



**GENERALITAT
VALENCIANA**

Conselleria de Educació,
Universitats y Empleo



1ST GREENMAT WORKSHOP

12TH DECEMBER 2024



Universidad de Valencia

Sala Vicente Such Belenguer, Departamento de Física Aplicada

C/Dr. Moliner 50, Burjassot, E-46100

Valencia, Spain

Introduction

The main objective of the GREENMAT project, supported by Conselleria de Educacion, Universidad y Empleo from Generalitat Valenciana with the PROMETEO grant CIPROM/2021/075, is the study, evaluation and optimization of materials for the development of green technologies in three areas of great industrial and domestic impact: photocatalysis, refrigeration, and thermoelectric generation. Since the beginning of the GREENMAT project, using high-pressure techniques, we have contributed to the development and characterization of new materials for the development of technologies that contribute to reducing the carbon footprint. The GREENMAT 2024 Workshop aims to bring together researchers who utilize extreme-conditions to study a wide range of material properties across various scientific disciplines such as condensed-matter physics, solid-state chemistry, geophysics, and materials science.

Venue

The GREENMAT 2024 Workshop will take place in Valencia December 12, 2024, at the Vicente Such Belenger seminar room (ground floor, Departamento de Física Aplicada, Universitat de Valencia).

Address: Edificio de Investigación, Dr. Moliner 50. 46100 Burjassot.

How to arrive: Visit <https://www.uv.es/uvweb/departament-fisica-aplicada-electromagnetisme/ca/departament-fisica-aplicada-electromagnetisme-1285858295693.html>

General Schedule

Morning – Chairman: Simone Anzellini (ICMUV)

9:00 Opening Session – Daniel Errandonea (ICMUV)

9:05 Raffaella Torchio (ESRF): The high-power laser facility at the ESRF

9:35 Dominik Spahr (Goethe University Frankfurt): Diversity of the geometry of the $[C_2O_5]^{2-}$ -groups in pyrocarbonates

10:05 Ganapathy Vaitheeswaran (Univ. of Hyderabad): Pressure-induced amorphization and robust hourglass dispersion in topological material: AuI

10:35 Benedito Donizeti Botan-Neto (ICMUV): High-pressure structural phase transitions in $MgCO_3 \cdot 3H_2O$ nesquehonite

10:50 Peijie Zhang (ICMUV): Post-synthetic transformations of hybrid metal halides via high-pressure polymerization

11:05 [Coffee Break](#)

11:30 Robin Turnbull (ICMUV): Pyramidal inversion in the solid state

12:00 Anna Herlihy (Diamond): High pressure total scattering using radial DACs

12:30 Josu Sanchez-Martin (ICMUV): Columbite single-crystal CoV_2O_6 under high pressure: An XRD and Raman spectroscopy study

12:45 Neha Bura (ICMUV): Pressure-dependent x-Ray diffraction analysis of scheelite-type perrhenates

13:00 [Lunch Break](#)

Afternoon – Chairman: David Santamaria (ICMUV)

14:45 Alberto Otero de La Roza (Univ. de Oviedo): Powder-diffraction-based structural comparison for crystal structure prediction under pressure

15:15 Juan Angel Sans (UPV): Helium trapping in Sr_2FeIrO_6 double perovskite under high pressure

15:45 Jose Luis Rodrigo (ICMUV): Thermal equation of state of rhodium characterized by resistively heated diamond-anvil cell

16:00 Pablo Botella (ICMUV): Structural and optical study on defect-functionalized multivariate modulated Zr UiO-66 under high-pressure

16:15 Enrico Bandiello (UPV): Transformation of electron-rich multicenter bonds into electron-deficient multicenter bonds in CsI_3 under compression

16:30 Hussien Osman (UPV): Chemical bonding in $CsIO_3$ under pressure

16:45 [Closing ceremony](#)

The High Power Laser Facility at the ESRF

R. Torchio¹, J.-A. Hernandez¹, N. Sevelin-Radiguet¹ and O. Mathon¹

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The High-Power Laser Facility at the ESRF [1] is a laser-driven dynamic compression platform coupled to the energy-dispersive X-ray absorption spectroscopy beamline ID24-ED at the ESRF and offers *in situ* high quality single-bunch (100 ps) XANES and EXAFS measurements between 5 and 28 keV. It enables the investigation of local microstructure and electronic structure of matter at extreme conditions of pressure and temperature, up to multi-Mbar and several 1000s K range.

HPLF drive laser currently delivers 60 J in 4 to 15 ns square pulses, producing ablation pressures up to 140 GPa in black kapton. The facility is equipped with two line-imaging VISAR and a line-imaging streak optical pyrometry system.

The science case ranges from fundamental science to planetary science and material/industrial science. In this presentation I will provide an overview of the facility, and a selection of scientific results obtained during the first two years of operation.

