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Italiadomani
PIANO NAZIONALE DI RIPRESA E RESILIENZA

VITALITY

High-Pressure dependence of structure evolution and adsorption behavior in Nano-Layered Double Hydroxides (LDHs): impact for their uses in Cements.

Fastelli, M.[1*], Vivani, R.[2], Di Michele, A.[1], Schoubben, A.[2], Zucchini, A.[1], Mortaro, F.[1], & Comodi, P.[1]

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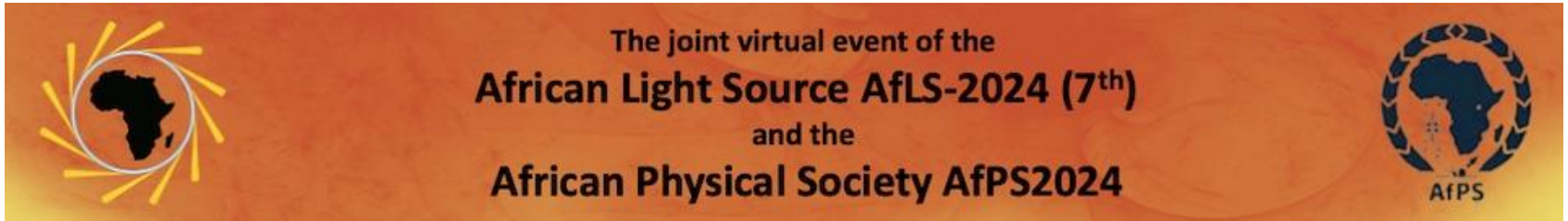

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VITALITY

VITALITY research project:

"Engineered sustainable concrete based on nanomaterials & recycled demolition waste"

(Principal Investigator: Prof. Paola Comodi)

DIPARTIMENTO DI FISICA E GEOLOGIA

Prof. Paola comodi
Dr. Azzurra Zucchini
Dr. Alessandro Di Michele
Prof. Francesco Frondini

