Towards large-scale hexagonal boron nitride 2D layers: a chemical approach

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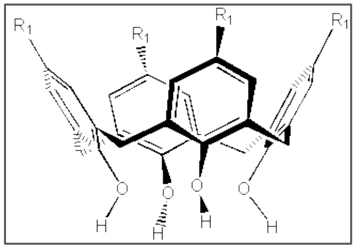
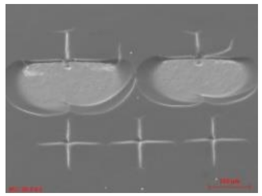
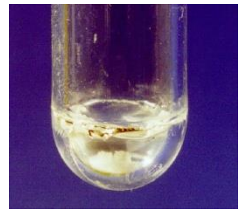
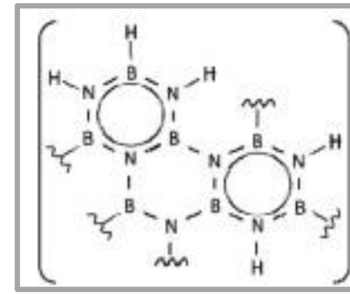
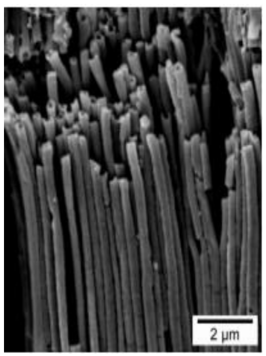
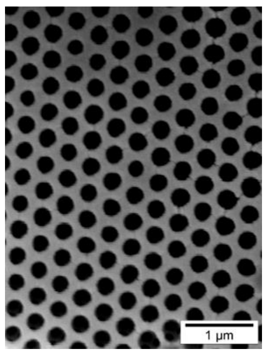
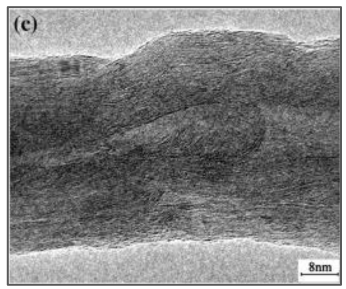
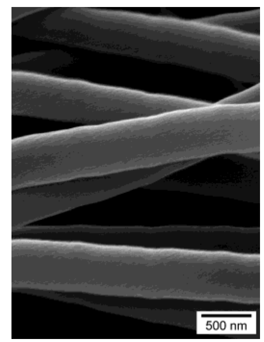
from molecule … … to material

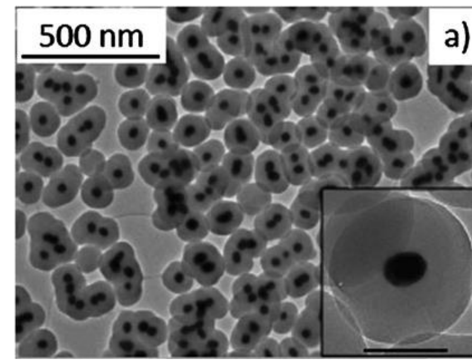




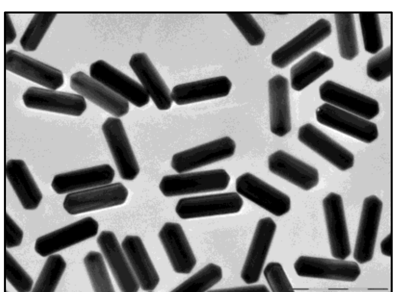



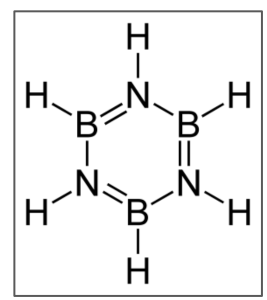
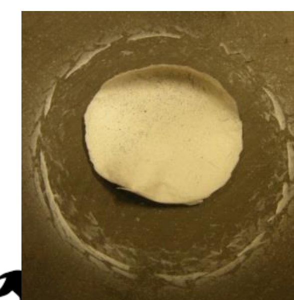










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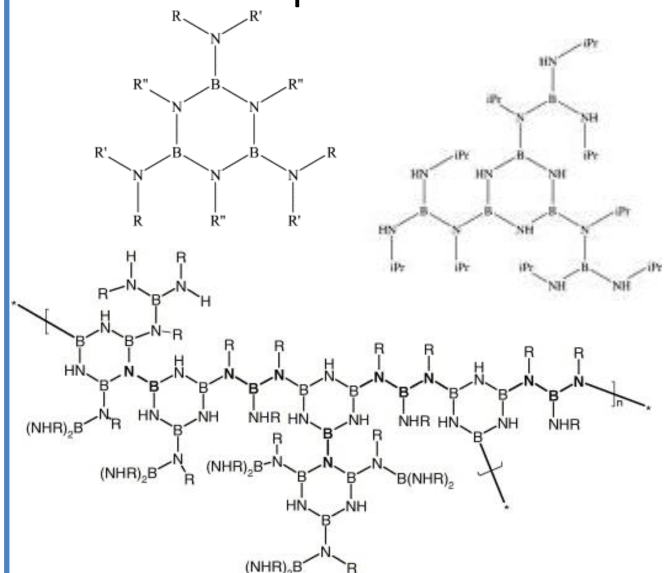
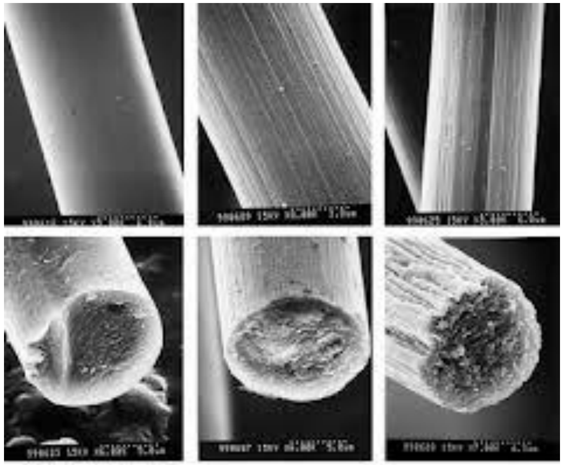
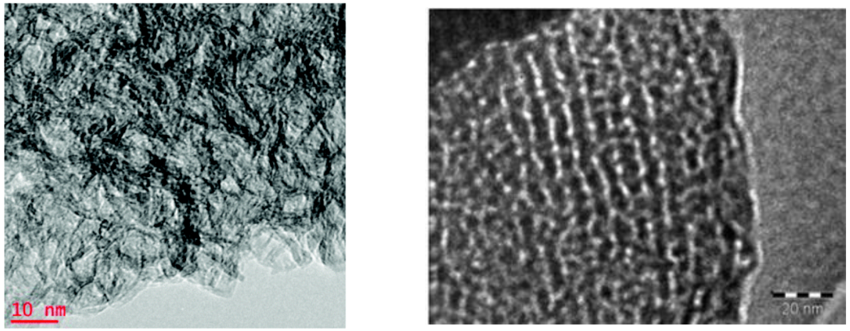
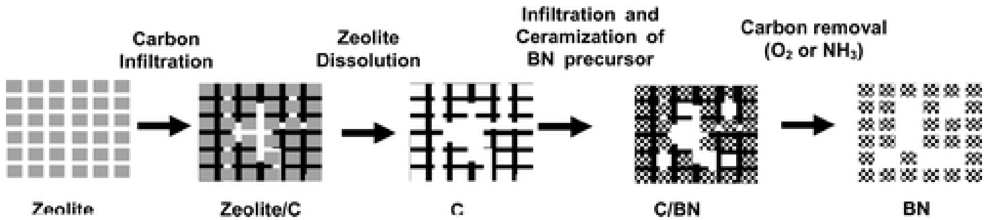
BN fibers new precursors



