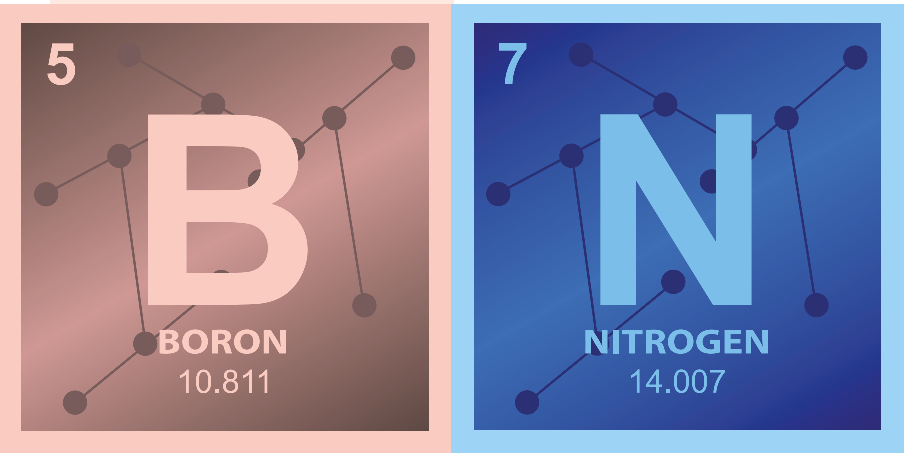
A new era for boron nitride

From medicine to quantum information

Hexagonal boron nitride is receiving increasing attention worldwide as a solid-state material for its unexpected and incredible potential in applications for optics, biology and the health sciences. Prof Bernard Gil (Centre National de la Recherche Scientifique) and Prof Guillaume Cassabois (University of Montpellier) have made pioneering contributions to the physics of this intriguing material and to the exploitation of its ability to interact with, and control, electromagnetic radiation. In collaboration with Prof James H. Edgar (Kansas State University), who has been developing advanced techniques for growing high-purity boron nitride crystals, they are studying the application of hexagonal boron nitride in emerging quantum information technologies.



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Hexagonal boron nitride (hBN) is a versatile solid-state material, which has found a central role in a number of traditional applications, ranging from lubrication to cosmetic powder recipes, thermal control and neutron detection. First synthesised in 1842 as a fragile powder, hBN exhibits a layered crystalline structure, not unlike that of graphite: tightly bound B and N atoms are arranged in weakly interacting reticular planes, which are stacked above each other. In a similar manner to the derivation of graphene from graphite, *monolayer* hBN can also be obtained. In fact, hBN sits at the intersection of two worlds, the classical four-fold coordinated wurtzitic semiconductors of the (Al, Ga)N type, which are used extensively in short-wavelength solid-state light emitters, and layered semiconductors like graphene and transition metal dichalcogenides. However, hBN shows a number of properties that are quite dissimilar from those of both these classes of materials and make it a peculiar and potentially unique candidate for a wide variety of applications.

HBN CRYSTAL GROWTH

A new phase in the study and application of hBN started in 2004 with the development of novel techniques for the growth of large (about 1×1×0.2 mm^3) single hBN crystals. Prof Edgar and his group at Kansas State University have played a pivotal role in this field. They have studied in detail the factors that determine, and can be used to control, the growth process and the final crystal size and quality, as well as the effect of incorporating impurities and varying the boron isotope ratio in the samples. hBN crystals are grown from molten metal solutions, such as chromium and nickel or iron and chromium, which have the ability to dissolve boron and nitrogen. Prof Edgar and his collaborators have shown that starting from pure boron produces crystals of better quality than that of those obtained from hBN powders. They have also examined the influence of the gas composition, choice of metal solvents and type of crucible on the growth process.