DIPARTIMENTO DI INGEGNERIA

Prof. Emanuela Speranzini

DIPARTIMENTO DI SCIENZE FARMACEUTICHE

Prof. Aurelie Schoubben
Prof. Riccardo Vivani

DIPARTIMENTO DI CHIMICA, BIOLOGIA E BIOTECNOLOGIE

Prof. Paola Sassi

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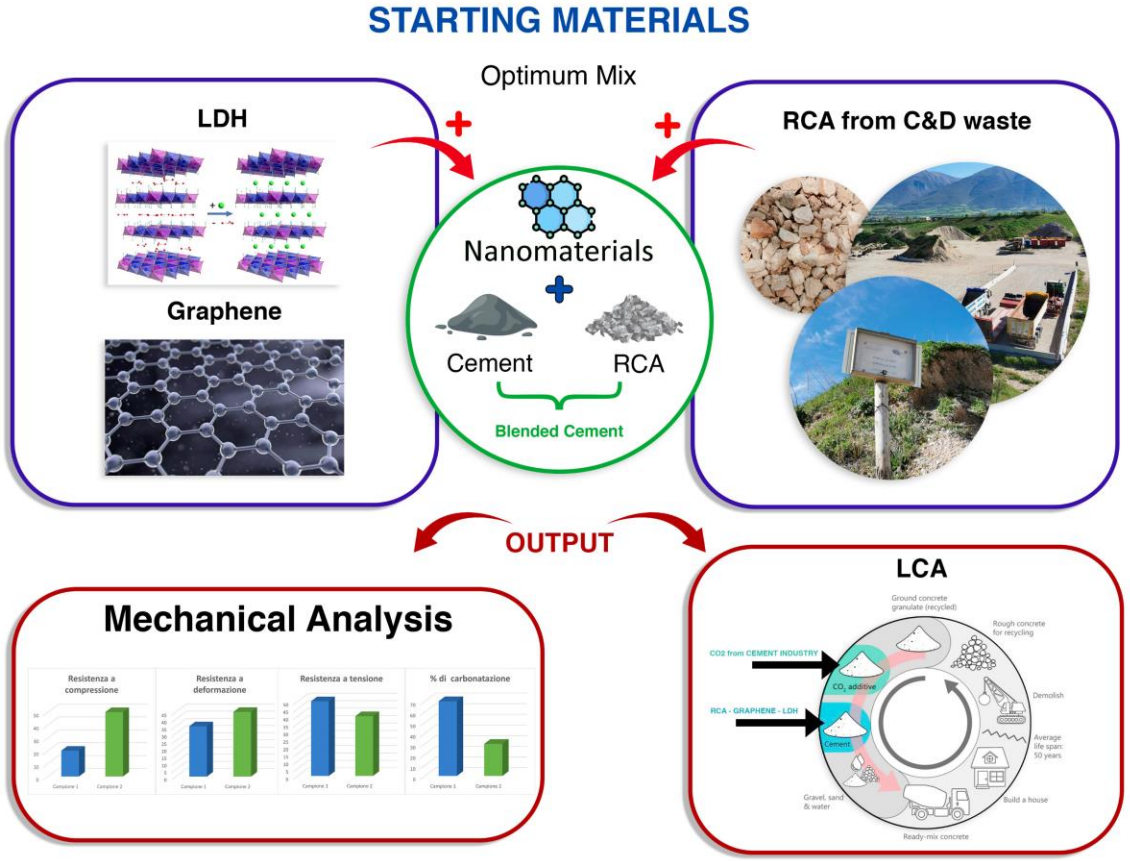
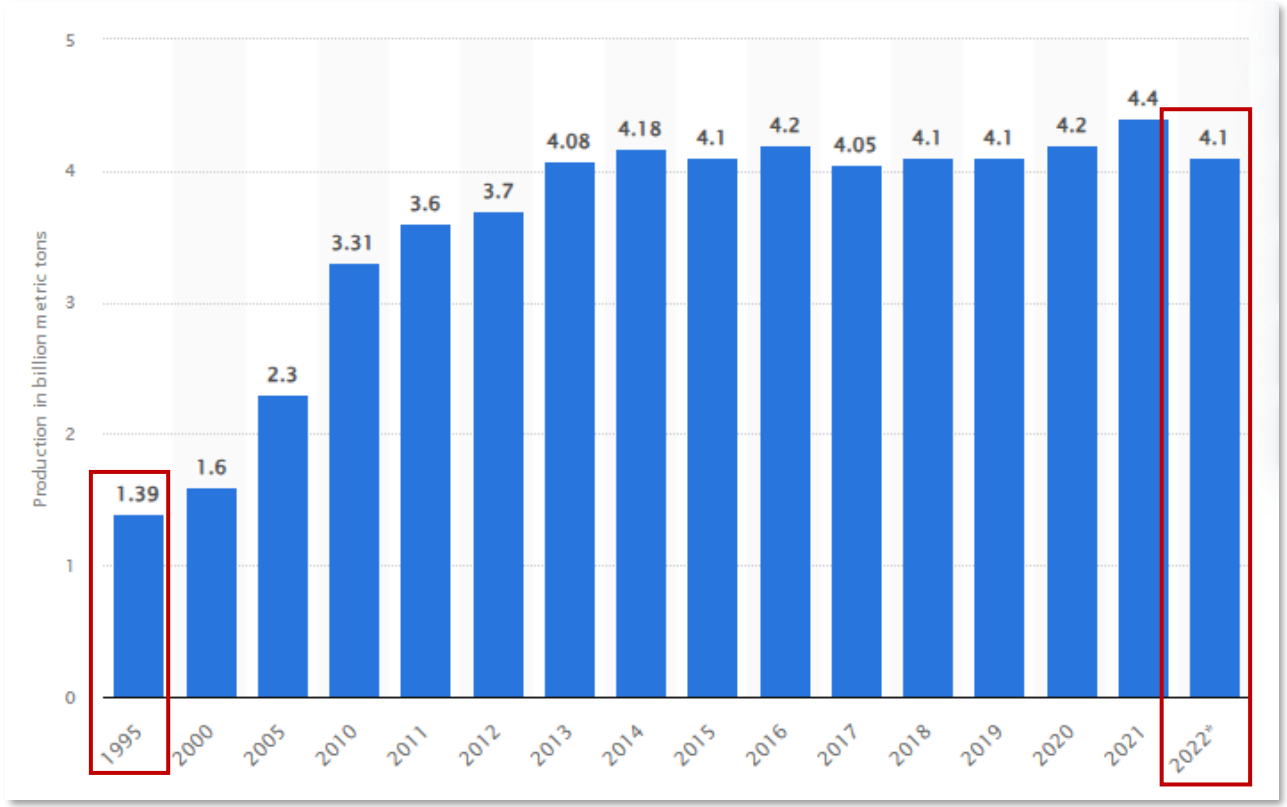
"Engineered sustainable concrete based on nanomaterials & recycled demolition waste"



Introduction

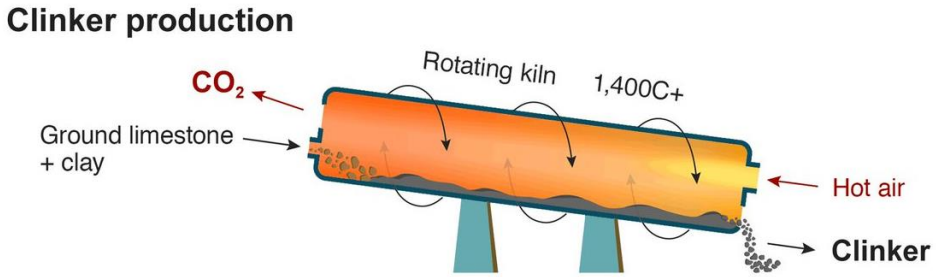
In recent decade,
demand and production of **cement** significantly **increased**