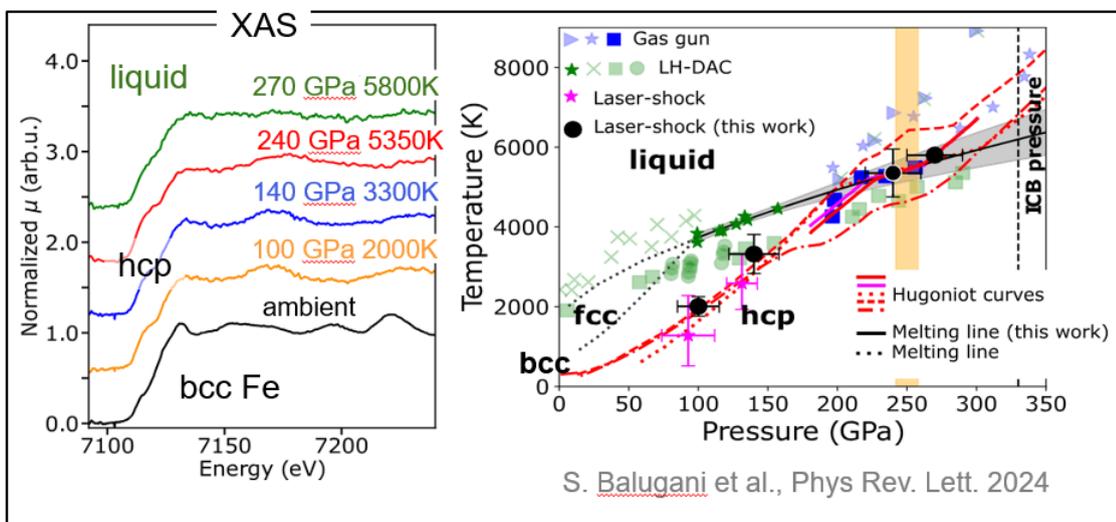
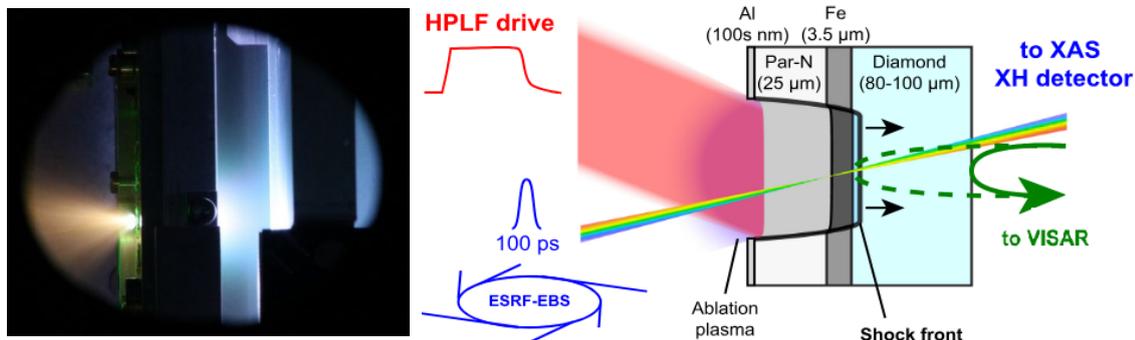


Fig. 1: top left: photo acquired during the shock event; top right: scheme of the laser-XAS-VISAR experiment. Bottom: results on laser shocked Fe up to 300 GPa and 6000K.

[1] J.-A Hernandez, N. Sevelin-Radiguet, R. Torchio et al., High Pressure Research 2024

Diversity of the geometry of the $[\text{C}_2\text{O}_5]^{2-}$ -groups in Pyrocarbonates

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Carbonates are the major reservoir of carbon in the Earth's crust. Hence, understanding their behaviour at different p, T -conditions and reactions with other phases is of great interest to understand the deep carbon cycle. The well-known sp^2 -carbonates contain trigonal planar $[\text{CO}_3]^{2-}$ -groups. Initially these were found to be stable up to high pressures (~ 70 GPa) and high temperatures. However, reactions of $\text{Ca}[\text{CO}_3]$ with oxides or CO_2 demonstrated that new carbonates ($\text{Ca}_2[\text{CO}_4]$ and $\text{Ca}_2[\text{C}_4\text{O}_{10}]$) can be obtained at lower pressures [1-3]. In these sp^3 -carbonates $[\text{CO}_4]^{4-}$ -groups can polymerize by corner-sharing, which was not observed in sp^2 -carbonates. During experiments exploring reactions of CO_2 with sp^2 -carbonates at moderate p, T -conditions we found a novel type of sp^2 -carbonates called pyrocarbonates [4]. In pyrocarbonates two $[\text{CO}_3]^{2-}$ -groups are linked by sharing one oxygen atom forming a $[\text{C}_2\text{O}_5]^{2-}$ -group. We solved the crystal structures of pyrocarbonates with different geometries of the $[\text{C}_2\text{O}_5]^{2-}$ -groups (Fig. 1) by synchrotron single crystal diffraction, and supported our SC-XRD-data by DFT-calculations and Raman spectroscopy [4,5].

