O, 0.3*X*) contain impurities, but bear no indication of their composition and structure, on which the performance characteristics of the materials depend. The purpose of this work was to develop an method and program for determining the alloys' composition. The use of a complex of X-ray phase and elemental (EDX) analyses, crystal chemical calculations (the theory of closest packing—CP, metal radii—r(*M*)Å, and Vegard's—*V* or Retger's—*R* rules) allowed us to determine the compositions of these alloys.

Al-1. Substitutional solid solution (SSS) ($Al_{1-x}Mg_x$) (sp.gr. Fm3m; a_{exp}=4.088(7)Å) with type (ST) of Cu (98%) + impurities (2%): a_{CP}(Al)=4.045Å, "a_{CP}(Mg)"=4.526Å - **$(Al_{0.90}Mg_{0.10})_{CP+V}$** (~350°C) [1]; EDX (wt.%): **91Al, 8Mg**, 0.2Fe, 0.3Si, 0.5Mn.

Al-2. SSS ($Al_{1-x}Cu_x$) (STCu; a_{exp}=4.036(4)Å): a_{exp}(Al)=4.049Å, a_{exp}(Cu)=3.615Å; a_{CP}(Al)=4.045Å, a_{CP}(Cu)=3.620Å - **$(Al_{0.97}Cu_{0.03})_V$ =$(Al_{0.98}Cu_{0.02})_{CP+V}$** (~500°C) [2]; EDX (wt.%): **98.3Al,** 0.7Mg, 0.3Fe, 0.4Si, 0.1Mn, **0.1Cu**, 0.1Ni.

Ti. SSS ($Ti_{1-x}Al_x$) (sp.gr. $P6_3/mmc$; a_{exp}=2.942, c_{exp}=4.678Å, c/a=1.590, V=35.064Å^3) with ST derived from Mg (c/a=1.633): a_{exp}(Ti)=2.950Å, c_{exp}(Ti)=4.684Å, V=35.300Å^3; a_{CP}(Ti)=2.940Å, c_{CP}(Ti)=4.675Å, V_{CP}=34.994Å^3; "a_{CP}(Al)"=2.860Å, "c_{CP}(Al)"=4.547Å, V_{CP}=32.208Å^3 - **$(Ti_{0.92}Al_{0.08})_{CP+R}$**; "$a_{CP}$(Mn)"=2.540Å, "$c_{CP}$(Mn)"=4.039Å, V_{CP}=22.566Å^3 - **$(Ti_{0.98}Mn_{0.02})_{CP+R}$**; **$(Ti_{1.00-0.80}Al_{0-0.12}Mn_{0-0.08})$** (700°C) [3]; EDX (wt.%): **84.6Ti, 2.5Al, 1.0Mn**, 0.2Si, 0.1Fe, 11.6O.

Thus, the composition of **Al-1, Al-2, and Ti** alloys are different from those indicated by the certificates.

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sciforum-094236: Integrated Data-led modelling of M7C3 carbides alloys

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M7C3 carbides (where M could be Fe, Cr, i.e. (Fe, Cr)7C3) or other solution elements replacing Cr or Fe are a special group of carbides, widely used in materials such as white cast iron and welded hardfacings. Normally, the structure of hypereutectic Fe–Cr–C alloy consists of a high quantity of large primary M7C3 carbides within an eutectic matrix. The morphologies of primary M7C3 carbides directly influence the hardness, wear resistance, fracture toughness of the alloy as well as the physical properties such as thermal conductivity and electrical resistance. It is essential to develop a systematic data-led modelling framework to assess the effect of the morphologies on the key properties and functionalities of M7C3 carbides under different loading conditions.