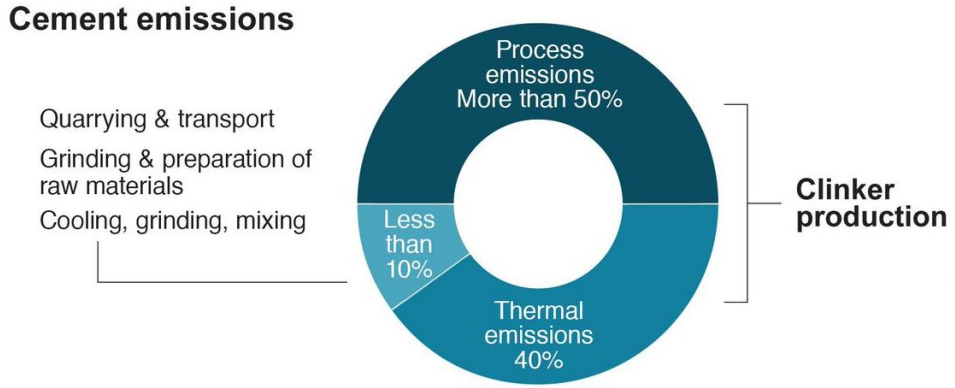


Statista.com

Cement production is responsible for approximately **7%** of global **CO_2** emissions

More than 50% of CO_2
arise from **clinker** production processes





Fastelli, M. et al.

High-Pressure dependence of structure evolution and adsorption behavior in Nano-Layered Double Hydroxides (LDHs): impact for their uses in Cements.

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Cement issue

- **Corrosion** of steel rebars caused by aggressive ions such as Cl^- , $CO_3^{-2}$and SO_4^- in reinforced concrete

- In **alkaline environment**, such as that of concrete, the steel bars a secured by a thin **protective layer**

- In **harsh environment**, acids can react with various cement hydration products so that the **pH** value of concrete pore solution is significantly **reduced**

Introduction

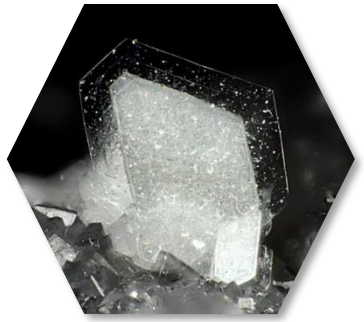
It is essential the development of new **strategies**

Incorporation of appropriate **nano-materials** into standard cement pastes

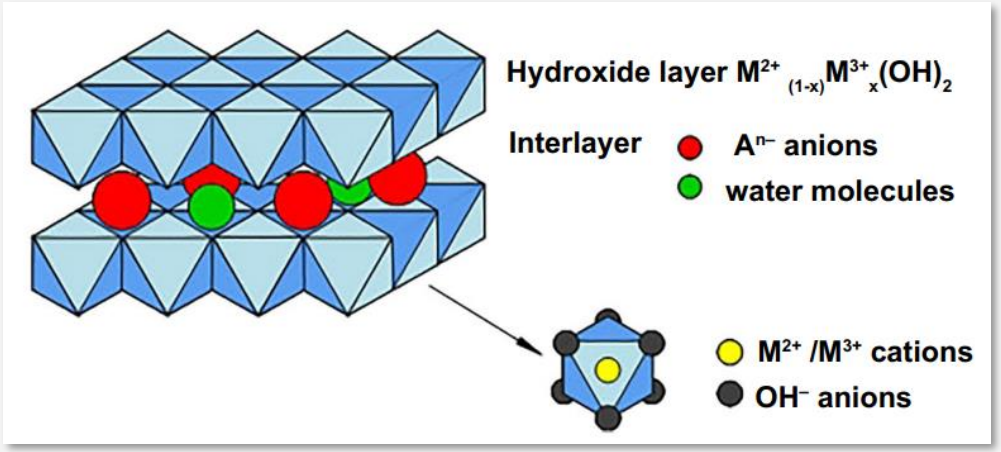
Improvement of **physical** and **chemical properties**

Layered double hydroxides (LDHs)

Also referred to as **anionic clays**, are emerging as excellent additives, thanks to their **structure** and interesting **properties**



LDHs consist of **positively charged** layers with intercalated **anions** in the inter-layer spaces.