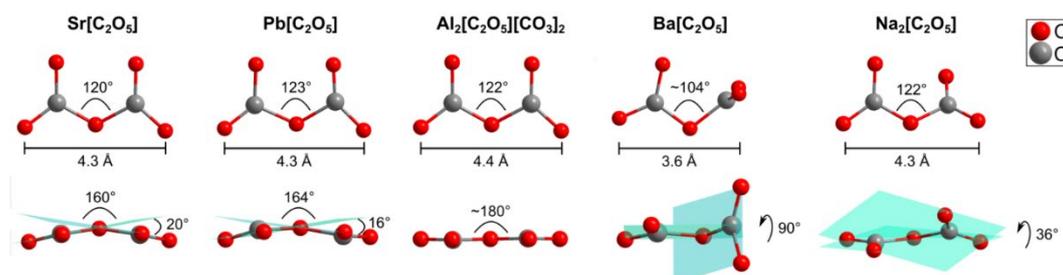


Fig. 1: Geometry of the $[\text{C}_2\text{O}_5]^{2-}$ -groups in different pyrocarbonates [5].

We acknowledge funding from the DFG (BA4020, WI1232, FOR2125/CarboPaT, BY101/2-1, BY112/2-1) and acknowledge DESY and ESRF for the provision of experimental facilities and beam time. B.W. is grateful for support by the Dassault Systemes Science Ambassador program.

[1] Bayarjargal et al. *Phys. Earth Planet. Inter.*, **281**, 31 (2018), [2] Binck et al. *Am. Mineral.*, **107**, 336 (2022), [3] Binck et al. *ACS Earth Space Chem.*, **6**, 73 (2022), [4] Spahr et al. *J. Am. Chem. Soc.*, **144**, 2899 (2022), [5] Spahr et al. *Chem. Commun.*, **59**, 11951 (2023)

Pressure-Induced Amorphization and Robust Hourglass Dispersion in Topological Material: AuI

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Pressure-induced amorphization (PIA) is a critical area of research in materials science with significant implications for both fundamental understanding and practical applications. This study investigates the PIA and topological behavior of the aurophilic material AuI using first-principles calculations. AuI consists of polymeric Au–I zigzag chains linked via Au⋯Au aurophilic interactions forming 2D layers, which are held together by weak van der Waals forces among I atoms (see Fig. 1). Our calculations show that, in ambient conditions, the elastic constants and phonon dispersion curves confirm the mechanical and dynamical stability of AuI. However, under pressure, we observe a dynamical instability characterized by the softening of an acoustic E_u mode around 7 GPa. The deviation of the calculated elastic constants from the Born stability criterion at this pressure indicates mechanical instability, aligning with experimental findings related to PIA attributed to phonon softening and elastic instability. Additionally, our electronic band structure calculations indicate an indirect bandgap of 2.31 eV. In the presence of spin-orbit coupling, the Z_2 invariants confirm that AuI is a non-trivial topological material, exhibiting a type-A hourglass dispersion with a movable Dirac point. Moreover, pressure-dependent electronic structure analysis reveals that band topology remains stable up to the amorphous transition, indicating unique structural and electronic properties that merit further investigation into this class of aurophilic materials.

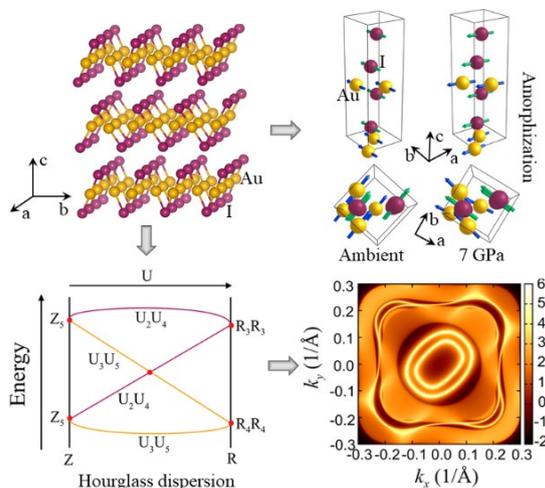


Fig. 1: Crystal structure of AuI, acoustic doubly degenerate mode (E_u) of AuI at 0 and 7 GPa, schematic figure showing the hourglass dispersion, and the Fermi arcs corresponding to the movable Dirac point.

Dense hydrated carbonates: The case of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ Nesquehonite

Benedito Donizeti Botan-Neto^{1,*}, Lkhamsuren Bayarjargal², Elena Bykova², Javier Gonzalez-Platas³, Alberto Otero-de-la-Roza⁴ and David Santamaría-Pérez¹

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*Corresponding Author: bebone@uv.es

Magnesium carbonates are among the most abundant carbonates in the Earth's mantle and play a crucial role in the Deep Carbon Cycle [1]. Nesquehonite ($\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$) stands out as the predominant and stable hydrated magnesium carbonate phase under ambient conditions, rendering it a promising material for long-term CO_2 capture and storage (CCS) applications [2]. High-pressure experiments confirmed two pressure-induced phase transitions in nesquehonite at 2.4 and 4.0 GPa, named HP1 and HP2 phases, respectively [3]. In this talk we will focus on the structural determination and physical characterization of these post-nesquehonite's HP1 and HP2 phases [4]. Structural analyses were conducted through in-situ synchrotron single-crystal X-ray diffraction in diamond-anvil cells. As illustrated in Fig. 1, denser phases of nesquehonite were determined at 3.1 and 11.6 GPa. The first pressure-induced phase (HP1) is described with an enlarged cell ($Z = 16$) and the complex $\text{MgCO}_3 \cdot 2\text{H}_2\text{O}$ double chains of nesquehonite, consisting of $[\text{CO}_3]$ trigonal planar and distorted $[\text{MgO}_6]$ octahedral groups, approach apically and the $[\text{CO}_3]$ carbonate groups are no longer coplanar. The HP2 phase exhibits a cell with $Z = 8$, accompanied by an increase in coordination number from 6 to 7, leading to distorted $[\text{MgO}_7]$ pentagonal bipyramids. The apical approximation of the chains causes a higher directionality of the H-bonds along the longer crystallographic axis. Density Functional Theory (DFT) calculations conducted on nesquehonite polymorphs confirm that the HP2 phase is energetically more stable at high pressures and suggest that the HP1 is an intermediate metastable phase.

