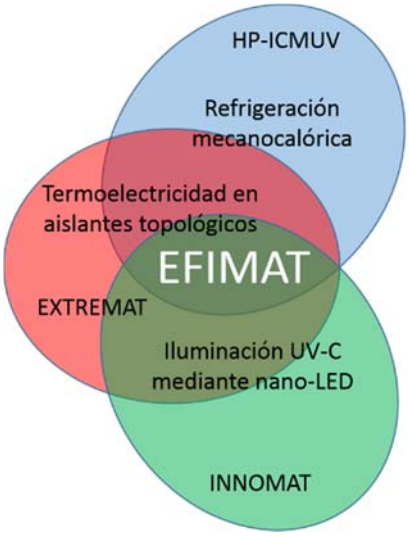
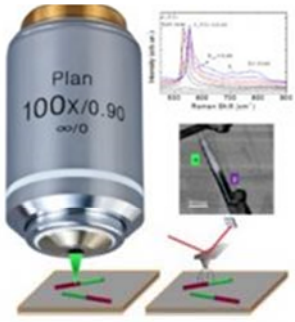
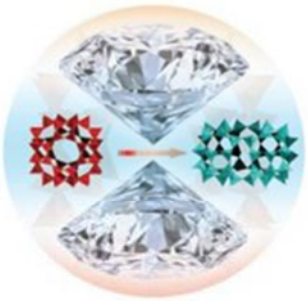
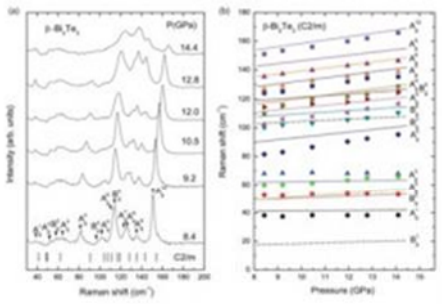


Program Book

FIRST EFIMAT WORKSHOP







GENERALITAT VALENCIANA | Proyecto EFIMAT PROMETEO 2018 / 123

PARC CIENTÍFIC VNIVERSITAT DE VALÈNCIA

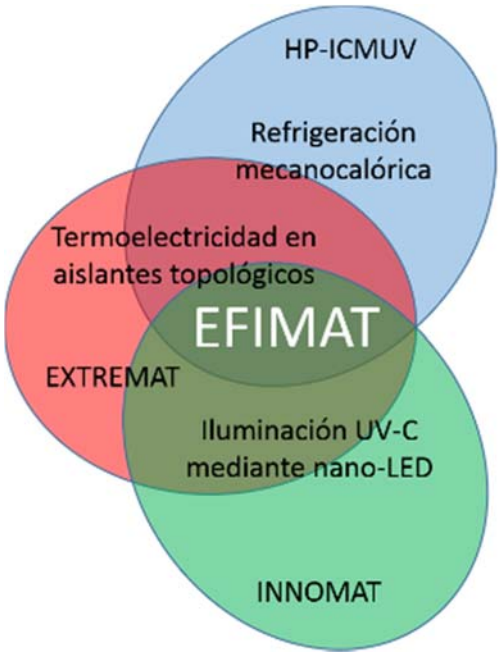
ICMUV

Parc Científic de la Universitat de València

November 29 to 30, 2018

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 first 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.



General Schedule

November 29

Morning – Chairman: Juan Ángel Sans

9:30 Opening Session – Carles Padilla, Vicerrector de Internacionalización y Cooperación; Ana Cros, Directora ICMUV.