$$[M^{2+}_{1-x}\, M^{3+}_{x}\, (OH)_2]^{x+}\, (A^{n-})_{x/n} \cdot nH_2O$$

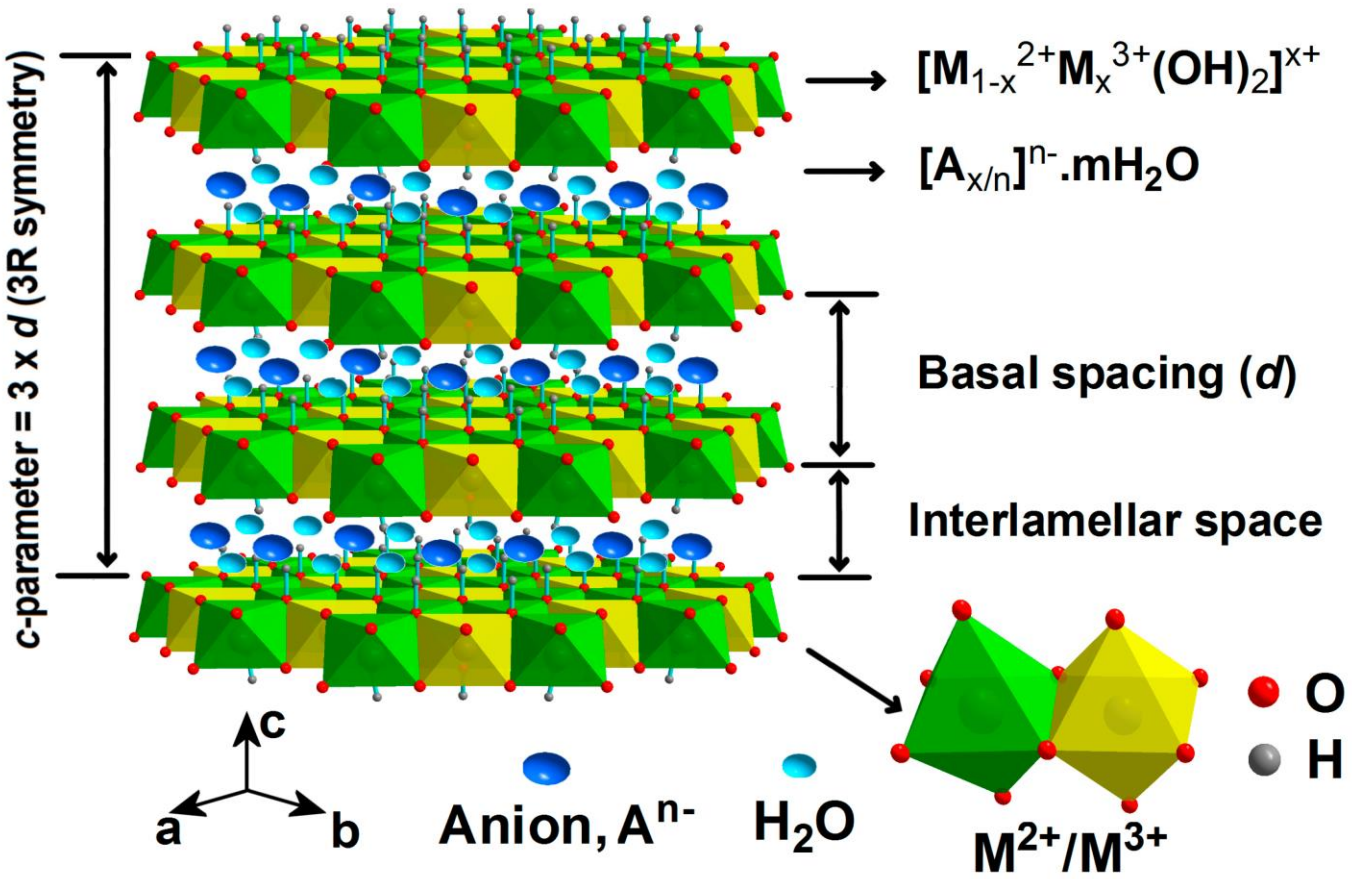
M^{2+} = divalent cation

M^{3+} = trivalent cation

A = inter-layer anion

x = cations molar fraction

LDH *Characteristics and properties*



Li et al., 2017

Environmental applications of LDHs

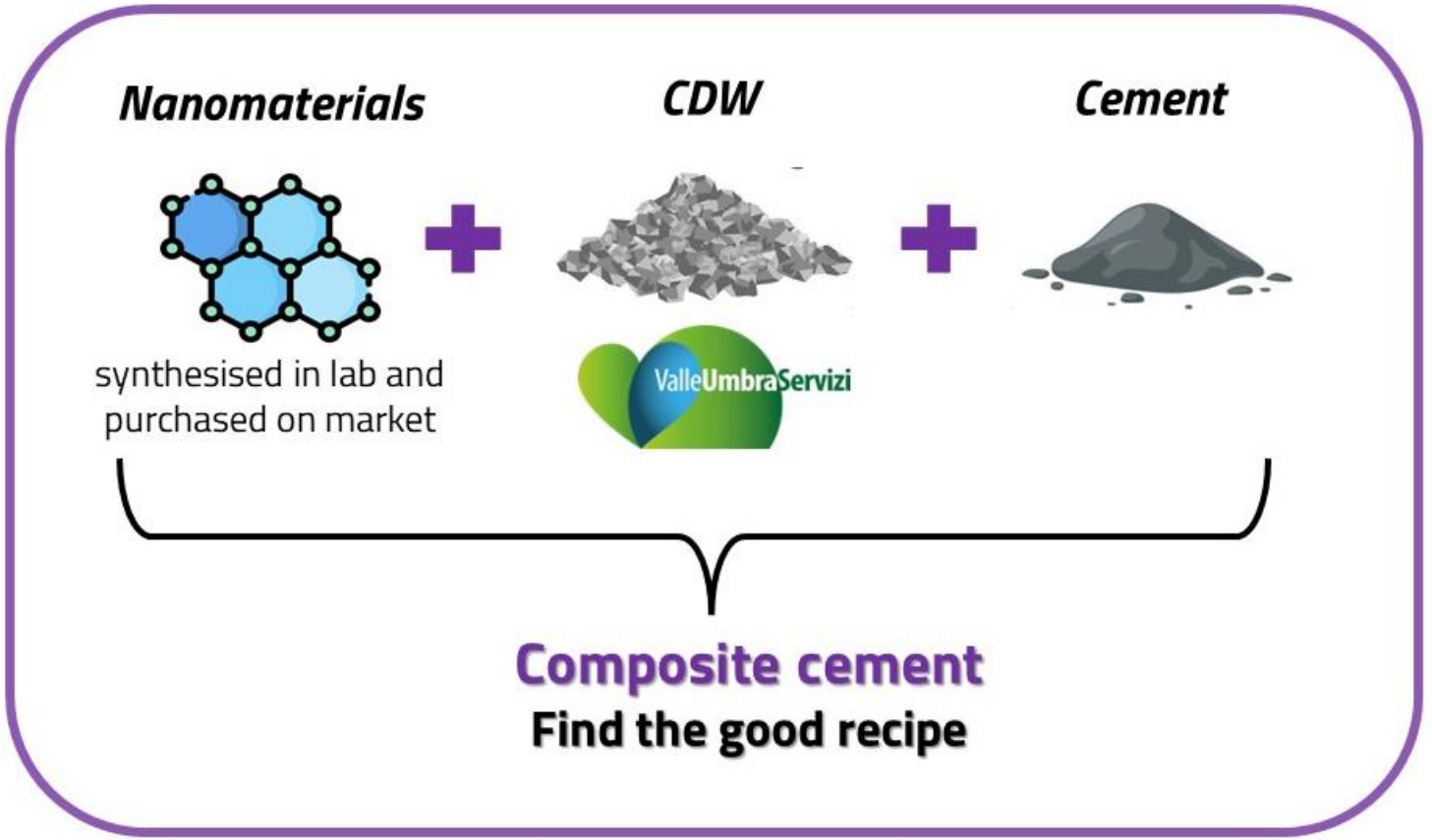
LDHs

- Gas adsorption **[adsorbents]**
  Recovery of CO_2
- Ion exchange (including capture through reconstruction) **[adsorbent]**
  Removal of ionic contaminants and selective ion tuning
- Reduce porosity and great specific surface **[nanomaterials]**
  Improve mechanical properties of concrete

LDH *inside cement paste*

1. Enhance in **early** and **late strength** of cements