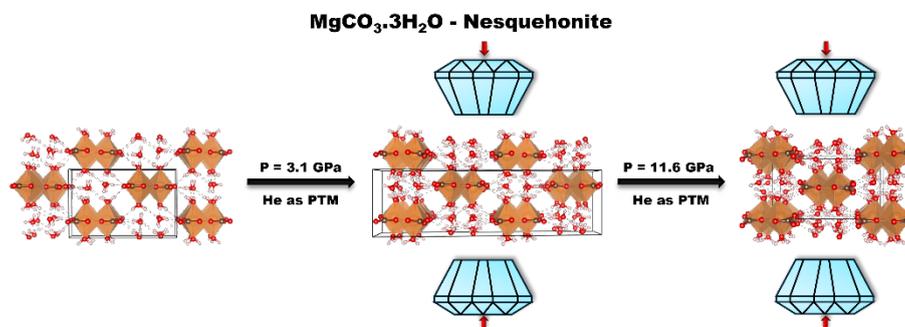


Fig. 1: Schematic representation of dense post-nesquehonite phases at 3.1 and 11.6 GPa.

- [1] R. Dasgupta, *Reviews in Mineralogy and Geochemistry* **75(1)**, 183 (2013).
 [2] A. Kastrinakis, *et al.*, *International Conference on Raw Materials and Circular Economy* **5(1)**, 60 (2021).
 [3] D. Santamaría-Pérez, *et al.*, *Crystal Growth & Design* **24(3)**, 1159 (2024).
 [4] B. Botan-Neto, *et al.*, *Inorganic Chemistry* **63**, 15762–15771 (2024).

Post-synthetic Transformations of Hybrid Metal Halides via High-Pressure Polymerization

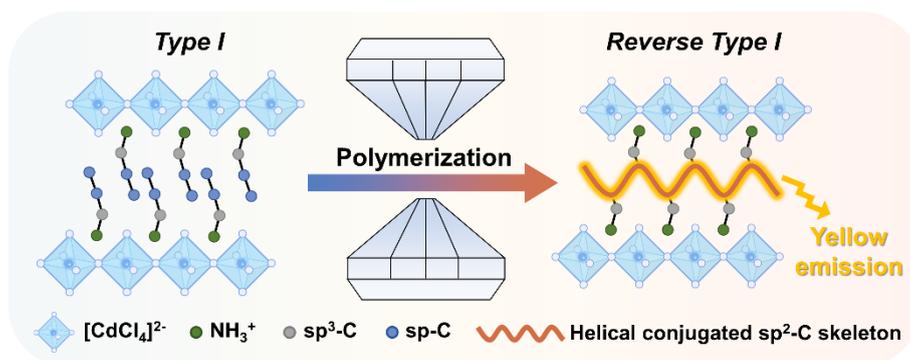
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Hybrid metal halides (HMHs) with typical host-guest structures exhibit intentional, unique, and synergistic features of organic and inorganic components. Here, a novel 2D HMH with conjugated polyacetylene skeleton is synthesized by pressure-induced solid-state topochemical polymerization (SSTP) of $(\text{C}_3\text{H}_6\text{N})_2\text{CdCl}_4$ ($\text{C}_3\text{H}_6\text{N}^+$ = propargylamine cation, **PA-CdCl**). Compared with the faint blue emission, polymerized $(\text{C}_3\text{H}_6\text{N})_2\text{CdCl}_4$ (**P-PA-CdCl**) exhibits a strong yellow emission that originates from helical polyacetylene skeletons. Furthermore, **P-PA-CdCl** exhibits the narrowed bandgap of 2.26 eV, which is almost half of initial **PA-CdCl**. Theoretical calculations reveal that the transformation of optical properties is due to the reconstruction of the band alignment from type-I to reverse type-I via SSTP. Such SSTP can be replicated in other 2D HMHs to yield polymerized HMHs with identical emissive polyacetylene skeletons. This study showcases the potential of pressure-induced SSTP in developing novel materials with intriguing properties, establishing it as a valuable platform for structural regulation of HMHs and polymer synthesis.



[1] P. Zhang, X. Xu, Y. Li, Y. Fei, J. Liu, B. Xu, S. Guo, J. Zhu and Z. Quan. Polymerized Hybrid Metal Halides with Yellow Emissive Helical Polyacetylene Skeleton via Pressure-Induced Polymerization. *Chem. Mater.* **2024**, 36, 8504-8513.

Funding: CIPROM/2021/075, PID2022-138076NB-C41, RED2022-134388-T, and MFA/2022/007 projects.