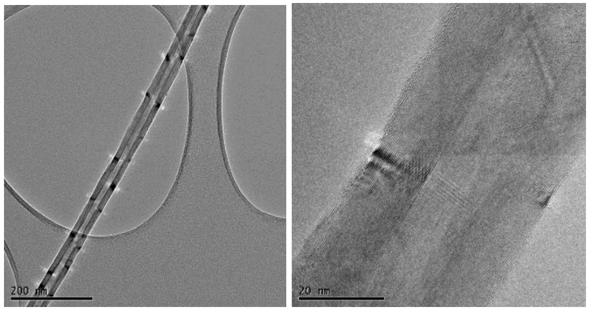


micro- and meso-porous BN by *template* or direct synthesis

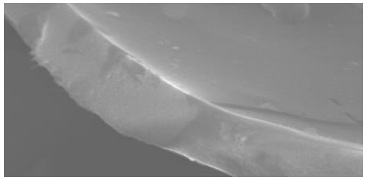




BN nanotubes

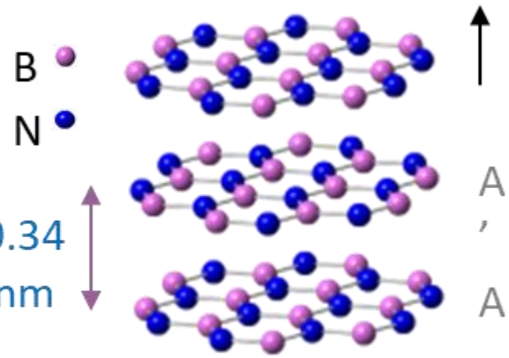


h-BN coatings

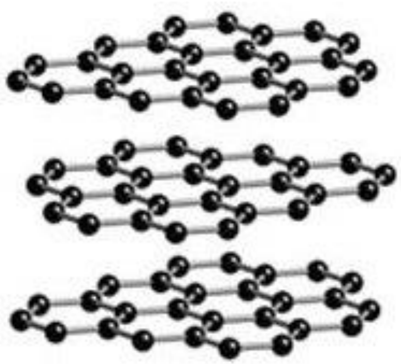


General context

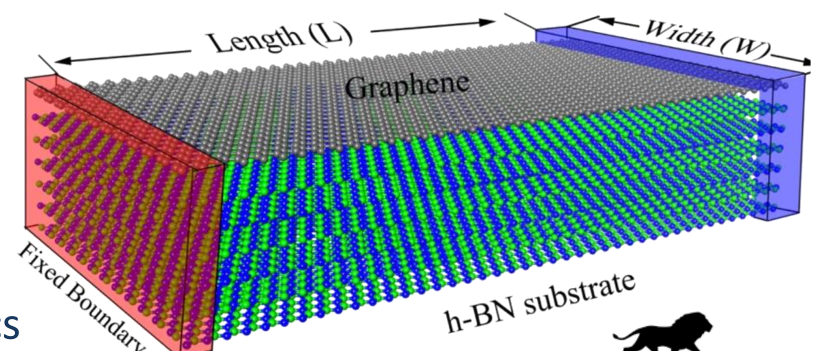
***h*-BN** also called white graphite



Graphite



- Electronic insulator ~ 6.0 eV
- Lattice matching with that of graphene
- Refractory behavior
- h-BN
- Hexagonal structure
- High thermal conductivity
- Chemical stability > 900°C under air

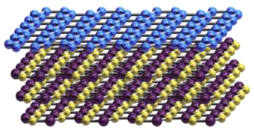


Zhongwei Zhang et al 2017 Nanotechnology **28** 225704

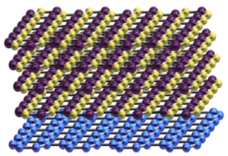
➢ Great potential for electronics and optics

Towards layered hBN

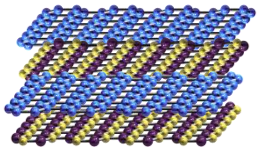
Several needs of h-BN samples :



Thick layers to be used as substrate for graphene



Encapsulating layers of graphene and other 2D materials



Dielectric layers in heterostructures

Need of both monolayers and thick layers (> 10 – 50 nm)

Our approach

High quality h-BN source

Polymer Derived Ceramics (PDCs)

- Tailored molecular precursor
- Non-oxide system for high purity
- Liquid precursors easy to handle
- Possibility for various shaping methods for specific ceramic shape

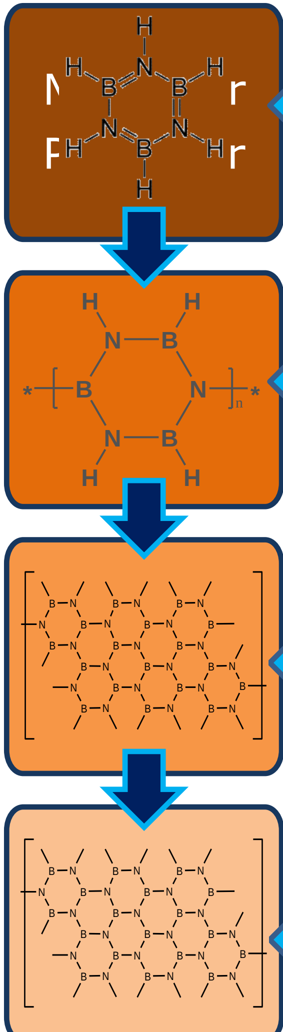
*S. Yuan, et al. Crystals. **2016**, 6, 55*
*S. Yuan, et al. Nanoscale. **2014**, 6, 7838-7841*
*P. Colombo. J. Am. Ceram. Soc. **2010**, 93, 1805-1873*

Spark Plasma Sintering (SPS)

- Rapid and efficient processing method for densification on both lab scale and industrial level
- Softer condition compared with HPHT method (2100°C, 5.5GPa, 80h)

*S. Yuan, et al. Sci. Rep. **2016**, 6, 20388*
*E. Bernardo, et al. Ceram. Int. **2014**, 40, 14493-14494*
*K. Watanabe, et al. Nat. Mater. **2004**, 3, 404–409*