2. Act as **fillers**



3. Can be **seeds of nucleation**

4. Increase **the tortuosity of pore**

Workflow

1 **Synthesis of** nano-LDH-$\mathbf{NO_3^-}$ through different synthesis methods

- **Ultrasound-assisted co-precipitation**

MgAl-NO_3

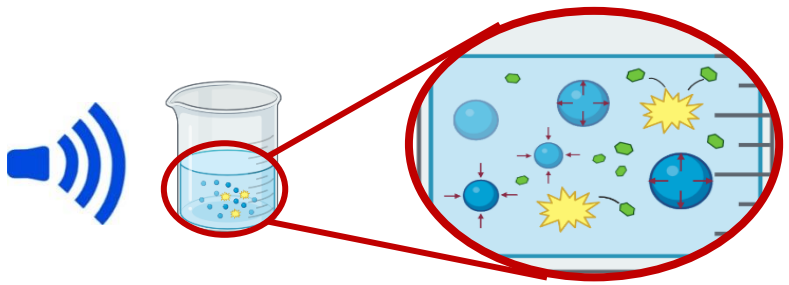
$[Mg_{0.67}Al_{0.33}(OH)_2](NO_3)_{0.33}$

2 **Characterization** of the synthesized samples through multiple analytical techniques

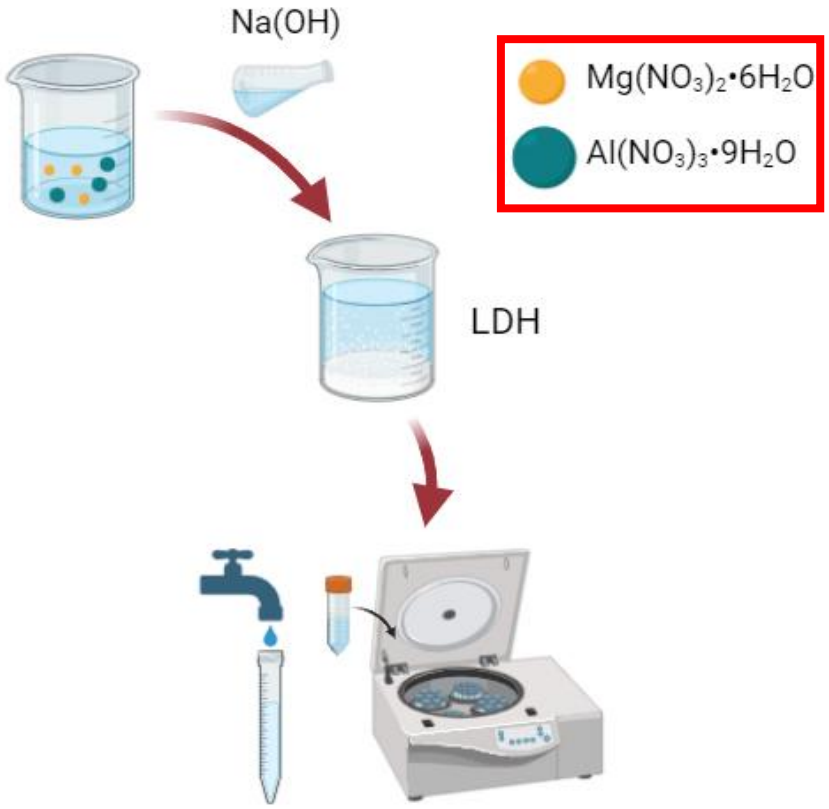
- **XRPD** (X-Ray Powder Diffraction)
- **FT-IR** (Infrared spectroscopy)
- **TGA** (Thermal Gravimetry Analysis)
- **SEM** (Scanning Electron Microscopy)
- **TEM** (Transmission Electron Microscopy)
- **DLS** (Dynamic Light Scattering)