ISOTOPIC PURITY

The research team have also developed unique techniques for growing isotopically pure hBN crystals. Natural boron is a mixture of two isotopes, boron-10 (20%) and boron-11 (80%), which differ in their nuclear mass, but show the same chemical properties and give rise to undistinguishable hBN crystal structures. However, the isotopic fraction in an hBN lattice has a profound influence on its vibrational modes, also known as phonons. Crystals that contain only boron-10 ($h^{10}BN$) or boron-11 ($h^{11}BN$) have longer phonon lifetimes. Boron isotopes randomly distributed within the crystal structure scatter the phonons modes more frequently and reduce their lifetime. Phonon scattering is reduced, and phonon lifetimes are longer when the hBN contains only a single boron isotope. This enhances hBN's thermal conductivity making it more efficient at dissipating heat. It also has important implications for its optical properties, particularly for its application in the field of nanophotonics, the study of light compression to dimensions lower than the wavelength of light in free space. In this context, a 150-fold decrease in the light wavelength was obtained in the case of $h^{10}BN$.

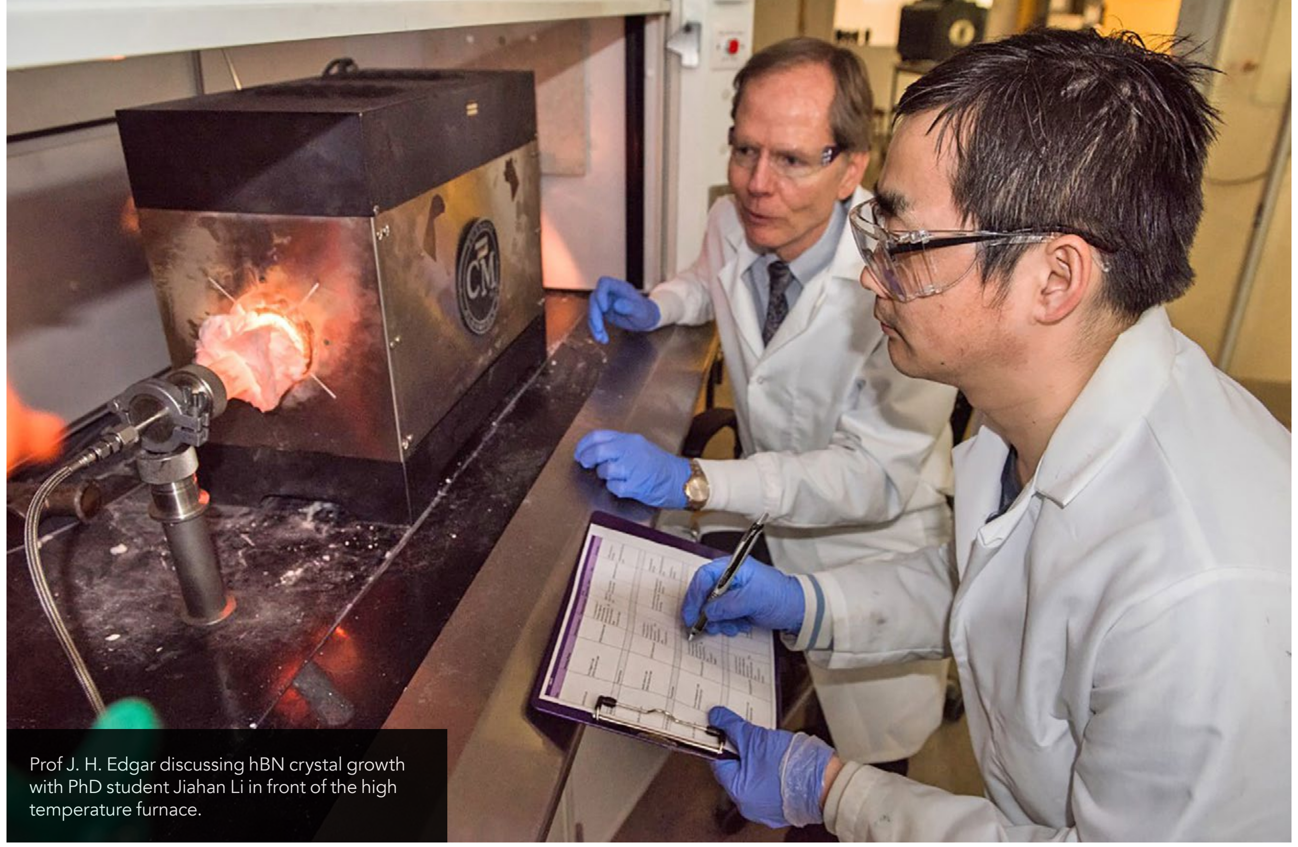


Photo courtesy of T. Theis, Kansas State University.

