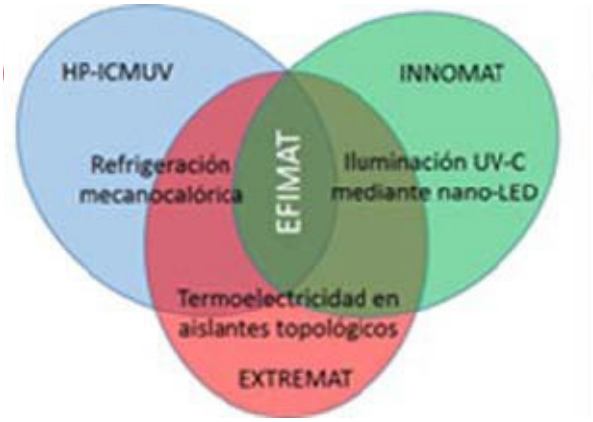
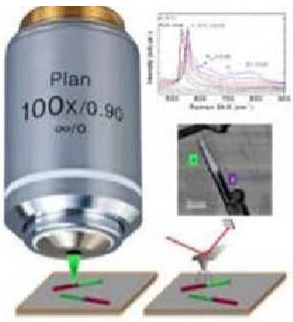
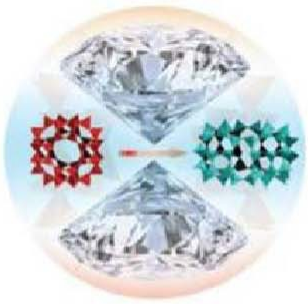


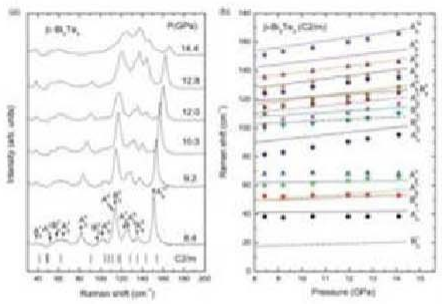
Program Book

FOURTH EFIMAT WORKSHOP









GENERALITAT VALENCIANA | Proyecto EFIMAT PROMETEO 2018 / 123

PARC CIENTÍFIC
VNIVERSITAT DE VALÈNCIA

ADEIT

Plaza Virgen de la Paz, 3. Valencia

November 4th, 2021

Introduction

EFIMAT is a research project supported by Generalitat Valenciana by means of a PROMETEO grant (Prometeo/2018/123 EFIMAT). This seeks to make a breakthrough in the use of energy through innovative but realistic proposals that take advantage of the synergy of three excellent research groups with complementary experiences. EFIMAT aims to develop advanced materials (LED-UV, materials with giant mechano-caloric effect, and thermoelectric materials based on topological insulators). The goal is to contribute to the development of efficient-energy applications highly demanded by industry and society, and which will allow our socio-economic environment to be at the vanguard of efficient-energy solutions. This fourth workshop covers almost all relevant research areas for EFIMAT and it is organized to boost the stimulating exchange of scientific ideas and results, creating new insights and collaborations.

Venue

The fourth edition of EFIMAT, Workshop for Advanced Materials for the efficient use of energy, will take place in Valencia November 4th 2021, at ADEIT, located at Plaza de la Virgen de la Paz 3, at the very center of Valencia:

https://www.adeituv.es/contacto/

General Schedule

November 4

Morning – Chairperson: Daniel Errandonea

9:30 Opening Session – Ana Cros (ICMUV)

9:40 Alberto Otero de la Roza (Univ. Oviedo, Spain)
Interatomic Delocalization in Solids Under Pressure

10:20 Robin Turnbull (ICMUV, Univ. Valencia, Spain)
Pressure-induced β→γ phase transition in copper(II) pyrovanadate ($Cu_2V_2O_7$) by single-crystal X-ray diffraction and absorption spectroscopy

11:00 Coffee Break

11:30 Valentín García Baonza (IGEO-CSIC, Madrid, Spain)
How much energy can a chemical bond withstand?