Synthesis of nano-LDH-NO_3

❑ **Ultrasound-assisted co-precipitation**



Acoustic cavitation



Results: XRPD and FT-IR

2) Ultrasound assisted direct co-precipitation in supersaturation conditions

- 1 M solution of nitrate salts precipitated by 6M NaOH under argon atmosphere followed by 24h ageing time at 80°C.

MgAl-NO_3

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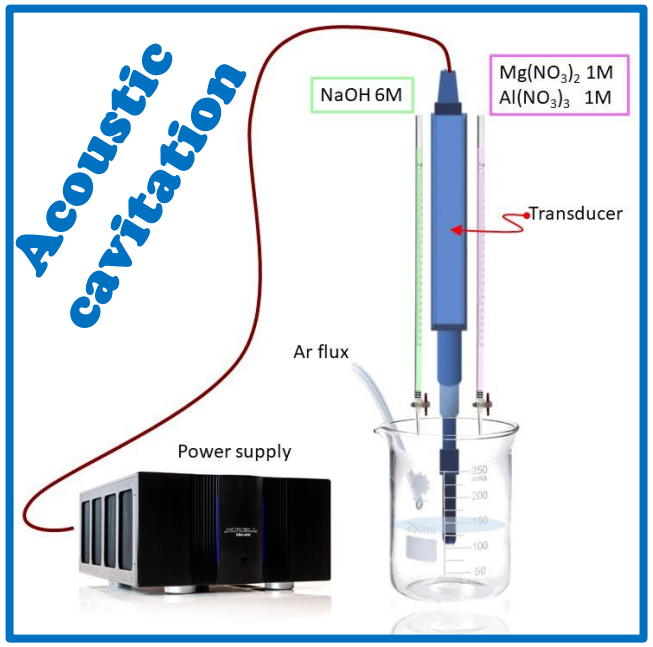
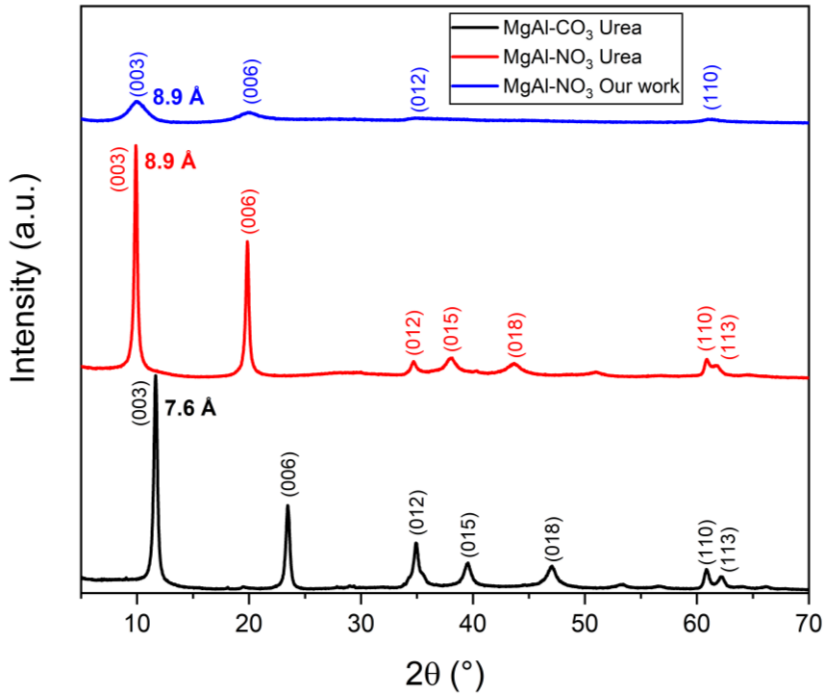
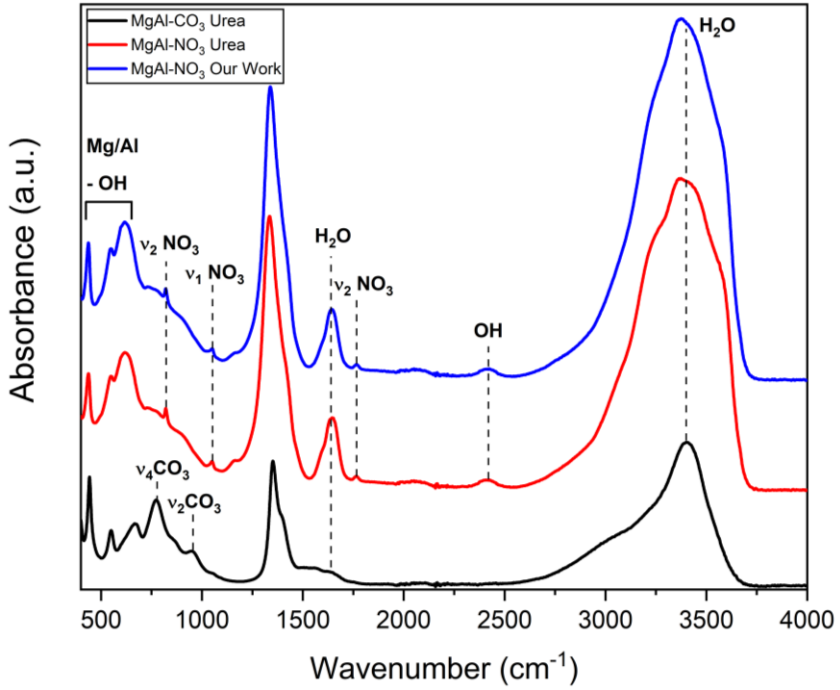