Prof J. H. Edgar discussing hBN crystal growth with PhD student Jiahan Li in front of the high temperature furnace.

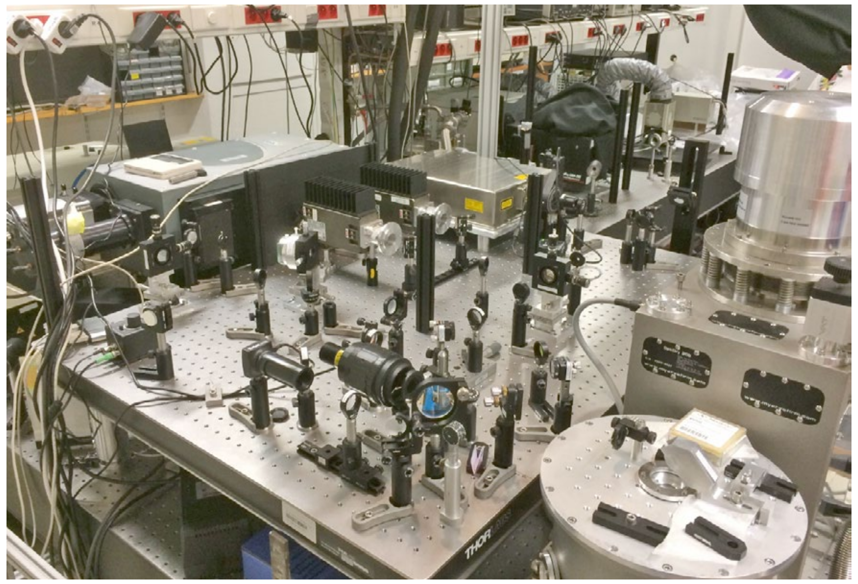
THE EXTRAORDINARY OPTICAL PROPERTIES OF HBN

The increasing availability of high-quality hBN crystal from 2004 led to a series of important findings concerning the complex physics driving light absorption and emission in hBN. One of the most important discoveries in this field was that of the existence of strong cathodoluminescence in hBN, first demonstrated at the National Institute for Materials Science, Japan by T. Taniguchi and collaborators in the same year. Cathodoluminescence is an optical phenomenon that causes the emission of light from a luminescent (that is spontaneously light emitting) material at wavelengths that can be in the visible spectrum when the material is exposed to a beam of electrons, similar to what happens in the cathode tube of a television set. In the case of hBN, the emission occurs in the deep ultraviolet with a wavelength of 215 nm, which is much shorter than that of any other competing luminescent material. Laser activity was also observed at the same short wavelength, a wavelength never achieved before. These findings can have important implications in the development of hBN-based devices for the study of nucleic acid (DNA and RNA) light absorption and their photo-induced decomposition, with the prospect of acting as efficient disinfection tools for viruses and pathogenic bacteria.

Prof Gil's group have made pioneering and crucial contributions to the physics of hexagonal boron nitride.

EXCITON-PHONON INTERACTIONS

Prof Gil's group have made pioneering and crucial contributions to the physics of hBN. In particular, in 2016 they