9:40 Alberto Otero (Universidad de Oviedo): Computational modeling and structural prediction in molecular materials

10:20 Francisco Javier Manjón (UPV): High-pressure study of high-mobility Bi_2O_2Se semiconductor

11:00 Coffee Break

11:30 Simone Anzelini (Diamond): Advances in LH-DAC Coupled with Synchrotron Radiation Techniques

12:10 Daniel Errandonea (ICMUV): Exploring the High-Pressure Behavior of Polymorphs of AMO_4 Ternary Oxides

12:50 Lunch Break

Afternoon – Chairman: Domingo Martinez García

14:50 Julia Contreras (CNRS-Sorbonne Université Paris): Quantum chemistry: enhancing the bidirectional experiment-theory interplay

15:20 Juan Angel Sans (UPV): Impact of the lone electron pair in the compressibility of group XV sesquioxides at extreme conditions

15:50 Alfredo Segura (ICMUV): Optical and electronic properties of 2H−MoS_2 under pressure

16:20 David Santamaria (ICMUV): Experimental approaches for silicate-carbonate formation

November 30 – Chairman: Nuria Garro

9:30 Pablo Ares (UAM): Electronic properties of 2D materials: tunable graphene doping with local ultrahigh pressure and few layer antimonene as a testbed material for topological surface state studies

10:10 Bruno Daudin (Univ. Grenoble Alpes): Why are nanowires attractive to design innovative visible and deep ultraviolet light emitting diodes?"

10:50 Coffee Break

11:30 Ana Cros (ICMUV): Nitride semiconductor nanowires for ultraviolet illumination: electrical and structural characteristics by Raman and EFM techniques

12:20 Juan Martinez-Pastor (ICMUV): Optical properties of 2D and near-2D Metal Halide Perovskites

13:00 Closing ceremony

Computational modeling of pressure-temperature phase diagrams in molecular materials

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In the past few years, great progress has been made concerning the development of computational methods based on density-functional theory (DFT) for the accurate description of intermolecular interactions. At present, it is possible to predict the relative stability of molecular clusters and crystals with reasonable accuracy, a fact that has been exploited recently to improve molecular crystal structure prediction protocols. In this talk, I address the question of whether it is possible to incorporate temperature and pressure effects to our computational simulations in order to predict the phase diagram of a given molecular compound from the knowledge of its chemical diagram alone. I will review some recent results concerning the exchange-hole dipole moment (XDM) model regarding crystal structure prediction and molecular crystal modeling, and present the computational prediction of the phase diagram and free energy landscape in two simple molecular compounds: carbon dioxide and benzene using a combination of XDM-corrected density functional energies with free energy contributions calculated in the quasiharmonic approximation. Our results demonstrate the feasibility of the prediction of phase diagrams and polymorph landscapes in molecular crystals with technological applications such as organic photovoltaics and other organic electronics materials.

Materiales avanzados para el uso eficiente de la energía

High-pressure study of high-mobility Bi_2O_2Se semiconductor

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We report a joint experimental and theoretical study of the structural, vibrational, elastic, optical and electronic properties of the layered high-mobility semiconductor Bi_2O_2Se [1,2] at high pressure by means of X-ray diffraction, Raman scattering and optical absorption measurements combined with ab initio theoretical calculations [3]. We report a complete and detailed description of the structural, vibrational and optical properties of Bi_2O_2Se under compression. The good agreement between experiments and calculations allows providing accurate equation of state, Raman-active mode assignation as well as the optical bandgap of the material. Both Raman-active modes and optical bandgap are described consistently in this material at room pressure for the first time. Bi_2O_2Se shows a remarkable structural stability up to 30 GPa, unlike other Sillén-type compounds [4], which transit from a tetragonal to a collapsed tetragonal phase at relatively low pressures, and unlike their parents Bi_2O_3 [5,6] and Bi_2Se_3 [7], which undergo several first- and second-order phase transitions at low pressures. Noteworthy, Bi_2O_2Se exhibits considerable electronic changes around 4 GPa, likely related to the progressive shortening and hardening of the long and weak Bi-Se bonds linking the Bi_2O_2 and Se atomic layers. Our understanding of Bi_2O_2Se under compression could help to improve the electronic and thermoelectric properties of similar materials and help to understand the behavior of other Sillén-type compounds under compression and in general that of layered materials lacking van der Waals forces between their layers.

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[2] J. Wu et al. Adv. Mat. 29, 1704060 (2017).
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Advances in LH-DAC Coupled with Synchrotron Radiation Techniques

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The characterization of materials under extreme conditions of pressure and temperature has always attracted the interest of the scientific community due to the numerous implications in fields ranging from condensed matter physics to Earth and planetary science. In particular, the determination of accurate melting curves and phase diagrams is of great importance to the study of planetary interiors since they are needed to better constrain thermal models of planets. The accurate determination of phase diagrams and equations of state is also of great relevance for metallurgy and the aerospace industry.