Pyramidal inversion in the solid state

Robin Turnbull*^a, Javier Gonzalez Platas^b, Alfonso Muñoz^c, Josu Sánchez-Martín^a, M. Jasmin^d,
Gaston Garbarino^e, Daniel Errandonea^a and Akun Liang^a

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Pyramidal inversion is a stereochemical phenomenon that describes the interconversion between two equivalent pyramidal configurations of the same chemical species. Using the IO₃ molecule as a prototypical trigonal pyramidal unit, pyramidal inversion has been observed in the solid state by applying hydrostatic pressure to crystals of barium di-iodate monohydrate, Ba(IO₃)₂·H₂O, without chemical reaction or the introduction/elimination of guest molecules (see Fig. 1). The pyramidal inversion was identified by high-pressure single-crystal synchrotron X-ray diffraction from the appearance of charge density on the unoccupied side of the IO₃ pyramid at pressures above 5 GPa. The percentage of inverted pyramids increases with pressure, from 2.5% at 5.10(5) GPa to 17.5% at 14.84(5) GPa. The energetic competition between the original and inverted IO₃ pyramids as a function of pressure is investigated by density functional theory calculations, finding the two configurations to be very close in energy. Factors contributing to the observation of pyramidal inversion in barium iodate monohydrate are discussed and it is suggested that hydrogen bonding due to the presence of water may play a significant role.

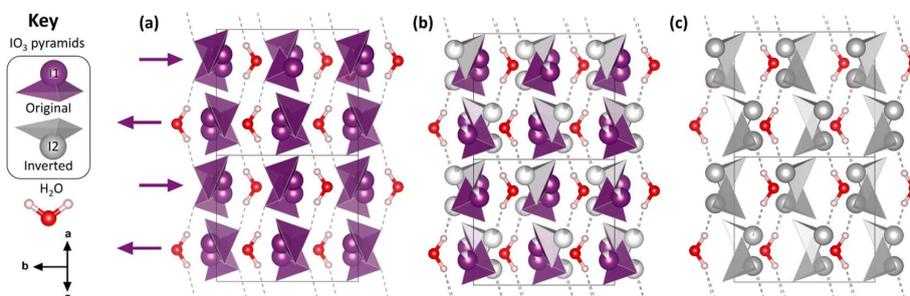


Fig. 1 | The crystal structure of Ba(IO₃)₂·H₂O with increasing pressure.

Funding: CIPROM/2021/075, PID2022-138076NB-C41, RED2022-134388-T, MFA/2022/007, and CIAPOS/2021/20 projects.

High pressure total scattering using radial DACs

Anna Herlihy^{1,*}, Silvia Boccato², Pablo Botella³, Phil Chater¹, Konstantinos Georgarakis⁴,
Jose Luis Rodrigo-Ramon³, Simone Anzellini³

¹ *Diamond Light Source Ltd., Harwell Science & Innovation Campus, Diamond House, Didcot, OX11 0DE, UK* ² *Sorbonne Université, Muséum National d'Histoire Naturelle, UMR CNRS 7590, Institut de Minéralogie, de Physique des Matériaux et de Cosmochimie, IMPMC 75005 Paris, France* ³ *Departamento de Física Aplicada - Instituto de Ciencia de Materiales, Matter at High Pressure (MALTA) Consolider Team, Universidad de Valencia, Edificio de Investigación, C/Dr. Moliner 50, Burjassot, Valencia, 46100, Spain* ⁴ *School of Aerospace, Transport and Manufacturing, Cranfield University, Cranfield, UK*

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Combined high-pressure and total scattering experiments are notoriously challenging due to the need to account for non-sample scattering. Measurements performed in diamond anvil cells (DACs) in a standard geometry contain significant “contaminant” scattering from the diamonds. Measuring radially through a weakly scattering gasket (Figure 1) provides a significant improvement on non-sample scattering, however, these weakly scattering materials are incompatible with many commonly used pressure-transmitting media.

We present results from recent experiments conducted at Diamond Light Source, where we explored the potential of using novel low-Z metallic glass gaskets to recover local structure information about amorphous and crystalline materials up to moderate pressures of ~10 GPa.

This work supports the importance of total scattering techniques in elucidating the complex interplay between pressure and atomic structure. Novel gasket materials and data processing procedures will facilitate a wide range of important endeavors including understanding fundamental processes in geophysics and materials science and the design of novel functional materials.

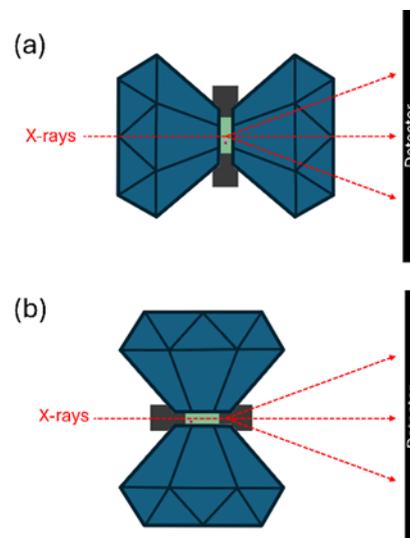


Figure 1: Diamond anvil cell set up for a) axial geometry

[1] S. Merkel and T. Yagi, *Rev. Sci. Instrum.*, 2005, 76, 7–10.