Polymer Derived Ceramics (PDCs) route



Borazine / Synthesis

$(NH_4)_2SO_4 + NaBH_4$ *in tetraglyme*

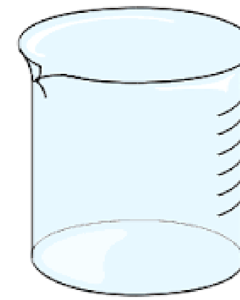
pressure vessel
50°C / 7 days

Polyborazilene / Polymerisation

Li_3N

cristallisation promoter
additivation

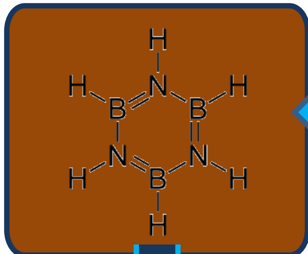
Ceramisation
1000-1200°C / N_2



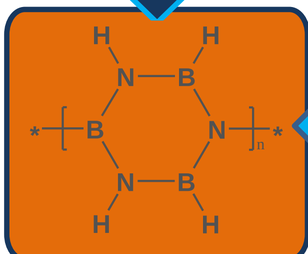
Bulk h-BN / Shaping

BNNS / Pyrolysis

Combination PDCs + SPS



Borazine

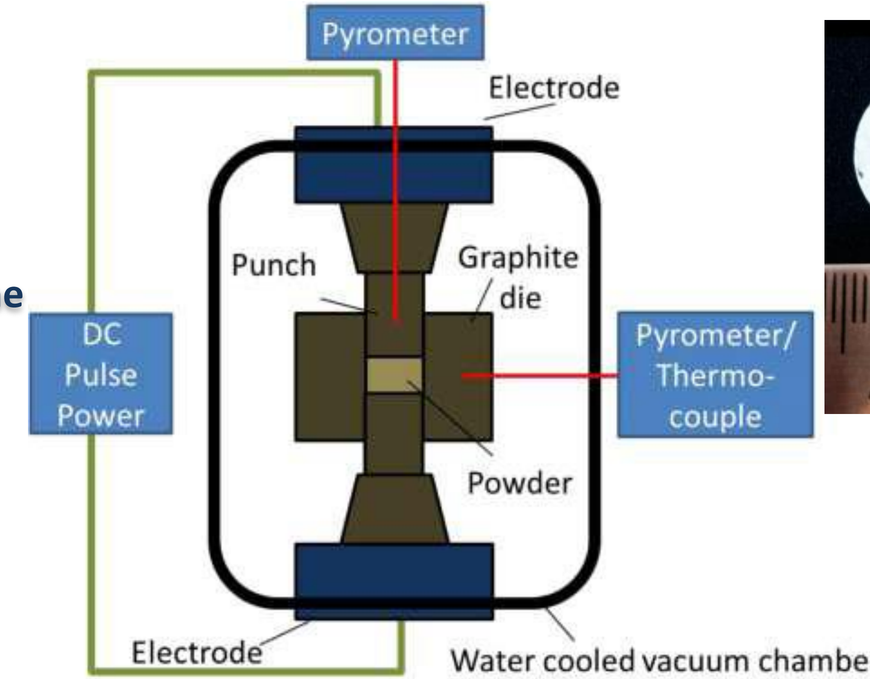


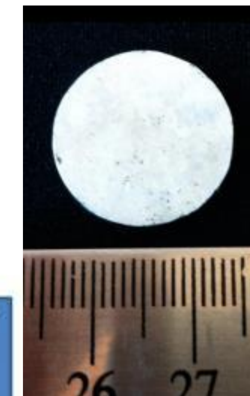
Polyborazilene
PBN + Li_3N

stabilized 600°C, 1h

Powder

O. Guillon, et al. Adv. Eng. Mat. ***2014****, 16, 831*



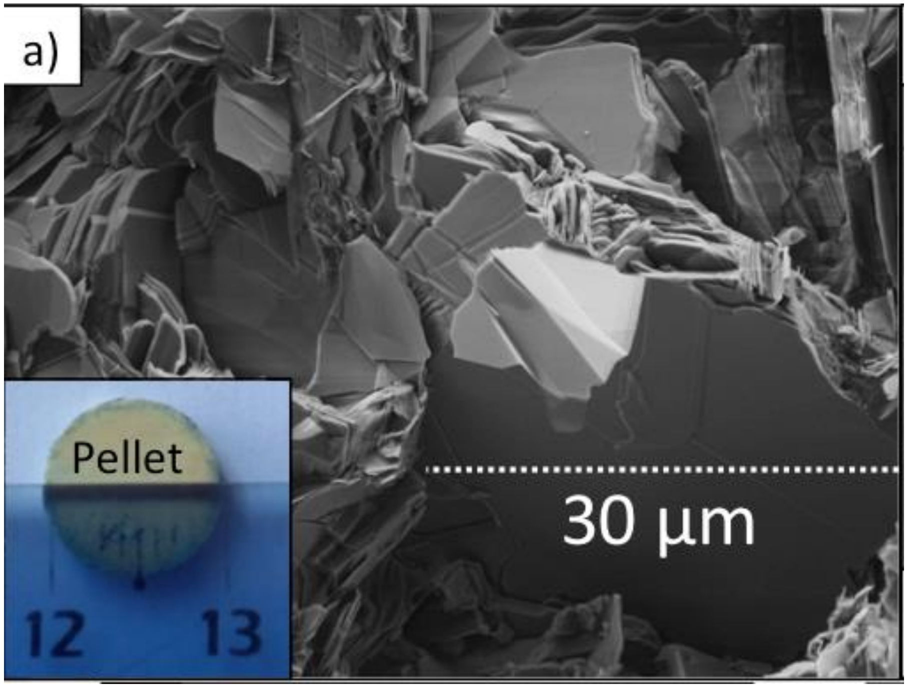


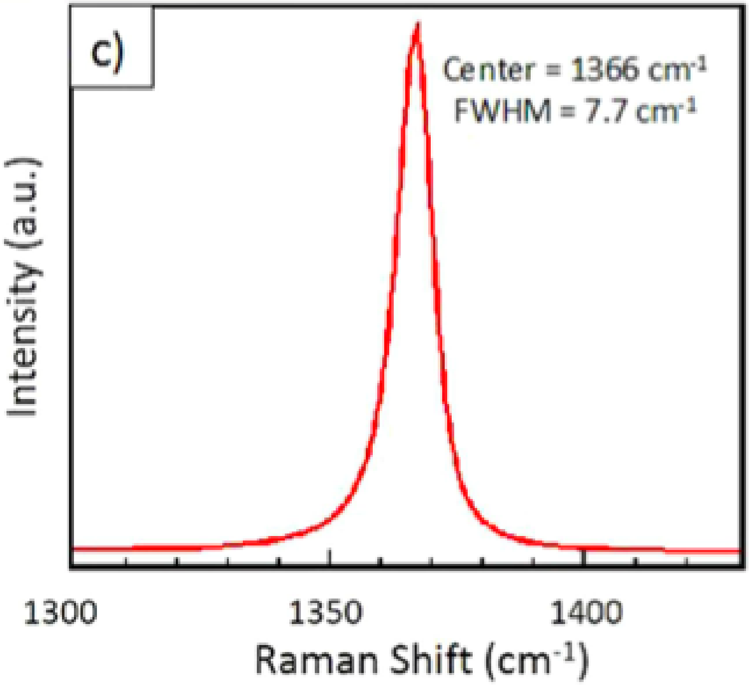
Spark Plasma Sintering (SPS)