12:10 Claudio Cazorla (UPC, Barcelona, España):
Strain Engineering of Photocatalytic Materials

12:50 Lunch Break

Afternoon – Chairperson: Núria Garro

15:00 Bruno Daudin (CEA, Grenoble, France)
Nanowire-specific electrical doping regime

15:40 Julie Villanova (ESRF, Grenoble, France)
Synchrotron X-Ray Nano-Imaging for Energy Materials

16:20 Pablo P. Boix (ICMUV, Univ. Valencia, Spain)
Limiting processes in perovskite optoelectronics: new structures for new challenges

Interatomic Delocalization in Solids Under Pressure

Alberto Otero de la Roza[1,*]

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Bader's localization and delocalization indices (DIs) measure interatomic electron localization and electron sharing. At zero pressure, DIs between covalently bonded atoms are similar to the bond order. However, DIs exist between any pair of atoms in the system, which means that they can be used to measure electron delocalization in systems where van der Waals, ionic, or metallic bonding is dominant. For this reason, DIs rank among the most popular real-space indices used to elucidate the nature of a chemical bond. In this talk, I will present a new method that has been implemented in the critic2 program that allows the efficient and accurate calculation of DIs in solids. This new method opens up a new avenue for the study of chemical bonding in materials under pressure. The behavior of DIs with pressure in several model materials is examined.

Pressure-induced β→γ phase transition in copper(II) pyrovanadate ($Cu_2V_2O_7$) by single-crystal X-ray diffraction and absorption spectroscopy

Robin Turnbull[1,*], Javier Gonzáles-Platas[2], Fernando Rodríguez[3], Akun Liang[1], Catalin Popescu[4], Zhangzhen He[5], David Santamaría-Pérez[1], Alfonso Muñoz[6], Daniel Errandonea[1]

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[2] *Departamento de Física - Instituto Universitario de Estudios Avanzados en Física Atómica, Molecular y Fotónica (IUDEA), MALTA Consolider Team, Universidad de La Laguna, Avenida Astrofísico Fco. Sánchez s/n, La Laguna, Tenerife E-38204, Spain.*

[3] *MALTA Consolider Team, Departamento de Ciencias de la Tierra y Física de la Materia Condensada, Facultad de Ciencias, Universidad de Cantabria, 39005 Santander, Spain.*

[4] *CELLS-ALBA Synchrotron Light Facility, 08290 Cerdanyola del Vallès, Barcelona, Spain.*

[5] *State Key Laboratory of Structural Chemistry, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China*

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We report an experimental high-pressure single-crystal synchrotron X-ray diffraction study of $Cu_2V_2O_7$ under compression to 4 GPa at ambient temperature. The results unambiguously reveal a previously unknown first-order pressure-induced phase transition from monoclinic β-$Cu_2V_2O_7$ to triclinic γ-$Cu_2V_2O_7$ at low pressures (< 0.40 GPa). The presentation will discuss the two structures and how they are related. The phase transition is associated with a volume collapse of approximately 7%, an increase in oxygen coordination (from 5 → 6) of half of the Cu^{2+} coordination complexes, and a reorientation of 1-dimensional chains composed of edge sharing CuO_6 units. The phase transition is also characterised by an indirect → indirect electronic bandgap decrease of approximately 0.2 eV as measured by absorption spectroscopy (1.93 → 1.75 eV) and calculated via density functional calculations (1.93 → 1.76 eV). The bandgap of γ-$Cu_2V_2O_7$, the pressure-induced structural evolution and isothermal compressibility tensor are reported here for the first time. β-$Cu_2V_2O_7$ is found to have by far the lowest bulk modulus (B_0 = 19(2) GPa) of any previously studied vanadate material.

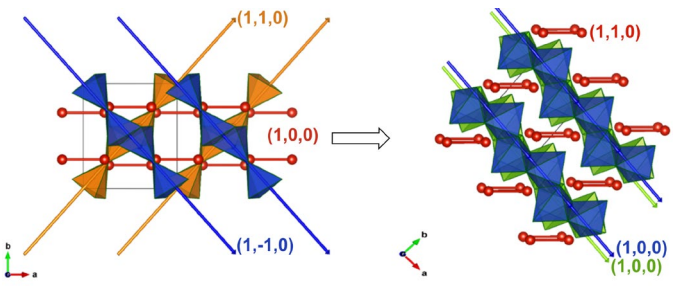


Figure 1: Crystal structures of β- and γ-$Cu_2V_2O_7$.

How much energy can a chemical bond withstand?