[2] W. Dong, K. Glazyrin, S. Khandarkhaeva, T. Fedotenko, J. Bednarčík, E. Greenberg, L. Dubrovinsky, N. Dubrovinskaia, H. P. Liermann and K. Kvashnina, *J. Synchrotron Radiat.*, 2022, 29, 1167–1179.

Columbite single-crystal CoV_2O_6 under High pressure: An XRD and Raman spectroscopy study

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Two new polymorphs of CoV_2O_6 starting in its columbite form were discovered via single-crystal X-ray diffraction and Raman spectroscopy by applying high-pressure conditions up to 54.9(1) GPa and ambient temperature. The first phase transition takes place at 19.9(1) GPa, preserving the space group ($Pbcn$) but undergoing a sudden symmetrisation of the polyhedra forming the structure, as well as a group shift of vibrational modes towards higher wavenumbers. The named columbite-II structure remains stable up to 45.6(1) GPa, where its Raman spectrum is totally shifted. The diffraction data have enough quality to be solved into a new monoclinic polymorph (space group $P2_1/c$). Both phase transitions are reversible when releasing pressure, but below 4.9(3) GPa the sample changes into a mixture of its natural brannerite structure, the initial columbite packaging and the $\gamma\text{-CoV}_2\text{O}_6$ polymorph. From the XRD analysis, the anisotropic compressibilities of all axes were obtained and the unit-cell volume vs pressure was fitted by a Birch–Murnaghan equation of state, obtaining the bulk moduli of both columbite polymorphs. Results for these two phases are also supported with DFT calculations showing good agreement.

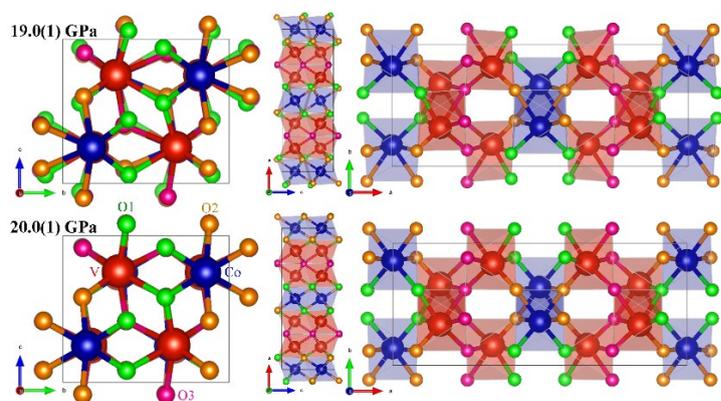


Fig. 1: The orthorhombic ($Pbcn$) crystal structure of CoV_2O_6 before (19.0(1) GPa) and after (20.0(1) GPa) the isostructural phase transition. Both structures are columbite-type, but the atom positions and unit-cell parameters vary significantly.

Pressure-Dependent X-Ray Diffraction Analysis of Scheelite-type Perrhenates

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Structural properties of Scheelite-type perrhenates were studied as a function of pressure using synchrotron radiation at the MSPD-BL04 beamline of ALBA using diamond-anvil cells. At ambient conditions, the three studied materials exhibit a tetragonal crystal structure with space group $I4_1/a$ (S.G. #88). However, with pressure a transition from Scheelite-to-M'-Fergusonite ($P2_1/c$, S.G. #14) structure has been observed at 7.4 GPa and 1.6 GPa for $KReO_4$ and $RbReO_4$, respectively with a 2.6 % decrease in volume. On the other hand, $AgReO_4$ shows a second-order transition to an M-fergusonite crystal structure ($I2/a$, S.G. #15). The bulk modulus for perrhenates was estimated using Birch Murnaghan equation of state. Bulk Modulus and compressibility analysis show that $RbReO_4$ is the most compressible of the three studied compounds followed by $KReO_4$ and $AgReO_4$.

Funding: CIPROM/2021/075, PID2022-138076NB-C41, RED2022-134388-T, and MFA/2022/007 projects.

Powder-Diffraction-Based Structural Comparison for Crystal Structure Prediction Under Pressure

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Crystal structure prediction (CSP) is a computational method for the prediction of the thermodynamical stable phase (or the energy landscape) from the stoichiometry of a compound. CSP is a hard problem because it involves a global search over the space of all possible structures, and it is computationally very demanding. It would be beneficial to be able to use experimental information, such as powder X-ray diffraction (XRPD) patterns, to inform and speed up the CSP search for the stable structure. This is particularly important in the field of high-pressure experimental X-ray diffraction experiments, where the powder data available is generally not of enough quality to allow the unequivocal determination of high-pressure crystal structures. To assist CSP, it is necessary to compare calculated structures with experimental patterns but, for achieving this, two problems need to be solved: i) lack of vibrational effects (and errors from the DFT method) may cause deformations in the unit cell relative to experiment, shifting peak positions, and ii) experimental patterns have peak shapes and widths that are directly not calculable from the structure. In this work, we present a crystal similarity index (VCGPWDF) for comparing structures with experimental patterns that allows for lattice deformations of the former. GPWDF is simple, efficient, fully automatic, and does not require indexing of the pattern. It gives meaningful results even if the experimental pattern is of very low quality. The development of VCGPWDF opens the door for XRPD-assisted CSP searches aimed at the solution of structures under high pressure.