90 MPa
770 A
1800°C
1h

Characterization of the bulk material

XR | SEM | s



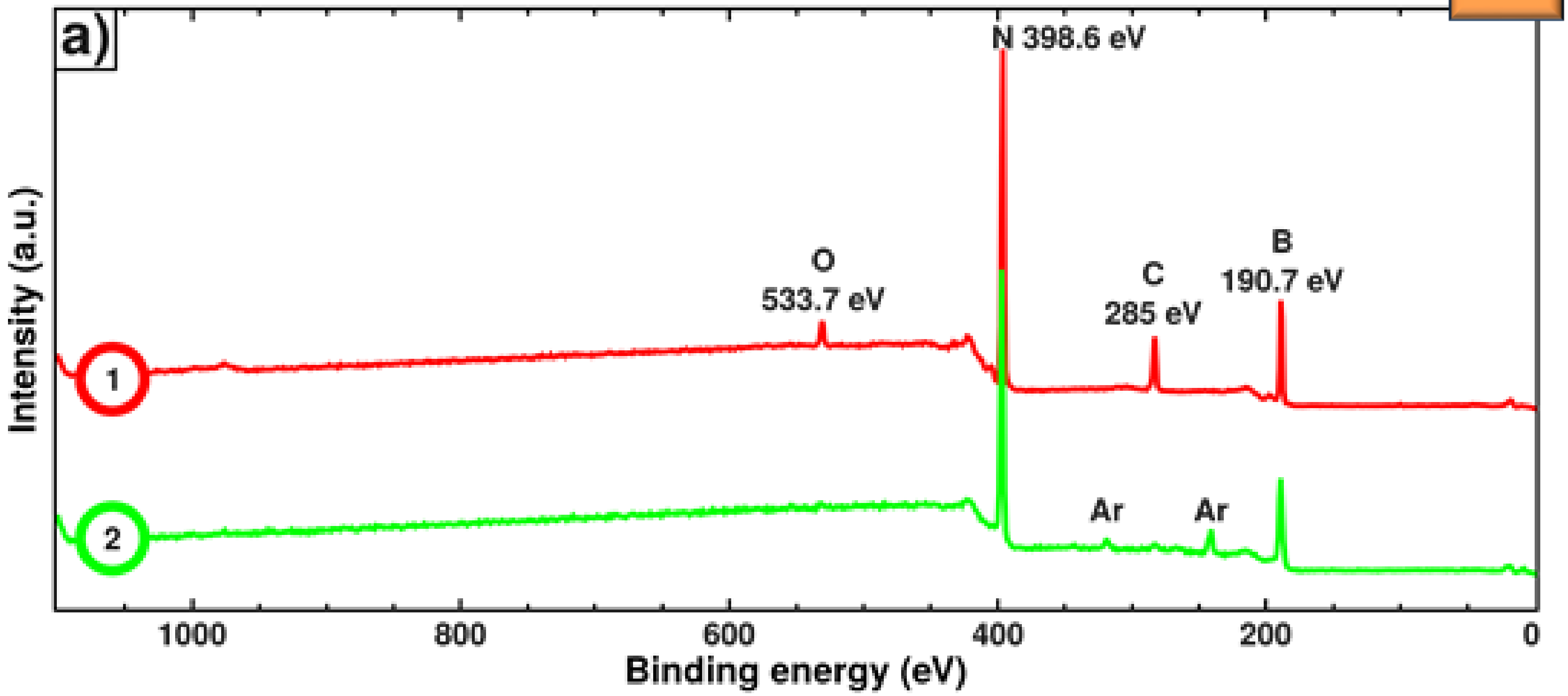


polycrystalline sample made of single crystal flakes

S. Yuan, et al. Sci. Rep. ***2016****, 6, 20388*

Characterization of the bulk material

XPS

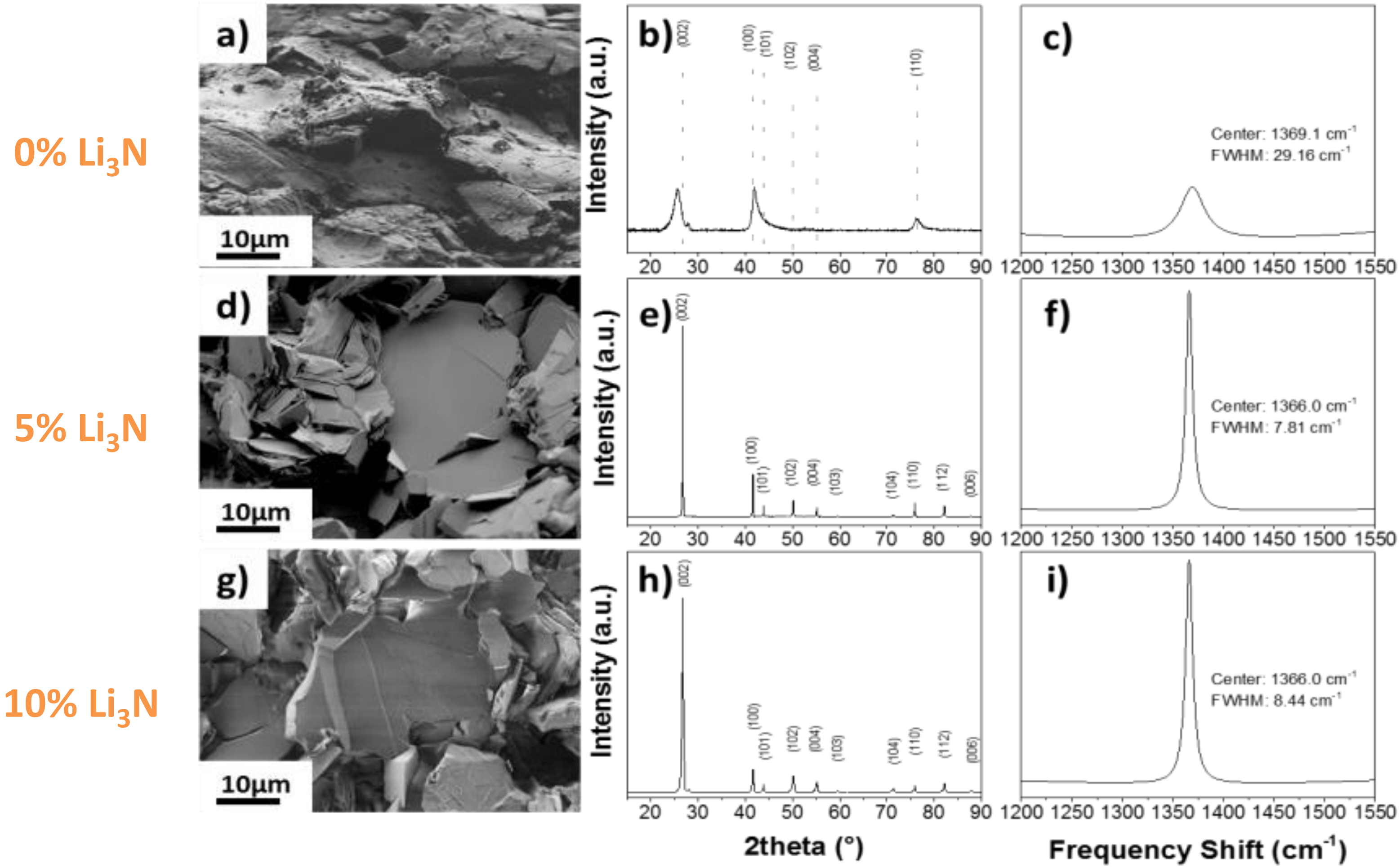


① Before abrasion :	ratio B/N = 0.97 (close to 1) < 0.5%at. for O1s and 1.3%at. for C1s
② After abrasion (1µm) :	elimination of C and O (just contaminants) preferential sputtering of nitrogen atoms

Influence of the crystallization promoter

No.	Pre-ceramic Composition	Li_3N wt. %	Temperature °C	Pressure MPa	Dwelling time hour
1	PBN	0	1800	90	1
2	PBN+Li_3N	5	1800	90	1
3	PBN+Li_3N	10	1800	90	1

Influence of the crystallization promoter

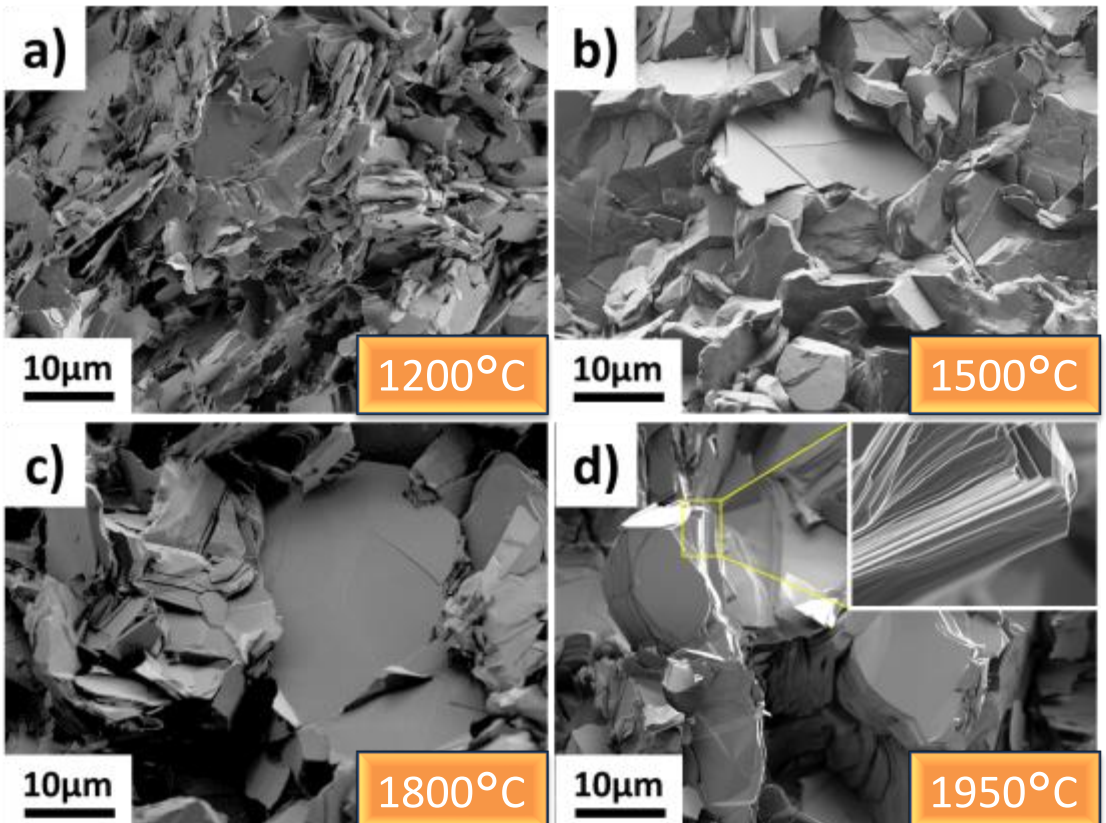


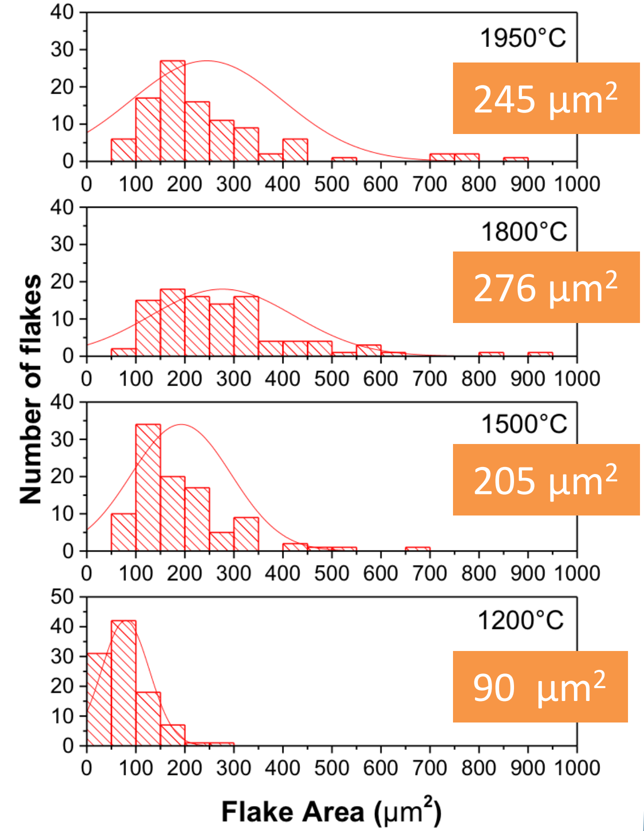
- Li_3N addition necessary for obtaining well-crystalized h-BN flakes
- No significant structural difference between 5% and 10 wt.%
- Ceramic yield decreases when increasing Li_3N amount