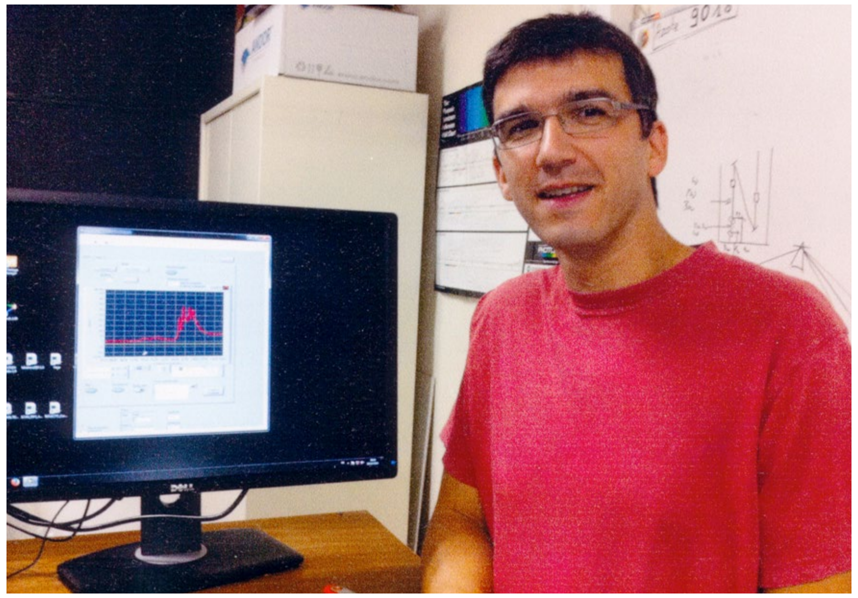


The deep UV microscope with ultimate spatial resolution at 200 nm limited by light diffraction. The low temperature chamber hosting the sample and the microscope objective is on the right of the picture.

demonstrated that hBN is an indirect bandgap semiconductor, in which the transitions between electronic states in the sample caused by the absorption of light occur through a coupling with lattice vibrational modes. This finding indicates the existence of an uncommonly strong and efficient interaction mechanism between the bound electron-hole pairs generated by photoexcitation (excitons) and the phonons in the crystal. Exciton-phonon interactions cause a number of observable phenomena, including a dependence of the optical transition energies on the sample temperature, a broadening of the absorption lines due to the finite lifetime of the excitons and the possibility to observe phonon-assisted exciton recombination. At present, no complete theoretical model of these phenomena has been proposed, owing to the enormous complexity of the interactions involved. The application of the physical principles governing the optical properties of hBN has recently allowed Prof Cassabois to develop a scanning confocal microscope dedicated to photoluminescence (which is the light-induced emission of light from a material) in the 200 nm wavelength range for samples at cryogenic temperatures (5-300 K). This unique instrument demonstrates the usefulness of photoluminescence in tomography, as an alternative to cathodoluminescence, and provides a powerful and versatile tool for materials science applications and in biological studies.

HBN AND QUANTUM INFORMATION TECHNOLOGIES

The ability to generate and manipulate single photons is at the very core of modern quantum technologies. At variance with conventional thermal light sources, like incandescent light bulbs, and coherent light sources (lasers), single-photon sources emit light as single quantum particles (photons), which interact with other single photons and can be used to store or produce new information in quantum computations. Defects in a crystalline structure, caused for instance by the incorporation of impurity atoms, can, in some cases, operate as single-photon sources. In the case of hBN,

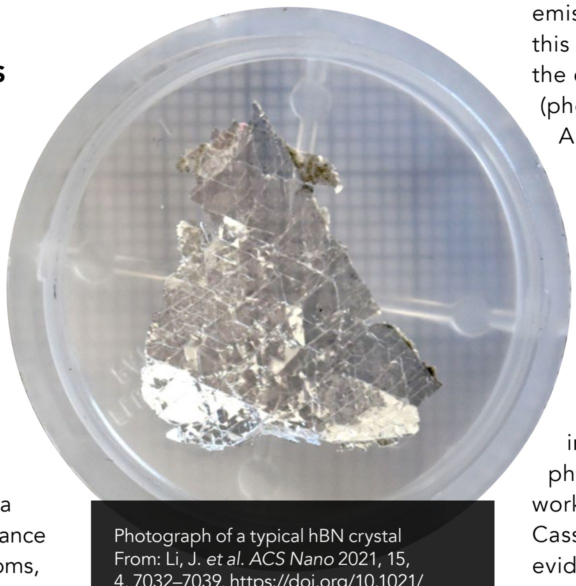


CNRS Research Engineer Pierre Valvin recording the photoluminescence spectrum that indicates the indirect bandgap structure of hBN.

the potentially high density of defects, combined with the large band gap, offers an opportunity to create an ideal support for single-photon sources. At variance with nanophotonics applications, which require extreme

The research team have also developed unique techniques for growing isotopically pure hBN crystals.

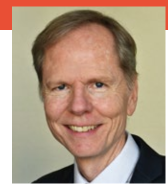
sample purities, quantum applications exhibit sharp enhanced spectral features with respect to pure hBN at a light energy of 4.1 eV.