Helium Trapping in Sr₂FeIrO₆ Double Perovskite Under High Pressure

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Our study investigates the effects of helium on the properties of the double perovskite Sr₂FeIrO₆, focusing on the potential for helium trapping within the lattice at high pressures. Double perovskites like Sr₂FeIrO₆ have garnered considerable attention due to their promising functionalities [1]. We employed synchrotron-based X-ray techniques alongside density functional theory (DFT) calculations to explore how helium affects the lattice structure, stability, and magnetic configuration of Sr₂FeIrO₆.

Our experiments revealed a notable volumetric anomaly above 5 GPa, suggesting helium's infiltration into the material's crystalline structure. This anomaly is characterized by an unexpected expansion in certain lattice parameters, implying that helium atoms are physically trapped within the perovskite framework. Further computational simulations support this observation, revealing specific atomic sites that are particularly susceptible to helium occupancy.

These results highlight the importance of selecting appropriate pressure media in high-pressure studies, as even inert gases can induce unexpected structural transformations in functional materials.

Thermal equation of state of rhodium characterized by resistively heated diamond anvil cell

Jose Luis Rodrigo Ramon^{1,*}, Simone Anzellini¹, Claudio Cazorla³, Pablo Botella¹, Aser Garcia-Beamud¹, Josu Sanchez-Martin¹, Gaston Garbarino², Angelika Rosa², Samuel Gallego-Parra², and Daniel Errandonea¹

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²European Synchrotron Radiation Facility, 71 Avenue des Martyrs, Grenoble, CS 40220, 38043, France

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The high-pressure and high-temperature structural, mechanical, and dynamical stability of rhodium has been investigated via synchrotron X-ray diffraction using a resistively heated diamond anvil cell and density functional theory. The isothermal compression data have been fitted with a Rydberg-Vinet equation of state (EoS) with best-fitting parameters $V_0 = 55.046(16) \text{ \AA}^3$, $K_0 = 251(3) \text{ GPa}$, and $K'_0 = 5.7(2)$. The thermal equation of state has been determined based upon the data collected following four different isotherms and has been fitted to a Holland and Powell thermal equation-of-state model with $\alpha_0 = 3.36(7) \times 10^{-5} \text{ K}^{-1}$. The measured equation of state and structural parameters have been compared to the results of ab initio simulations. The agreement between theory and experiments is generally quite good. The present results solve controversies between previous studies which reported values of the bulk modulus from 240 to 300 GPa.

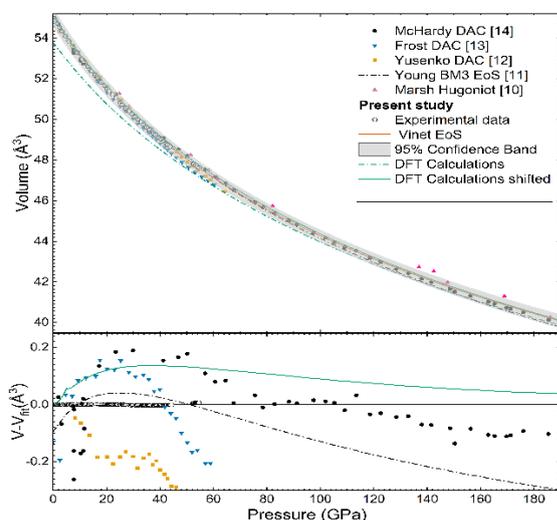


Fig. 1: (Top) Measured and calculated volume of rhodium as a function of pressure compared with literature data and ab initio calculations. (Bottom). Difference between measured and fitted volume, Vinet formulation with $V_0 = 55.046(10)$, $K_0 = 251(3)$, and $K' = 5.7(2)$

Structural and optical study on defect-functionalized multivariate modulated Zr UiO-66 under high-pressure

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Metal-organic frameworks (MOFs) are known for their versatile, tunable properties, enhancing performance in various applications. Recent studies demonstrate that defect-functionalized, multivariate modulated (MTVM) Zr UiO-66 structures can modify Zr₆ clusters, altering porosity and electronic structures [1]. This work explores high-pressure behavior in three Zr UiO-66 derivatives functionalized with *p*-substituted benzoate groups (-SO₃, -NO₂, -SH) using in-situ X-ray diffraction (XRD) with silicone oil and methanol-ethanol (4:1) as pressure-transmitting media (PTM). The alcohol mixture penetrates and stabilizes the structure up to 15 GPa, unlike silicone oil, and induces reversible chemical interactions. An unexpected volume increase was observed with the alcohol PTM, also observed in the pristine material [2], while the optical band gap decreased by ~1 eV at 20 GPa.