XRPD



FT-IR



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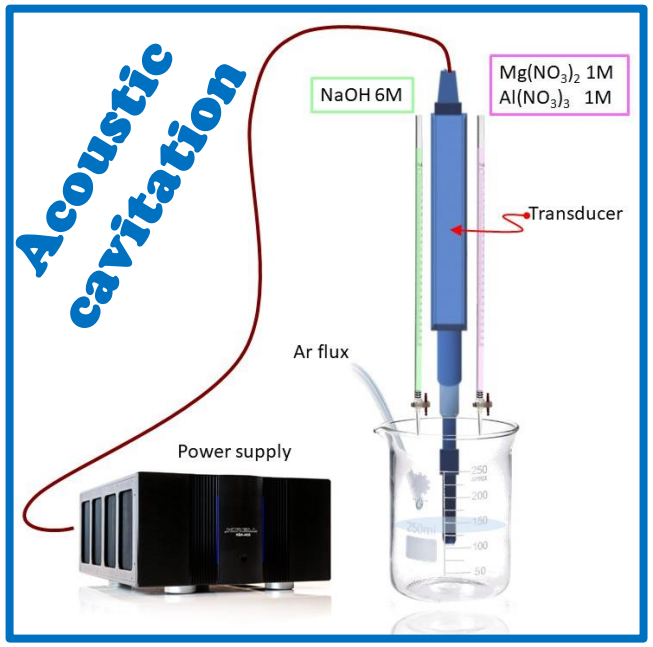
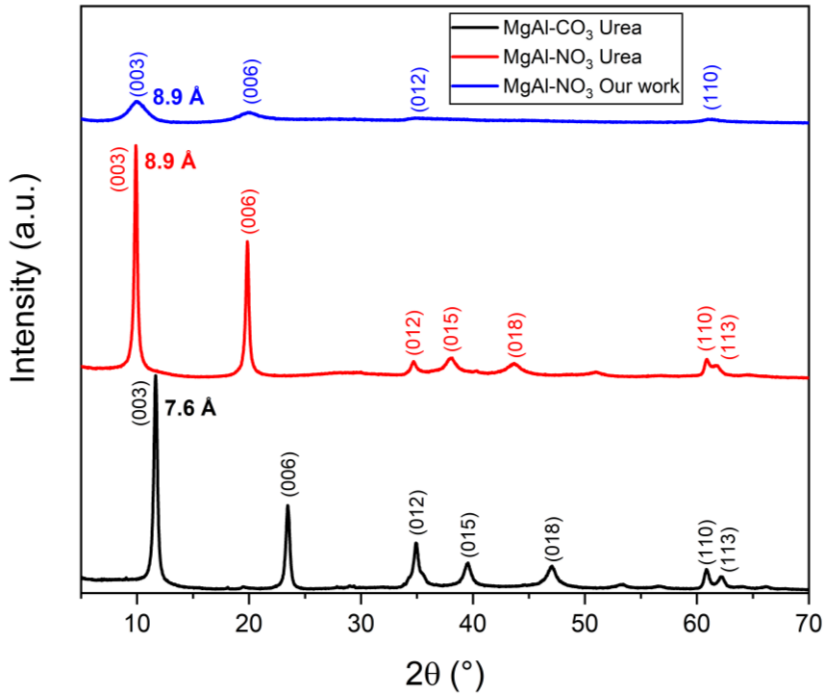
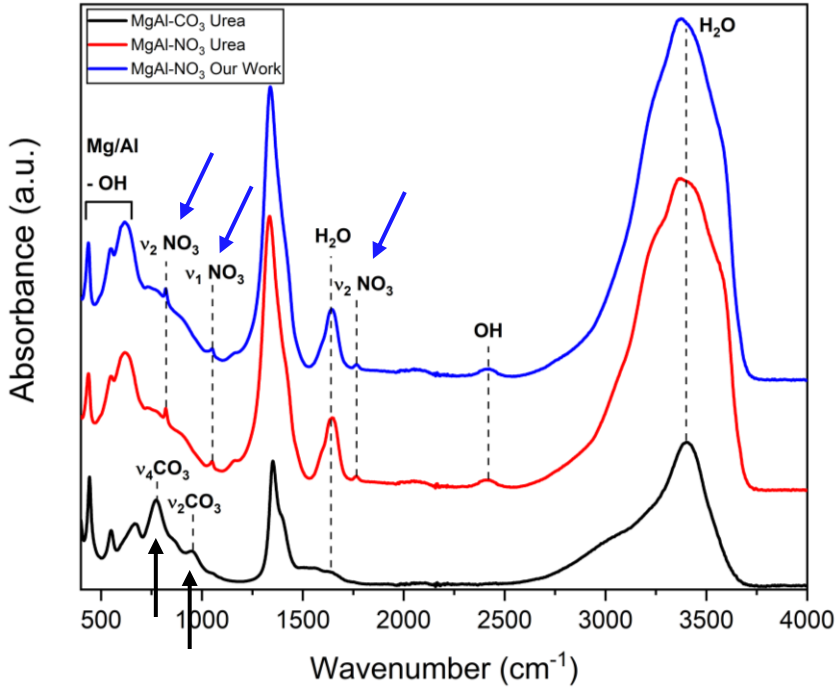