The laser-heated diamond anvil cell (LH-DAC) is the only static technique allowing temperatures and pressures in excess of 5000 K and 300 GPa to be achieved respectively.

Initially restricted to X-ray diffraction (XRD) [1], LH-DAC can now be combined with inelastic X-ray scattering [2], Mossbauer [3], X-ray fluorescence [4] and X-ray absorption spectroscopy (XAS) stations [5] at several synchrotron facilities worldwide. These new techniques enable the investigation of long and short-range structural modifications, chemical reactions, thermal and electronic excitations under extreme pressure–temperature (P-T) conditions. This opens up many opportunities for research under extreme P-T conditions.

Reliable *in situ* measurements in LH-DAC still remain very challenging and rely on identifying and solving several critical experimental problems. In this talk, a critical examination of these problems will be presented together with an overview of the advances achieved in the past years.

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Exploring the High-Pressure Behaviour of Polymorphs of AMO_4 Ternary Oxides: Crystal Structure and Physical Properties

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Compounds of the AMO_4 family have interesting properties, and indeed many of them are being employed in the industry [1]. For instance, orthovanadates have applications in green technologies as photocatalysts for degradation of C_3H_8 and H_2S and for hydrogen production by water splitting [2]. During the last decade, high-pressure (HP) techniques have played a crucial role for understanding the physical properties of AMO_4 oxides. They have been also used for synthesizing novel metastable polymorphs and for discovering a plethora of interesting phenomena. In particular, in compounds like $BiPO_4$ the polymorphism is very rich [3], occurring phase transitions at pressures as low as 2.4 GPa. In contrast, in other compounds, like $BiSbO_4$ [4], the ambient-pressure polymorph remains stable up to at least 70 GPa. Progress on the knowledge on the HP behavior of AMO_4 compounds has been recently achieved by combining experiments with theory.

The focus of this presentation, is to discuss the main characteristics of phase transitions induced under HP in AMO_4 oxides, emphasizing recent discoveries. Results from synchrotron x-ray diffraction (XRD) experiments carried out up to 50 GPa on vanadates and phosphates will be presented. The information from these experiments allow to identify several pressure-induced phase transitions and to determine the crystal structure of the new phases by means of Rietveld refinements. Raman and optical-absorption measurements were also performed. The combination of experimental results with density-functional theory calculations has allowed us obtaining a systematic understanding of the high-pressure behavior of AMO_4 compounds, improving the knowledge of their physical properties. A comparison of the HP behavior of different oxides will be presented. Crystal-chemistry arguments will be used for the systematic interpretation of the experimental evidence.

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Quantum chemistry: enhancing the bidirectional experiment-theory interplay

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Electron density is a quantum observable through X-rays, however, the mutual interaction of experiment and theory in Quantum Crystallography needs to understand what errors derive from the theoretical models used both in the direct calculation of solids. We will look at two different axes of the same question: "how does the method chosen affect the description of a solid"?

Firstly, we will dwell on the effects of the functional on the calculated properties of a system, such as the cell geometry or transition pressures. We will aim at providing insight into how trustworthy a DFT simulation is and how important is the input from the scientist (i.e. the parameters the computational chemist can tune) [1].

Secondly, we will try to see how the functionals chosen can affect the electron density we obtain. It has been shown that the quest for highly accurate functionals has led to big errors in the electron density [2]. But these errors have been looked at as overall errors (NRMSD), i.e. one number for a given system. However, not all parts are equally relevant for understanding the chemistry of a system: systematic errors in the core are not relevant for chemical transformations, whereas random errors in the valence can lead to unpredictable results. As an example, Figure 1 shows the localization in CO from a set of DFAs with similar RMSD. As can be seen, very different real space errors are at the base of their failure. Whereas some of them are localized in chemical regions (lone pairs, bond), some others seem more chaotic and their effect is more difficult to predict [3].