In this paper microstructure based modelling is applied to M7C3 carbides. An effective framework has been developed to transfer microstructure of M7C3 carbides into image databases for statistical structure analysis and modelling. A mechanical-thermal-electrical modelling approach has been developed and is applied to different carbide structures for predicting the effective properties including stiffness, thermal and electrical properties. A new approach is developed to model the structure of individual carbides including the stress concentration factors associated with the shapes and the internal features, which is critical to wear and fracture of the carbides. The key functional feature of the program is presented including microstructure data, image processing and structure models with different scales. The work show that the internal feature could cause significant variation of stress concentration factors under different loading and boundary conditions. The key issues in data development and analysis of the structures are outlined. The link between engineering simulation and first principle calculation of the properties is analysed. The use of modelling for data-driven materials development, quality and performance prediction is discussed.

sciforum-096481: Mineralogical Studies of Low-Grade Iron Ores from Daitari Iron Ore Deposit, Odisha, India

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Iron is one of the most important metallic elements and covers around 5.05% of the Earth's crust. It has widespread applications in our day-to-day life, from household equipment to large industries. Due to rapid increases in the demand for steel in both the global and domestic market, as well as due to an ongoing depletion of high-grade iron ores, industry actors and policy makers have started considering the utilization of low-grade iron ores. According to the National Steel Policy 2017, India aims to attain a steel production capacity of 300 MT by 2030. In order to achieve this target, we must improve the utilization of low-grade iron ores. In this study, we use a low-grade iron ore, specifically banded hematite jasper (BHJ) from Daitari Iron Ore Mines, Odisha, India. The aim of this study is to understand the morphology, mineralogy, texture, and chemistry of BHJ. The characterization of BHJ is carried out using X-ray diffraction (XRD), X-ray fluorescence spectroscopy (XRF), optical microscopy, and scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDS). The XRD results suggest that quartz is the major gangue mineral, while hematite is the major iron mineral. The XRF analysis shows that the Fe content of BHJ is around 30%, and its SiO_2 content is around 54%, along with minor elements in varying proportions. Optical microscopic studies indicate the presence of alternate bands of hematite and quartz in BHJ, while SEM-EDS demonstrates how iron and silicate phases are associated with each other. This study allows for the optimization of conventional liberation or beneficiation practices for low-grade iron ores.

sciforum-094289: Optical and pressure-induced investigations of double perovskite Ba_2TiMnO_6 from the first principles

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Double perovskite (DP) compounds have been reported to possess many valuable properties and are considered excellent candidates for magnetocaloric applications, high-performing semiconductivity in optoelectronic devices, and photo(electro)chemical energy storage systems [1-4]. To explore the physical properties of double perovskite Ba_2TiMnO_6, we examined its optical and pressure dependence utilizing PBE-GGA and PBE-GGA+U exchange—correlation energy functionals. Following previous findings, DFT calculations revealed direct semiconducting band-gaps of 0.82, 0.98, and 1.27 eV, respectively [5]. Moreover, the optical properties show high dielectric constants, a robust light absorption coefficient in the UV energy range, and a significant optical conductivity of 6.53 × 105 cm−1, making Ba_2TiMnO_6 a promising candidate for high-performance perovskite solar cells in optoelectric applications. We identified that optical properties below 10 eV are mostly due to intraband and interband transitions of Mn-3d electrons. Employing the Projected Augmented Wave (PAW) method, we also studied the impact of pressure on crystal structure and density of states. Notably, near 8 GPa, there appears to be a structural distortion, accompanied by a sharp increase in the semiconducting gap.

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sciforum-096551: Three-dimensional characterization of Fe-rich intermetallics in Al-Si-Mg (A6xxx) aluminium alloy DC cast billets with an increased scrap content by X-ray tomography

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The characterization of Fe-rich intermetallic compounds (Fe-IMCs) in DC casting billets of aluminium alloys is critical for understanding their downstream processing and the properties of the final components. The use of recycled aluminium scrap in the formulation of these alloys results in the accumulation of Fe and other elements and modifies the volume fraction, the size and the shape of these Fe-IMCs. Standard techniques, like optical or electronic microscopy, allow for 2D visualization and quantitative comparison but do not provide enough information about the real 3D morphology of the intermetallics or the connectivity between them. In this study, we have used X-ray computed tomography to evaluate the 3D features of the intermetallics in DC billets for an Al-Si-Mg alloy with different levels of Fe in the as-cast and homogenized conditions. The 3D analysis shows that increasing Fe in the alloy results in thicker, more elongated and more interconnected particles, while during homogenization, the particles become thinner and more rounded and fragmented. We also provide a detailed comparison between the 2D and 3D results. The use of real 3D morphology characteristics of the secondary phases is more accurate and will allow a better understanding of the solidification process forDC billets in industry, as well as the subsequent microstructure and the properties of the extruded components.

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