Influence of the sintering T

No.	Pre-ceramic Composition	Li_3N wt. %	Temperature °C	Pressure MPa	Dwelling time hour
1	PBN+Li_3N	5	1200	90	1
2	PBN+Li_3N	5	1500	90	1
3	PBN+Li_3N	5	1800	90	1
4	PBN+Li_3N	5	1950	90	1

Influence of the sintering T





- Flakes size ↗ with T to reach a maximum area of 276 µm² at 1800°C and ↘ at 1950°C
- When sintering T ↗ → nucleation rate ↗ faster than crystal growth rate, thus decreasing the flakes size

  - pellets show similar feature
  - composed of defined BN domains staked into flakes and growing in different orientations
  - flakes are significantly

best compromise between 1500 and 1800°C

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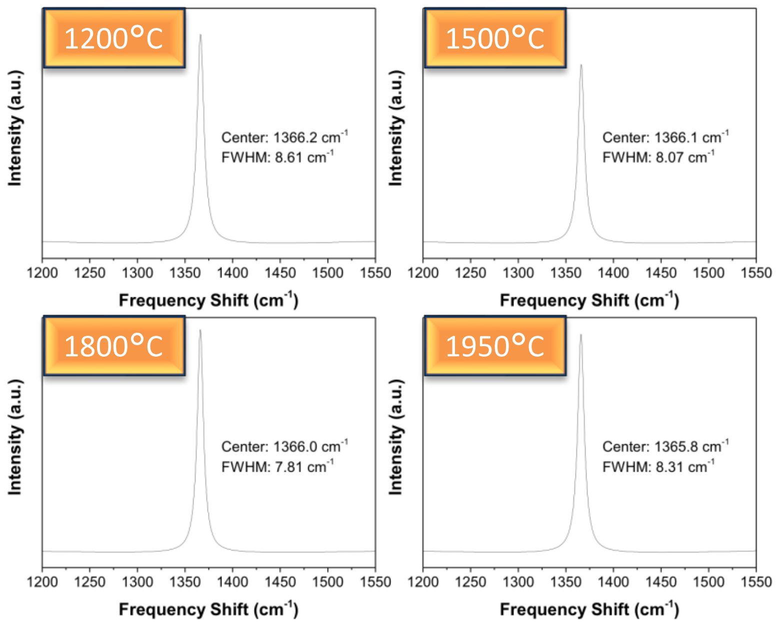
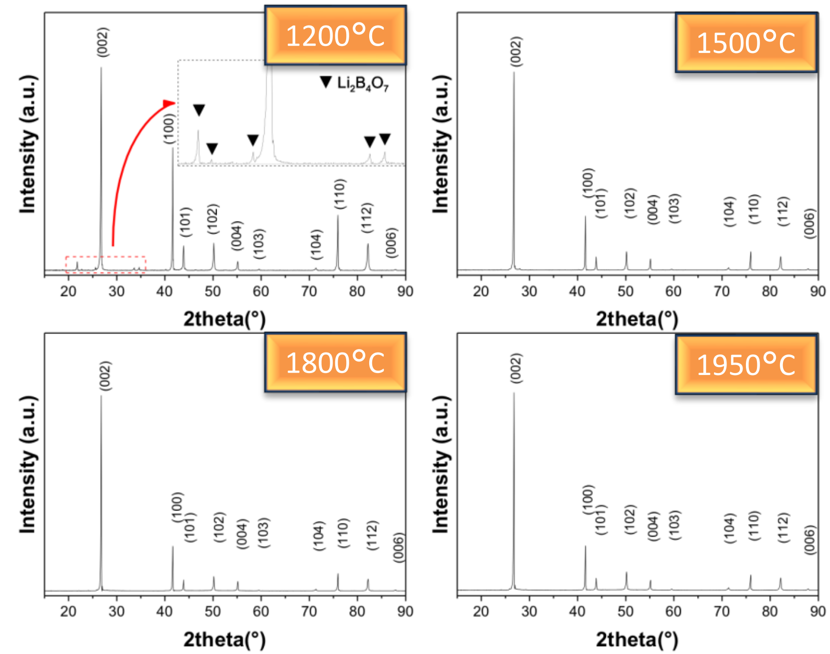
Influence of the sintering T

Raman



XRD



Very good Raman signature with a FWHM ≈ 8 cm^{-1}

Good crystalline structure of h-BN

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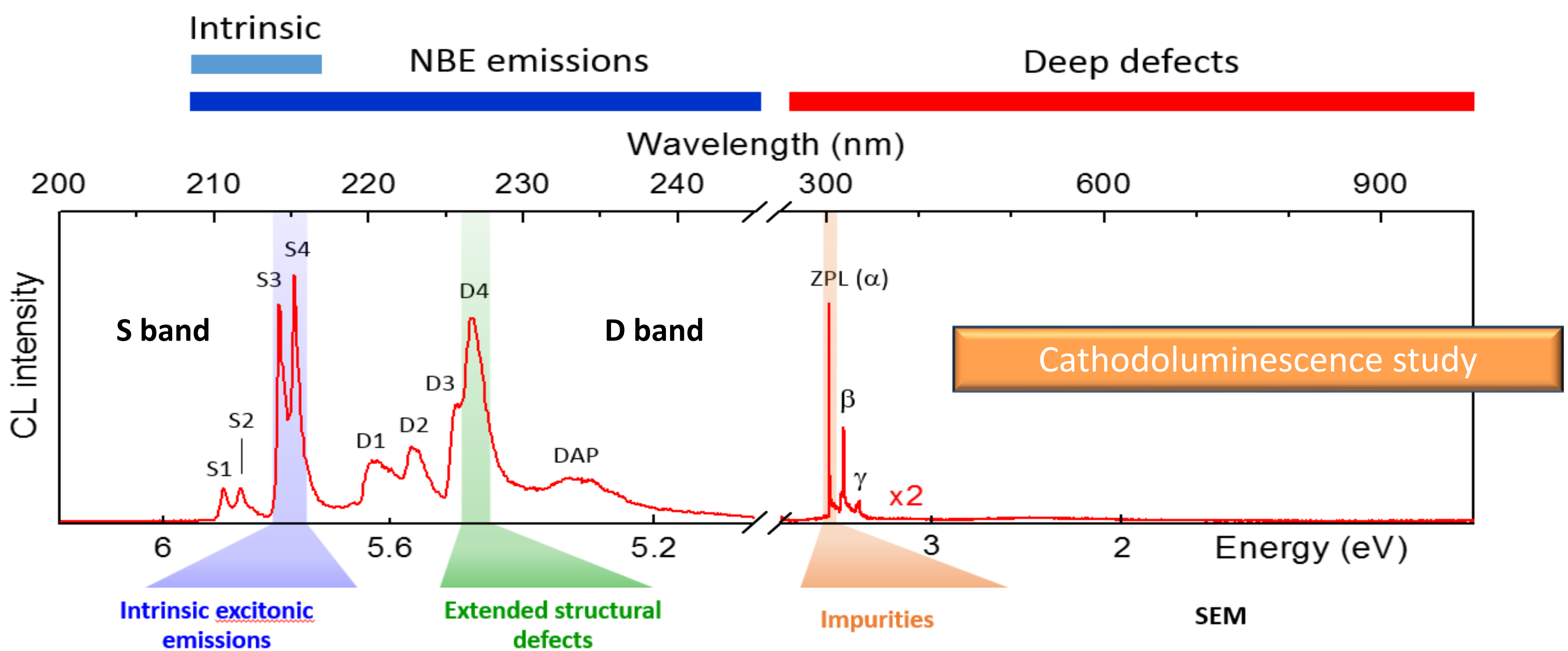
Influence of the crystallization promoter and sintering T