Photograph of a typical hBN crystal From: Li, J. *et al.* *ACS Nano* 2021, 15, 4, 7032–7039, https://doi.org/10.1021/acsnano.1c00115

Photoluminescence experiments carried out on hBN samples in the presence of C, Si and Mg impurities have been shown to exhibit sharp enhanced spectral features with respect to pure hBN at a light energy of 4.1 eV. Recent cathodoluminescence experiments (in which the emission of phonons is induced by an electron beam) have reported single-photon emission at this frequency, but this has not yet been observed in the case of laser-induced emission (photoluminescence) experiments. A number of spectral lines below 4 eV have also been observed in photoluminescence experiments, which could correspond to single photon emitting defect in this energy range. The origin of these defects however, is still widely debated. Despite the complexity of the phenomena involved in the study of single-photon emission in hBN, the work of Professors Edgar, Gil and Cassabois has put forward solid evidence for the extraordinary potential of this material in the field of quantum technologies.

Behind the Research



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Research Objectives

James H. Edgar's research goal is to improve hBN crystal growth, examining factors that control crystal size and quality, the incorporation of impurities with low concentrations, and with controlled concentrations of boron isotopes. The Montpellier group is an international leader in deep UV spectroscopy, based on the complementary skills of Bernard Gil in the field of materials sciences and of Guillaume Cassabois more specialised in the area of quantum optics for quantum technologies.

Detail

Bernard Gil, Centre National de la Recherche Scientifique Laboratoire Charles Coulomb.

James H. Edgar, Kansas State University, Tim Taylor Department of Chemical Engineering.

Guillaume Cassabois, Université de Montpellier, Laboratoire Charles Coulomb.

Bio

James Howard Edgar is a university Distinguished Professor in the Tim Taylor Department of Chemical Engineering at Kansas State University. His research is on the crystal growth and epitaxy of novel wide bandgap semiconductors. He is currently an Electronic and Photonic Materials program manager at the National Science Foundation.

Guillaume Cassabois is Professor at Montpellier University. His research activities deal with optical spectroscopy in semiconductor nanostructures for innovative applications in materials sciences and quantum technologies.

Bernard Gil is Director of Research at the National Center of Scientific Research (CNRS), the first French public research operator. He is Doctor Honoris Causa of the State University of Saint-Petersburg and of the Meijo University of Nagoya. He is the 2018 laureate of the Welker award.

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References

Gil B, *et al.* (2020). Boron nitride for excitonics, nano photonics, and quantum technologies. *Nanophotonics*, 9(11), 3483-3504.

Valvin P, *et al.* (2020). Deep ultraviolet hyperspectral cryomicroscopy in boron nitride: Photoluminescence in crystals with an ultra-low defect density, *AIP Advances* 10 (7), 075025.

Li J, *et al.* (2020). Single crystal growth of monoisotopic hexagonal boron nitride from a Fe–Cr flux. *J. Mater. Chem.* C, 8, 9931-9935.

Caldwell J, *et al.* (2019). Photonics with hexagonal boron nitride. *Nature Reviews Materials*, 4, 552-567.

Giles A, *et al.* (2018). Ultralow-loss polaritons in isotopically pure boron nitride. *Nature Materials*, 17, 134-139.

Vuong T, *et al.* (2017). Isotope engineering of van der Waals interactions in hexagonal boron nitride. *Nature Materials*, 17, 152-159.

Cassabois G, *et al.* (2016). Hexagonal boron nitride is an indirect bandgap semiconductor. *Nature Photonics*, 10, 262-266.

Gil B, (2021). Gil Bernard [online]. Laboratoire Charles Coulomb, Montpellier. https://coulomb.umontpellier.fr/user/bernard.gil.

Personal Response

According to your group's findings, hBN is an extremely promising material for quantum technologies. What factors set hBN apart from competing materials and what are the remaining issues that need addressing in view of its practical application in quantum computing devices?

" hBN is grown at high temperature, which favours the formation of defects giving birth to a large variety of mid band gap states. Such states can act as high rate single photon emitters useful for encrypted communications and they can operate at high temperatures, thanks to the large value of bandgap of their host material: hBN. Some of the electron energy levels in hBN are affected by the presence of a magnetic field: the emission spectrum changes according to the strength of the magnetic field. Thus, this property paves the way toward hBN's applications as a nanomagnetic sensor and for digital information storage. "