Valentín García Baonza[1,*]

[1]*Instituto de Geociencias IGEO (CSIC-UCM), C/ Doctor Severo Ochoa 7, Ciudad Universitaria, 28040 Madrid, Spain*

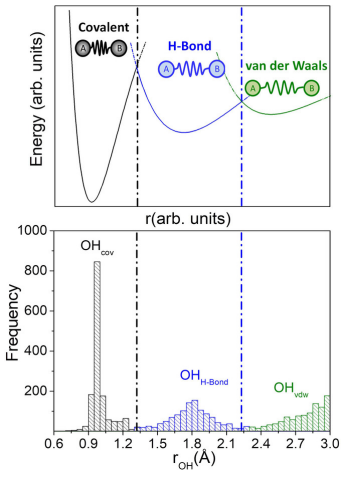
*E-mail: v.g.baonza@csic.es

The interrelationship between bond dissociation energies, bond orders or bond strengths and bond distances reflects the well-known correlation between atomic-level configurations and macroscopic observable properties. Surprisingly, while equilibrium bond distances and energies have been comprehensively studied, characterized, and tabulated, bond-breaking (or -formation) distances and energies have been marginally explored, even though they provide key information for synthetic routes of novel materials or for improving certain catalytic processes. In fact, the question "*At which interatomic distance a chemical bond disappears?*" is still controversial [1] despite of being crucial to understand and define the extent of chemical interactions and reactivity.

This talk aims to introduce a novel practical route to calculate bond critical distances and distances. The rationale behind our model is the existence of a formally universal generic (or universal) analytical function describing the potential energy curve of a pairwise interaction reference molecule. Here we will show that two distinct points on the potential energy curve of a pairwise interaction, namely the zero-energy crossing point (hard sphere) and the point where the stretching force constant vanishes (spinodal), allow us to anticipate the range of possible distances between two atoms in diatomic, molecular moieties and crystalline systems. Examples will be worked out to demonstrate convincingly the range of distances in which stable single covalent bonds in a number of systems, from diatomic molecules to crystalline solids under extreme conditions.

We will also discuss that the multimodal distribution found in the O−H distance histogram (reflects changes in the nature of the covalent O−H bond caused by hydrogen bonding or van der Waals interactions with the surrounding atoms), can be explained within a generalized *chained-interactions conjecture*.

These models can be used as a guide to determine the distances that will be unreachable (unstable) in the laboratory and anticipate restrictions to the synthesis of novel compounds (either molecules or crystals).



[1] L. Zhao, M. Hermann, W. H. E. Schwarz, G. Frenking, Nat. Rev. Chem. 2019, 3, 48–63.

[2] A. Lobato, M.A. Salvadó, J. M. Recio, M. Taravillo, V. G. Baonza, Angew. Chem. Int. Ed. 2021, 60, 17028-17036.

Strain Engineering of Photocatalytic Materials

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Photocatalytic materials are pivotal for the implementation of disruptive clean energy applications like conversion of H_2O and CO_2 into fuels and chemicals driven by solar energy. However, efficient and cost-effective materials able to catalyze the chemical reactions of interest when exposed to visible light are scarce due to the stringent electronic conditions that they must satisfy. Chemical and nanostructuring approaches are capable of improving the catalytic performance of known photoactive compounds, however, the complexity of the synthesized nanomaterials and sophistication of the employed methods make systematic design of photocatalysts difficult. Here, we present the results of recent first-principles studies on semiconductor materials that have the potential to improve the rational and systematic engineering of photocatalysts[1,2]. First, we show that application of biaxial stress on binary oxides can modify their optoelectronic and catalytic properties in a significant and predictable manner. In particular, upon moderate tensile strains CeO_2 and TiO_2 become suitable materials for photocatalytic conversion of H_2O into H_2 and of CO_2 into CH_4 under sunlight. The band gap shifts induced by biaxial strain are qualitatively reproduced by a simple analytical model that only depends on structural and dielectric susceptibility variations. And second, we assess the water-splitting photocatalytic potential of piezoelectric materials that, despite may react to mechanical stimuli by noticeably adjusting their band gaps and band alignments, have been seldom investigated to date. In particular, we present a high-throughput screening of piezo-photocatalyst materials performed over ~1,000 piezoelectrics that relies on a simple electrostatic model and first-principles calculations. A number of overlooked binary and tertiary piezo-photocatalysts emerge as very promising from our analysis, among which SiC stands out due to its superb optoelectronic tunability under uniaxial strain and facile synthesis.

[1] Liu, Z., Shenoy, J. N., Menendez, C., Hart, J. N., Sorrel, C. C. & Cazorla, C**.** *Strain engineering of oxide thin films for photocatalytic applications*. Nano Energy **72**, 104732 (2020).

[2] Liu, Z. & Cazorla, C**.** *First-principles high-throughput screening of piezo-photocatalyst materials for water splitting under visible light*. Submitted (2021).