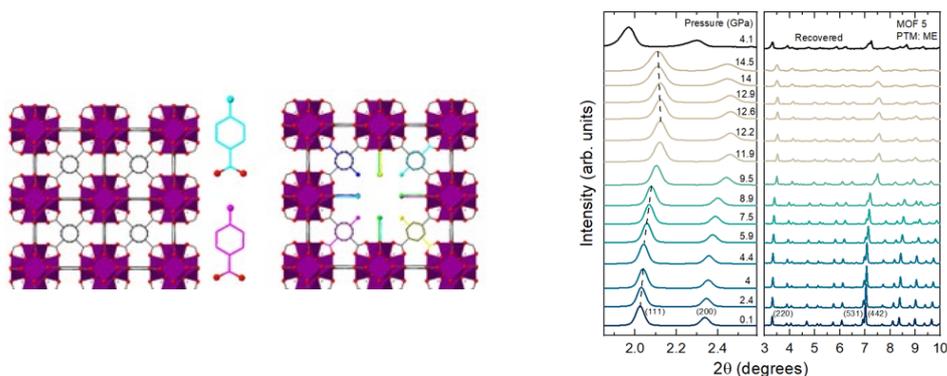


Fig. 1. Schematic representation of MTVM MOF with defect-induced reo topology compared with the pristine MOF [1]. XRD patterns under compression.

[1] Carmen Rosales-Mártinez *et al.* Chem. Commun., 2024, 60, 8280

[2] Georgina P. Robertson *et al.* Inorg. Chem. 2023, 62, 10092–10099

Funding: CIPROM/2021/075, CIAPOS/2023/406, PID2022-138076NB-C41, RED2022-134388-T, and MFA/2022/007 projects.

Transformation of electron-rich multicenter bonds into electron-deficient multicenter bonds in CsI₃ under compression

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We present a joint experimental and theoretical study of the structural, vibrational and chemical behavior of cesium triiodide (CsI₃) and of the I-I bonds in its high-pressure (HP) phases. At ambient conditions, CsI₃ crystallizes in an orthorhombic *Pnma* structure, with asymmetric linear I³⁻ units found in a herringbone motif (Fig. 1) [1,2]. CsI₃ gradually and

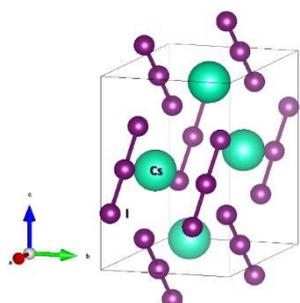


Fig. 1: *Pnma* phase of CsI₃.

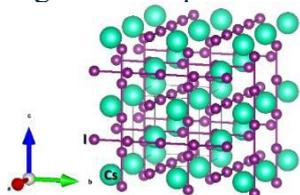


Fig. 2: *Pm-3n* phase of CsI₃.

reversibly symmetrizes with pressure, going to a trigonal *P-3c1* phase above 1.3 GPa, in which symmetric linear I³⁻ units are arranged in a linear fashion. Finally, a cubic *Pm-3n* structure occurs above 22 GPa [1,2]. Interestingly, the I³⁻ units polymerize in the cubic HP phase forming infinite linear iodine chains (I_∞) along the three coordinated directions (Fig. 2) [3]. We show that a change in the character of the I-I bonds in CsI₃ occurs from the electron-rich multicenter bonding (ERMB) in the single I³⁻ units of the low-pressure phases to the electron-deficient multicenter bonding (EDMB) in the I_∞ chains of the cubic HP phase [4].

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[2] N. N. Patel, M. Sunder, A. B. Garg, H. K. Poswal, *Phys. Rev. B* 96, 174114 (2017).

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Chemical Bonding in CsIO₃ under Pressure

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In this contribution, we conduct a joint high-pressure experimental and theoretical study of the distorted perovskite CsIO₃ since this compound with rhombohedral $R3m$ structure (see **Fig. 1**) was assumed to transform into a cubic $Pm\bar{3}m$ perovskite on increasing pressure, as already predicted for isostructural RbIO₃ [1]. Interestingly, we have obtained that the $R3m$ phase of CsIO₃ at room conditions undergoes two second-order pressure-induced phase transitions. The first one occurs around 14 GPa to an orthorhombic ($Pmn2_1$) phase while the second one is to a tetragonal ($P4/nmm$) at around 50 GPa. With increasing pressure, the original IO₃ units present in the rhombohedral phase at room pressure transform gradually into IO₆ units as the tetragonal (quasi-cubic) phase is approached. Concomitantly, the chemical I—O bonds change from the classical simple covalent 2c-2e bonds in IO₃ units towards electron-deficient multicenter bonds (EDMBs) in slightly distorted IO₆ units [2,3]. This behavior has been recently discussed in Sr(IO₃)₂HIO₃[4].

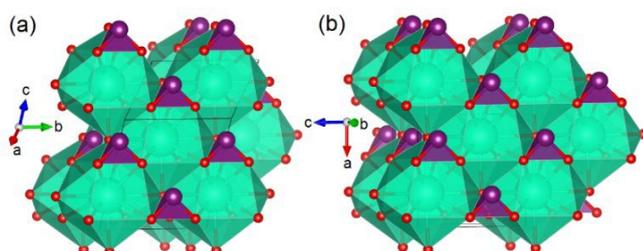


Fig. 1: Crystal structure of CsIO₃ in the $R3m$ phase (a) and $Pmn2_1$ phase (b). Polyhedra of CsO₁₂ (green) and IO₃ (violet) are shown. The Cs, O, and I atoms are shown in green, red, and violet, respectively.

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Funding: CIPROM/2021/075, PID2022-138076NB-C41/42, RED2022-134388-T, MFA/2022/007, and MFA/2022/025 projects.