A tool of interest

Collab. GEMAC & ONERA (A. Plaud, L. Schue, J. Barjon, A. Loiseau)

- Investigation of optical and excitonic properties
- identification of different classes of defects and their impact on optical properties



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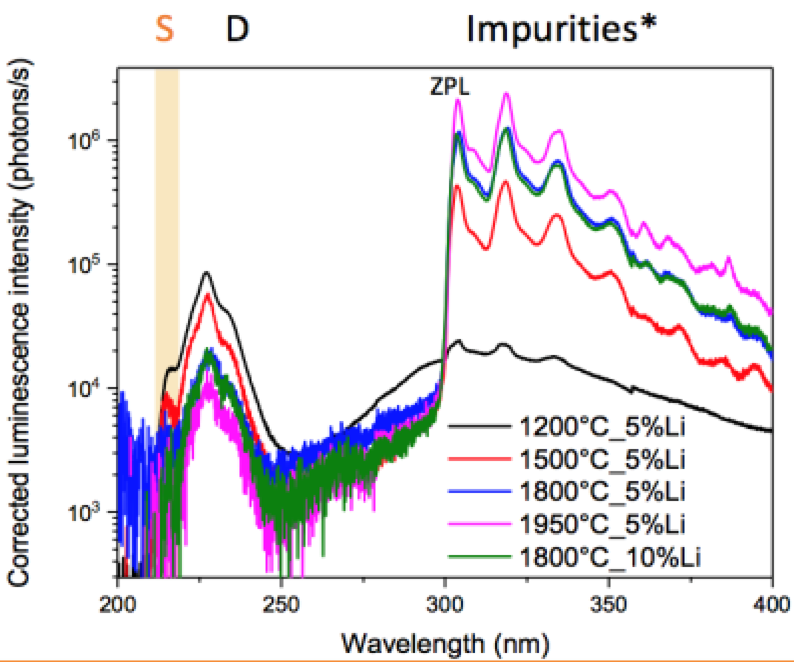
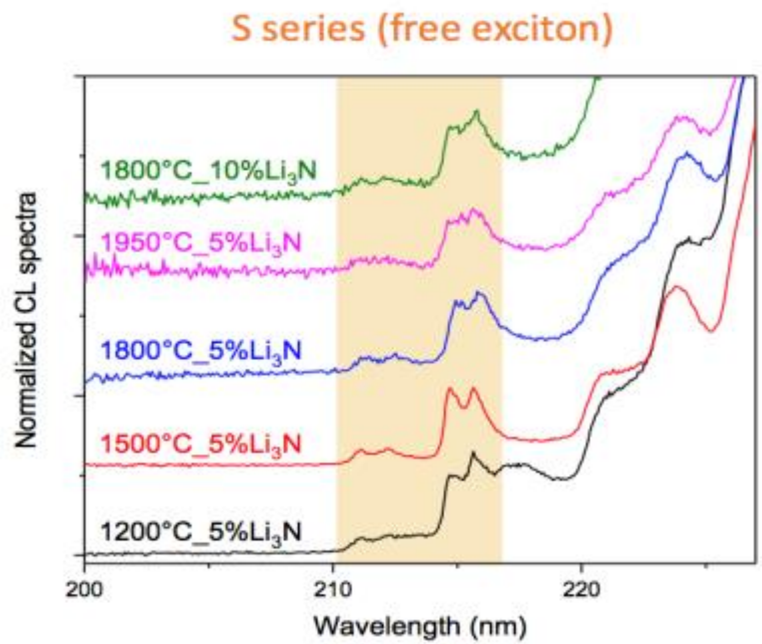
Influence of the crystallization promoter and sintering T

Indication of the overall material quality, accounting for both purity and crystallinity



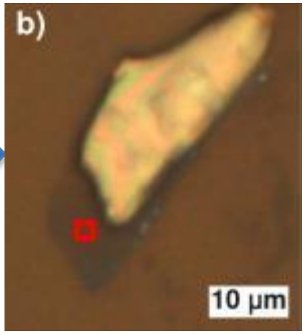


- Observation of intrinsic exciton emission (S-lines)
- Absence of defect-related emissions (D-lines)
- Presence of impurities when increasing the sintering temperature : contamination ?

Collab. GEMAC & ONERA (L. Schue, J. Barjon, A. Loiseau)

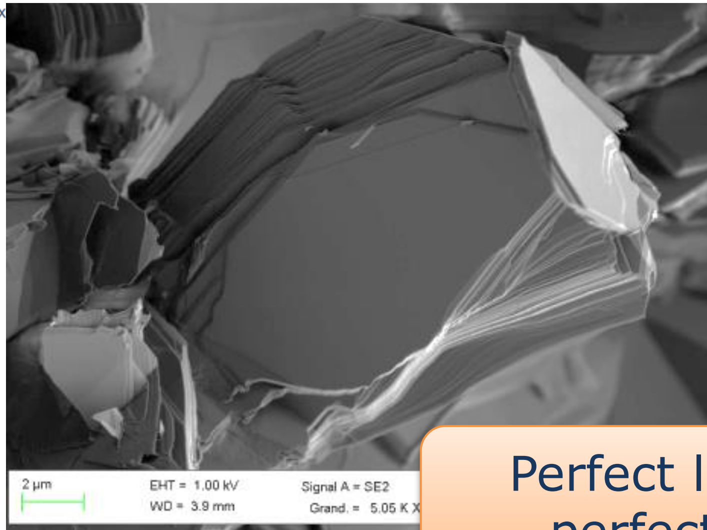
From h-BN pellets … towards flakes

well-crystallized
h-BN bulk sample
(pellet)

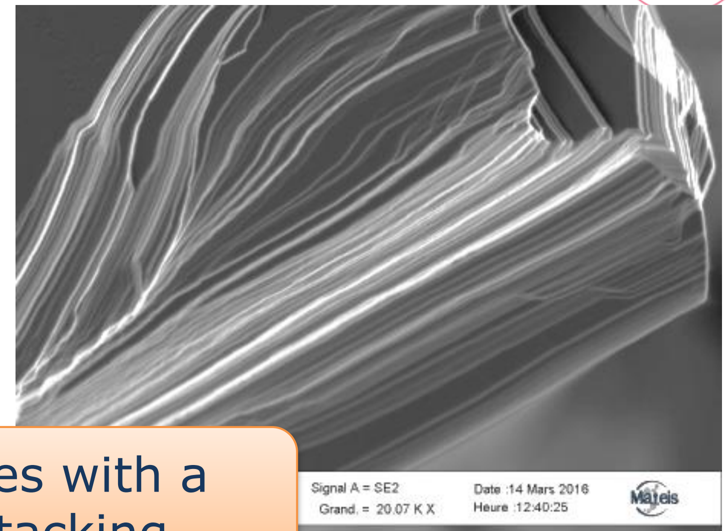


flake
(single crystal)