Nanowire-specific electrical doping regime

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Introduction of electrical dopant species in semiconductors generally results in increasing built-up strain for increasing dopant densities, till reaching the solubility limit and/or a strain relaxation stage associated with extended defect formation. By contrast doping in nanowires (NWs) obeys a specific regime, associated with their unique morphology. In the case of GaN NWs grown on Si (111) by molecular beam epitaxy, the eased strain relaxation due to the large amount of free surface favors the incorporation of Si dopant at concentrations higher than in layers [1]. Also, specific adatom surface diffusion and reconstruction-stabilized sidewall stoichiometry are affecting dopant incorporation. Hence, atom probe tomography [2] and energy-dispersive X-rays spectroscopy (EDX) [3] experiments at the nanoscale demonstrate that preferential Mg incorporation through the m-plane side walls of GaN NWs leads to a higher Mg density in the NW periphery, about ten times larger than in the NW core. Scanning spreading resistance microscopy (SSRM) experiments were performed to investigate the effect of inhomogeneous dopant distribution on the electrical transport properties of n-type and p-type GaN NWs at the nanoscale. In Si-doped GaN NWs a conductive core surrounded by a more resistive shell was put in evidence, which is assigned to the depletion resulting from Fermi level pinning on m-plane surface states. By contrast, in the case of Mg-doped GaN NWs, the SSRM is one order of magnitude smaller at the periphery than at the centre of the Mg-doped GaN. This experimentally demonstrates that peripheral Mg incorporation in GaN NWs indeed counterbalances the depletion resulting from Fermi level pinning on m-plane surface states, which results in preferential current flow in the highly doped shell. For the same samples as measured by SSRM, EDX reveals a Mg concentration of about 2-4 $\times$ 10^{20} /cm^3 in periphery, higher by more than one order of magnitude compared to the NW centre where the Mg content is below the experimental detection limit of 10^{19}/cm^3. The coexistence of these different electrical conduction channels, specific to NWs, opens new prospects on the full understanding of the opto-electrical properties of NW-based devices such as visible or UV light emitting diodes.

[1] Z. Fang et al, Nano Lett. 15, 6794 (2015)

[2] A.M. Siladie et al, Nanotechnology, 29, 255706 (2018)

[3] E. Aybeke et al, submitted

Synchrotron X-Ray Nano-Imaging for Energy Materials

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X-ray characterization provides opportunities for scientists in the exploration of materials and living matter in many fields: chemistry, material physics, archaeology and cultural heritage, structural biology and medical applications, environmental sciences, information science and nanotechnologies. In this context, synchrotron X-ray beams offer the ultimate state-of-the-art instrumentation, especially in terms of resolution. The seminar will present the nano-analysis beamline ID16B at the ESRF. This beamline presents a multi-modal approach to determine elemental and chemical composition, crystallographic phases and 3D microstructure of materials using a combination of several nano-scale techniques such as X-ray fluorescence (XRF), X-ray absorption spectroscopy (XANES), X-ray diffraction (XRD), and 3D phase contrast imaging. Each technique will be detailed and illustrated with energy materials studies. Finally the last developments and new possibilities opened by the Extremely Brilliance Source upgrade program at the ESRF will be discussed.

Limiting processes in perovskite optoelectronics: new structures for new challenges

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The use of metal halide perovskites for optoelectronic applications has experienced an unprecedented expansion in the last nine years. These materials can form polycrystalline thin films with outstanding semiconducting properties from low-cost fabrication methods, yet their current development has not impacted the commercial applications yet.

Our research lines focus on identifying the physical processes limiting current perovskite-based devices and developing advanced manufacturing methods to fabricate device-oriented metal halide monocrystals (Figure 1) in the macro and nanoscale. We will present optical and electrical characterization techniques which can unveil current perovskite solar cells' working mechanisms [1], while exploring the potential of nano and macro crystals in new applications -catalysis, sensing, X-ray imaging and neuromorphic circuits which will leverage the monocrystalline halide perovskites advantages.

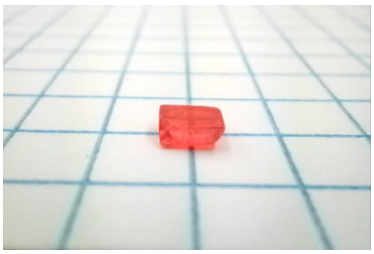


Fig. 1: Centimeter-scale $CH_3NH_3PbBr_3$ monocrystal.

[1] S. M. Yoo, S. J. Yoon, J. A. Anta, H. J. Lee, P. P. Boix, I. Mora-Seró, Joule 2019, 3, 2535.