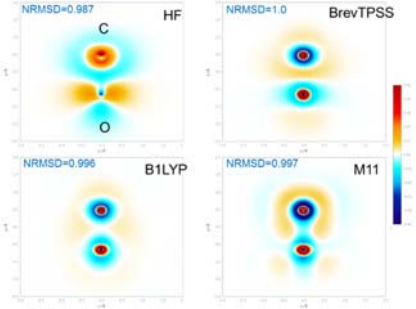

Fig. 1: Errors in the electron density of N_2 (ρ_i-ρ_{CCSD}) calculations for several functionals with similar integrated errors.

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[3] R. Laplaza, J. Contreras-Garcia (to be submitted).

Materiales avanzados para el uso eficiente de la energía

Impact of the lone electron pair in the compressibility of group XV sesquioxides at extreme conditions

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The different polymorphs of sesquioxides formed by group XV elements (As, Sb and Bi) have recently attracted an increasing interest with the aim to understand the effect of the lone electron pairs in their behavior at extreme conditions.

α-As_2O_3 is one of the most compressible solid inorganic compounds and crystallizes in a cubic structure with strong molecular character that becomes amorphous around 20 GPa. In turn, isostructural α-Sb_2O_3 shows two 2nd-order phase transitions driven by dynamical instabilities, below 10 GPa, and a 1st-order phase transition above 20 GPa. The completely different behavior of both compounds with the same structure points out that the strength of the lone electron pair effect could play an important role when pressure increases. Intermediate symmetric structures such as orthorhombic β-Sb_2O_3 and tetragonal β-Bi_2O_3 seem to be more prone to undergo different compressibility behaviors. In particular, the anomalous compressibility of β-Sb_2O_3 has revealed an electronic change associated to a transition of order higher than 2, which is hidden by the larger compressibility of the structural voids in the crystal lattice. Finally, polymorphs belonging to the monoclinic family like α-Bi_2O_3 (β-As_2O_3) exhibits a pressure-induced amophization (2nd-order phase transition) at high pressures.

In summary, this work will show some guidelines in the stability of sesquioxide polymorphs and how the stereochemically active lone electron pair distribution affects the stability of the different structures, paying special attention on the intermediate symmetric structures where the most striking results have been observed.

Electronic structure of centrosymmetric MoS_2 under pressure: absorption measurements and ab-initio band structure calculations

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In this talk we present an investigation of the electronic structure of MoS2 under high pressure by means of absorption measurements and ab-initio band structure calculations. Monolayers of transition-metal dichalcogenide semiconductors present spin-valley locked electronic bands, a property with applications in valleytronics and spintronics that is usually believed to be absent in their centrosymmetric (as the bilayer or bulk) counterparts. Results here presented are consistent with spin-polarization of the states determining the direct band gap of bulk 2H-MoS_2 with the spin sequence of valence and conduction bands expected for its single layer [1,2]. This relevant finding is attained by investigating the behavior of the binding energy of A and B excitons under high pressure, by means of absorption measurements and density-functional-theory calculations. These results raise an unusual situation in which bright and dark excitons degeneracy is naturally broken in a centrosymmetric material. Additionally, the phonon-assisted scattering process of excitons has been studied by analyzing the pressure dependence of the linewidth of discrete excitons observed at the absorption coefficient edge of 2H-MoS_2. Also, the pressure dependence of the indirect optical transitions of bulk 2H-MoS_2 has been analyzed by absorption measurements and density-functional-theory calculations. These results reflect a progressive closure of the indirect band gap as pressure increases, indicating that metallization of bulk MoS_2 may occur at pressures higher than 26 GPa.