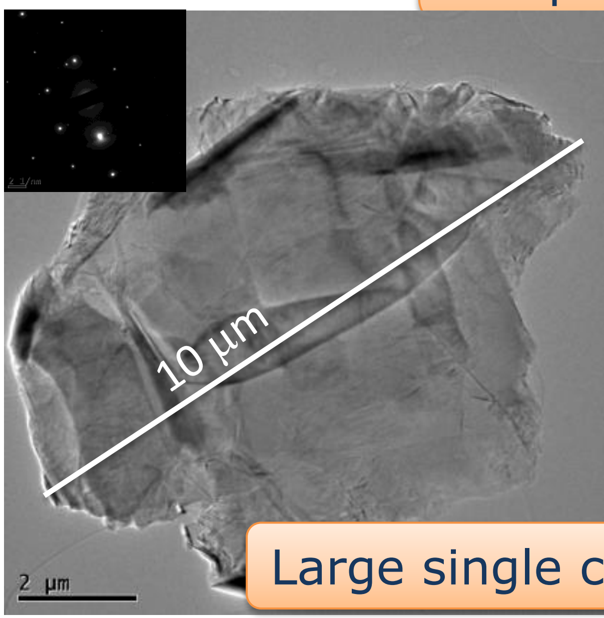
Characterization of the flakes



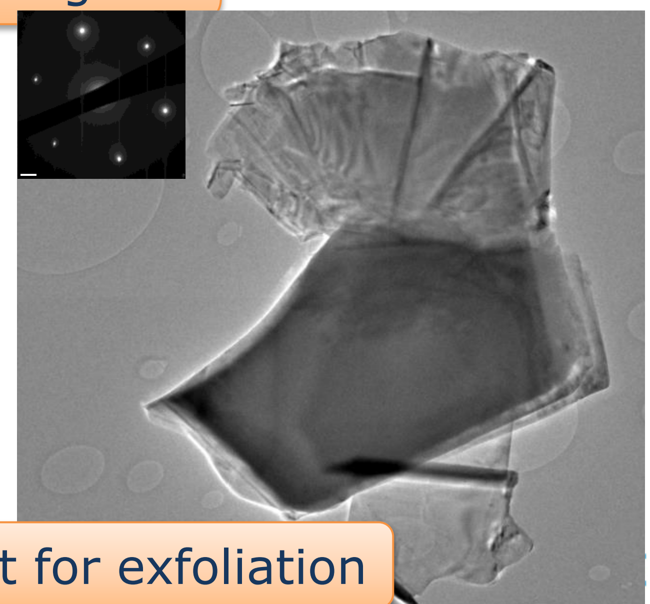
SEM



Perfect large flakes with a perfect layers stacking

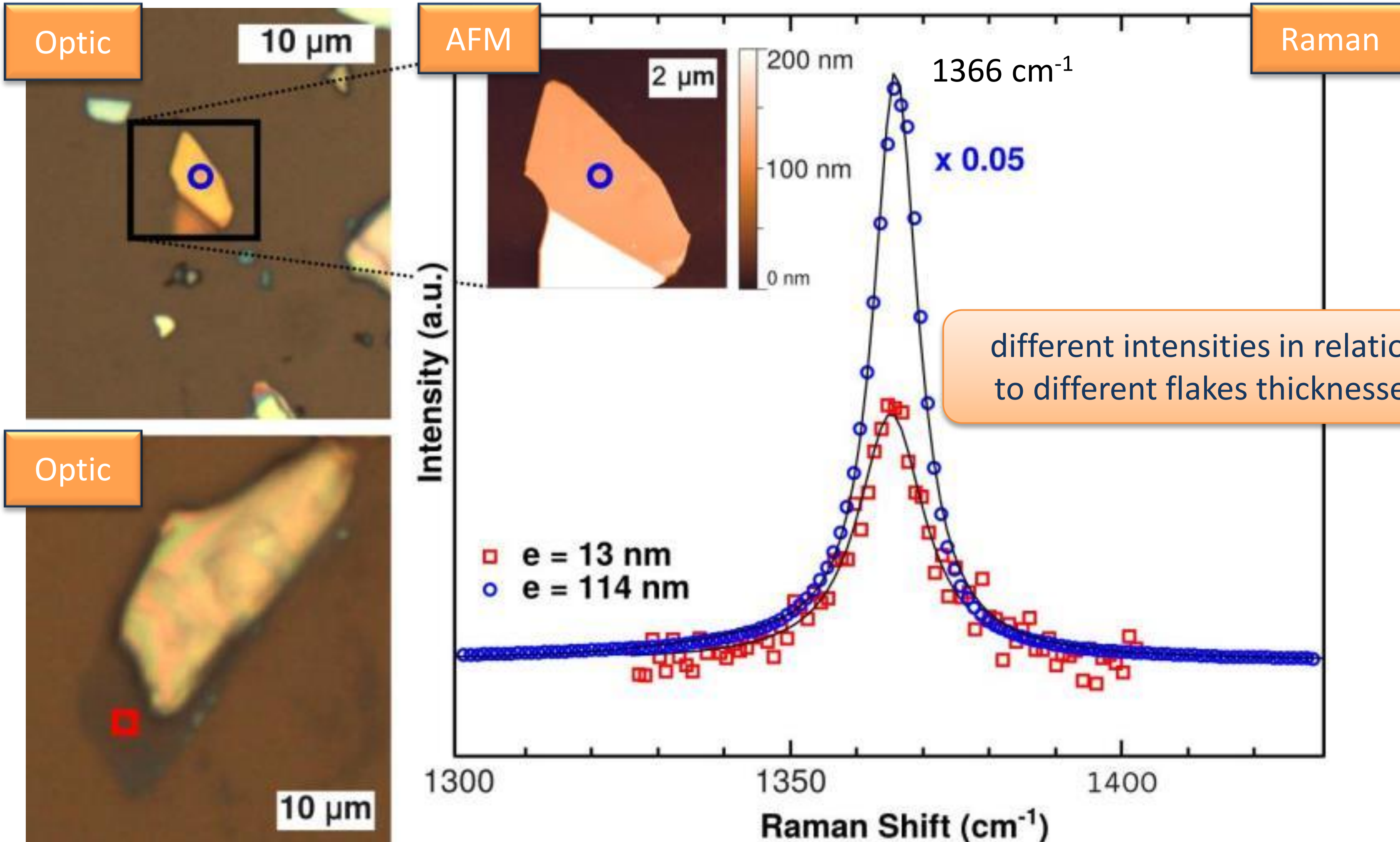


TEM



Large single crystal convenient for exfoliation

Characterization of the flakes

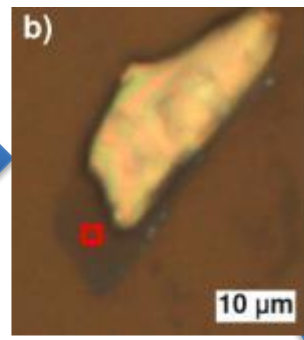


different intensities in relation to different flakes thicknesses

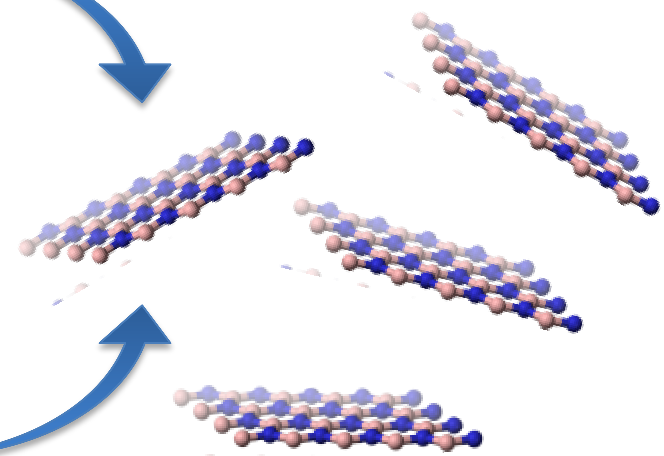
From h-BN pellets … towards flakes

mechanical exfoliation
using the tape method

well-crystallized
h-BN bulk sample
(pellet)



flake
(single crystal)