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Experimental approaches for silicate-carbonate formation

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Carbon dioxide (CO_2) in its free and anionic forms (carbonates) is an essential component of Earth's carbon cycle and a major contributor to climate change. A detailed knowledge of CO_2 dynamics and stability under high pressure and temperature is essential to understand the carbon cycle as well as to design new strategies for separation and capture of CO_2. Silica and carbon dioxide are traditionally perceived as being incompatible, but recent high-pressure experiments have altered this perception [1]. We explore the reactivity of carbon dioxide (CO_2) with silica and silicates, particularly regarding carbonation and CO_2 reduction [2], and the stability of silicate-carbonate phases as a function of temperature, pressure, and composition. For this purpose, we use an experimental approach in which we map out the phase stability of compositionally relevant silicate-carbonates under different thermodynamic conditions. Structural studies on silicate-carbonate minerals $Ca_5(SiO_4)_2(CO_3)$ spurrite and $Ca_5(Si_2O_7)(CO_3)_2$ tilleyite with 3-coordinated carbon and 4-coordinated silicon atoms as initial samples have been performed [3]. In addition, we explore the chemical interaction between open framework silicates and molecular CO_2. Experimental data on adsorption processes and potential chemical reactions could also help in the design of carbon capture strategies using porous solids. For instance, our experiments allow accurately determining the content of adsorbed CO_2 and the location of molecules in silica zeolites [4,5].

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Electronic properties of 2D materials: tunable graphene doping with local ultrahigh pressure and few layer antimonene as a testbed material for topological surface state studies

Pablo Ares[1,†*], Michele Pisarra[2], Cristina Díaz[2,3,4], Fernando Martín[2,3,5], Pilar Segovia[1,3], Enrique G. Michel[1,3], Wendel Silva[1], Sahar Pakdel[1], Irene Palacio[6], José A. Martín-Gago[6], J. J. Palacios[1,3], Cristina Gómez-Navarro[1,3], Félix Zamora[3,4,5,7], Julio Gómez-Herrero[1,3]

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The possibility to control graphene properties is crucial to promote its use in a variety of applications [1]. In the first part of this talk I will present a procedure to achieve fine tuning of graphene effective doping. By applying ultrahigh pressures (> 10 GPa) using Atomic Force Microscopy (AFM) diamond tips [2], we irreversibly flatten specific areas of graphene against a SiO_2 substrate, creating p-doped graphene regions. Within these areas we improve the contact resistance between graphene and a metal electrode, a paramount issue in the field of graphene electronics, as verified by Conductive AFM measurements.

In the second part of the talk I will present the first isolation and high stability of a novel 2D material, antimonene [3], which indeed has been shown recently to be a highly promising material for energy storage applications [4]. I will present preliminary results on the conductive properties of few-layer antimonene in ambient conditions. They point to be governed by topologically protected surface states, thus opening antimonene a convenient venue for the study of these phenomena.

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Materiales avanzados para el uso eficiente de la energía

Why are nanowires attractive to design innovative visible and deep ultraviolet light emitting diodes?

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III-nitrides are the base of visible and white LEDs currently available on the market, with the prospect of replacing all incandescent bulbs at short term. The external efficiency of such LEDs is already very high (around 80%). This is not the case of UV LEDs: only a few groups worldwide are able to reach 10 % but most devices exhibit an efficiency below 5 %, such figures being drastically dependent on the emission wavelength, with a marked decrease in the 250-270 nm range, which corresponds to important applications such as air and water sanitization. The main reasons for the dramatic decrease in efficiency for shorter and shorter emission wavelengths (obtained by incorporating more and more Al) has been assigned i) to the increasingly detrimental effect of structural defects leading to non-radiative recombination, ii) to difficulties in p-type doping for increasing Al content in the heterostructures, associated with increasing electrical contacting difficulties, and iii) to limitations in the light outcoupling efficiency. The low optical power of a single device is a consequence of the currently low efficiency but also of the limitations in contact size and heat extraction efficiency.

In this context, the exceptional structural, optical and electrical transport properties of III-nitride nanowires (NWs) make them of potential interest for a new generation of optoelectronic devices in the visible/ultraviolet range. In particular n-type and p-type doping of GaN and AlN NWs will be discussed, putting in evidence both a high solubility limit of dopants in NWs and specific spatial inhomogeneities in dopant incorporation, assigned to NW morphology [1, 2]. EBIC experiments will be shown: they provide a direct evidence of p-n junction formation and give quantitative access to doping level and carrier diffusion length. As concerns ternary alloys, the growth of InGaN/GaN and AlGaN/GaN NW heterotructures will be discussed. Morphology engineering of InGaN section by playing with growth conditions will be demonstrated [3]. Finally, composition fluctuations at the nanoscale put in evidence in both InGaN and AlGaN NWs as well as the spontaneous formation of superlattices alternating Al-rich/Al-poor sections in AlGaN NWs will be shown to provide a carrier localization mechanism leading to high IQE [4].