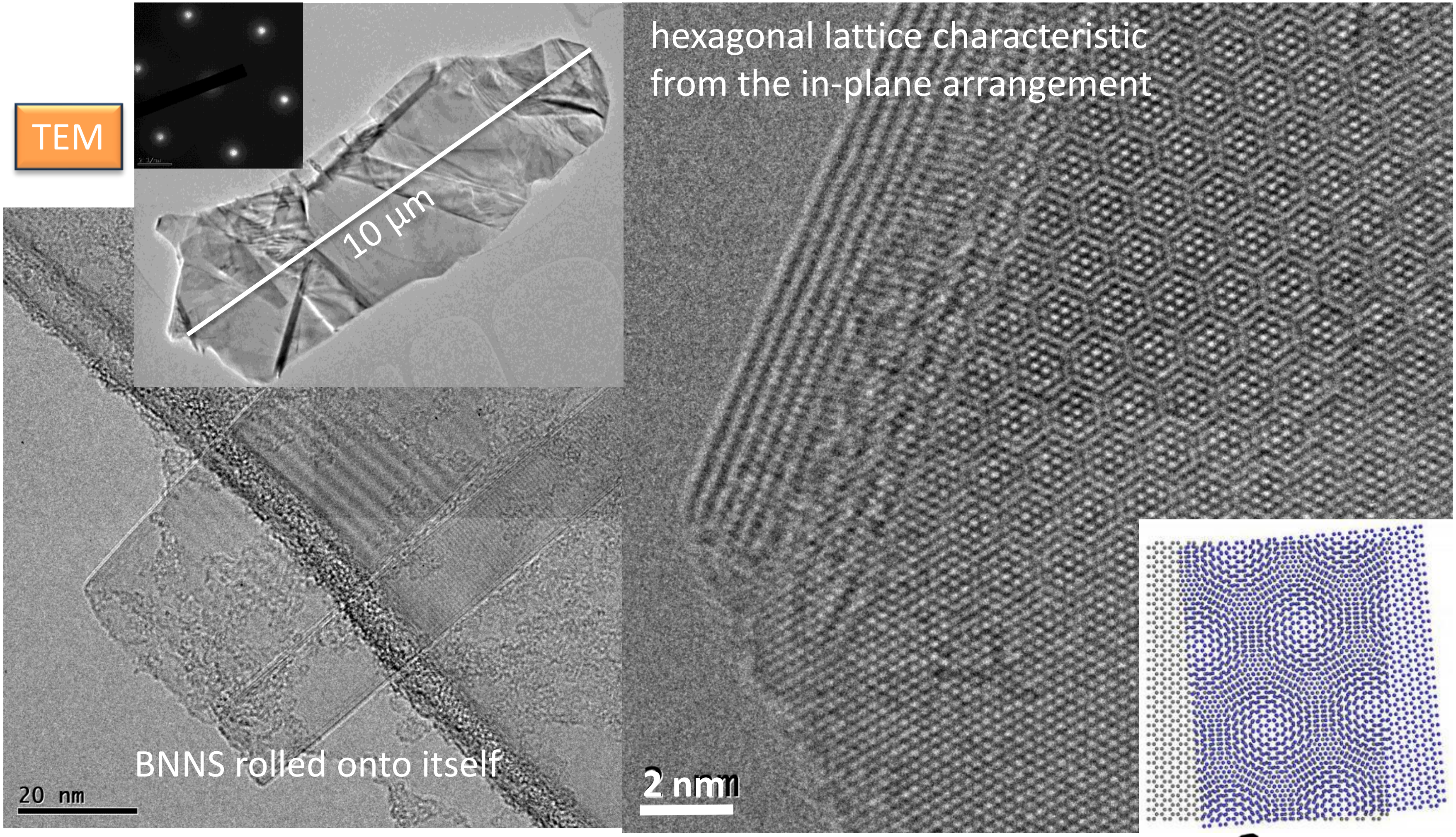


BNNSs

« chemical » exfoliation
in a solvent under sonication

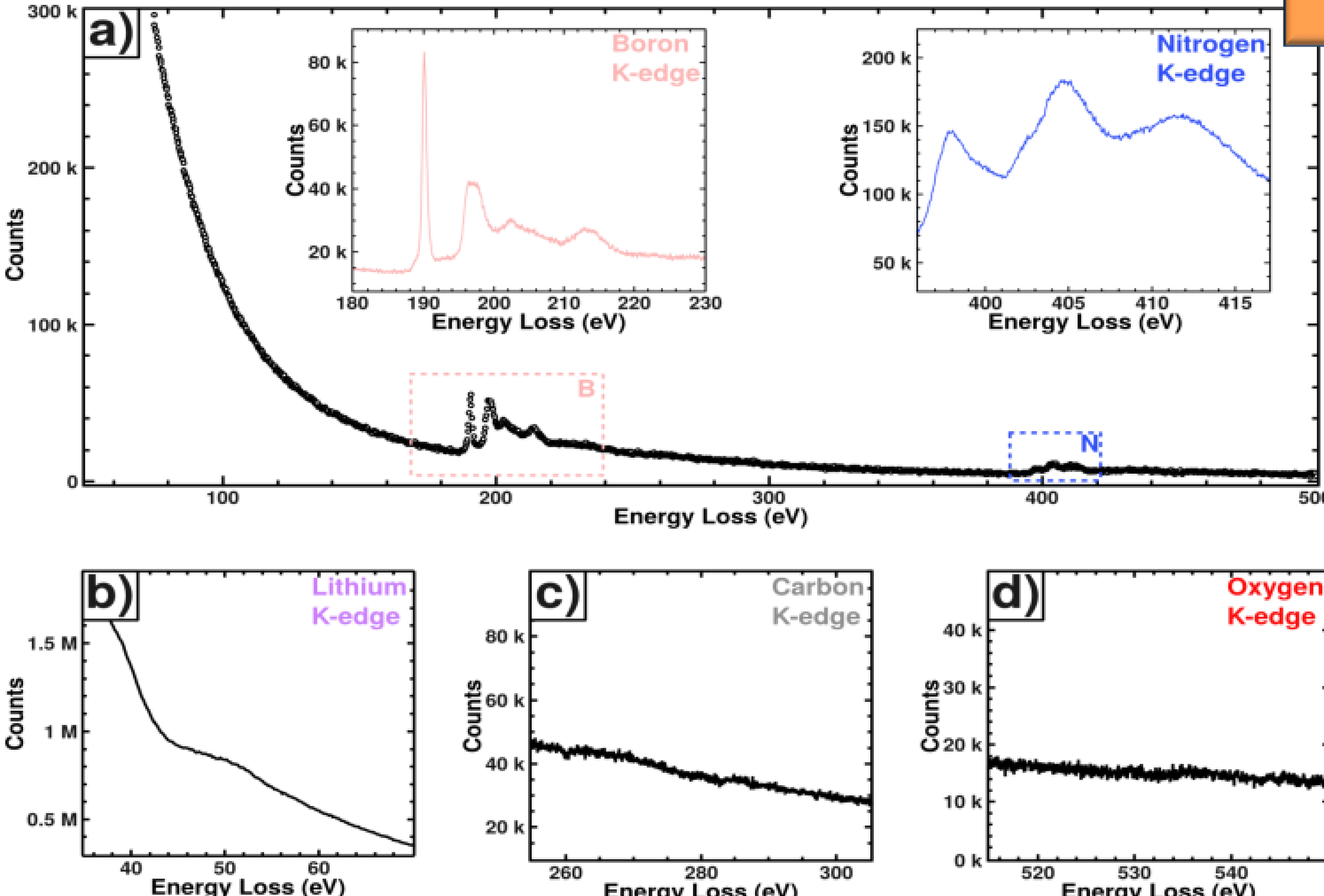
Characterization of the BNNSs

TEM



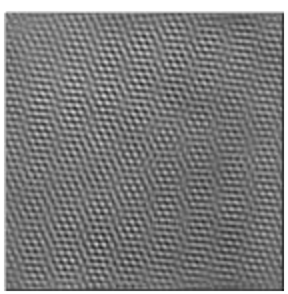
Characterization of the BNNSs

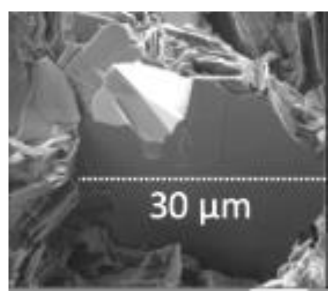
EELS

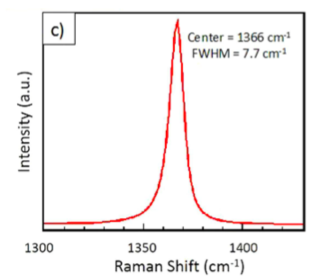


Conclusions & Outline

- BNNS as ideal candidate for graphene substrate / encapsulating layer / 2D layers staking
- Increase of the crystallinity by adding Li_3N
  - Higher crystallinity at lower temperature
- Interest in combining the PDCs route & the SPS to get h-BN large single crystals
- After exfoliation, large (tens of µm) and defect-free BNNSs obtained







*S. Yuan et al. Crystals, **6**, 55 (2016)*

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- Philippe Steyer
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- Annick Loiseau
- Alexandre Plaud
- Julien Barjon

Thank you for your attention !