[1] Z. Fang et al, Nano Lett. **15,** 6794 (2015)
[2] A.M. Siladie et al, Nanotechnology, **29,** 255706 (2018)
[3] X. Zhang et al, Nanotechnology **27,** 455603 (2016)
[4] A. Pierret et al, Pss RRL **7**, 868 (2013)

Nitride semiconductor nanowires for ultraviolet illumination: electrical and structural characteristics by Raman and EFM techniques

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The realization of electrically driven ultraviolet light emitting diodes in the 300-200 nm range based on nitride semiconductors relies on the adequate control of p- and n-type doping, alloy homogeneity, density of defects and elastic relaxation of built in strain fields. With this target in mind, nanowires (NWs) are advantageous due not only to their ability to grow free of extended defects on a large variety of substrates, but also to the easier doping of NWs with respect to layers, as recently shown for n-type doping [1]. In this work, we report on the electrical characteristics of GaN NW p-n junctions grown by molecular beam epitaxy [2,3]. Light assisted Kelvin probe force microscopy allows the location of the space charge region and the direct measurement of the depletion width and the junction potential. Raman spectra taken at different locations along the axis of single AlGaN NW p-n junctions allow the identification of three NW segments with different composition: a strained GaN basis, the n-type AlGaN middle region and the p-type AlGaN top. The distinction between n- and p-type AlGaN sides is based on the change of intensity of a low-frequency band and of disorder activated modes in the spectral region corresponding to the longitudinal optical phonons, a feature characteristic of strong Mg incorporation, the impurity used as p-type dopant [4].

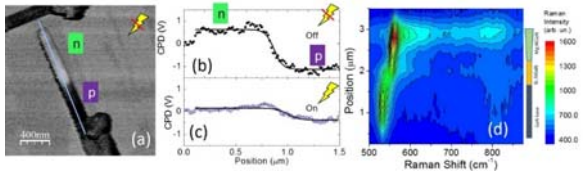

Figure 1. (a) KPFM image of a GaN NW p-n junction with no illumination. Corresponding KPFM profile along the NW axis of (b) dark and (c) above band-gap illuminated GaN NW pn junction. (d) Raman line-map along the NW axis of an AlGaN NW p-n junction.

[1] Z. Fang et al., Nano Letters 15, 6794 (2015)
[2] A. Minj et al., Nano Lett. 15, 6770 (2015)
[3] A. Minj et al. Nanotechnology 27, 385202 (2016)
[4] A.-M. Siladie et al. Nanotechnology 29, 255706 (2018)

Materiales avanzados para el uso eficiente de la energía

Optical properties of 2D and near-2D Metal Halide Perovskites

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The application of bulky aliphatic cations in the manufacture of stable lead halide perovskites against ambient conditions was opened a growing interest in the development and application of near-2D (or 2D-3D) perovskites for solar cells. However, it is also true that the photovoltaic performance of 2D-3D perovskites is limited by the strong quantum size and dielectric confinement effects associated to these new multi-quantum-well (MQW) perovskites. However, 2D-confinement is good for photonic applications due to the strong oscillator strength achieved in 2D-related optical transitions. Here we present the optical properties (extracted from absorption, photoluminescence and time resolved photoluminescence experiments as a function of temperature) of thin films prepared by spin-coating using as cations butylammonium, phenethylammonium (PEA) and anilinium (Any). If only these cations are used (namely, n = 1), PEA-PbI_3 and BA-PbI_3 results in strictly 2D (Ruddlesden-Popper) perovskite structures, whereas a mixture of these cations with methylammonium will produce MQW-structures with different n-values, where n is the number of perovskite monolayers that define the thickness of the quantum well.