XRPD



FT-IR



Results: SEM

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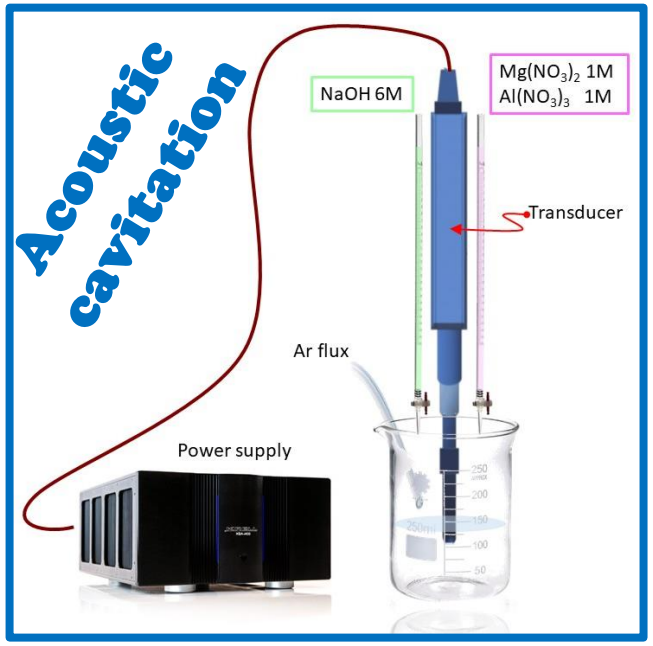

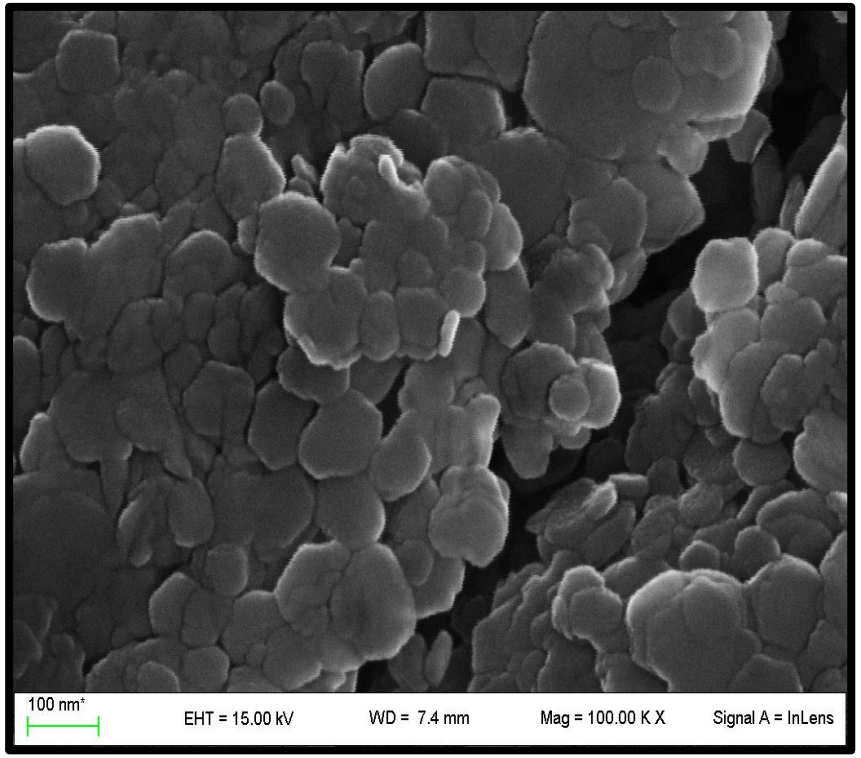

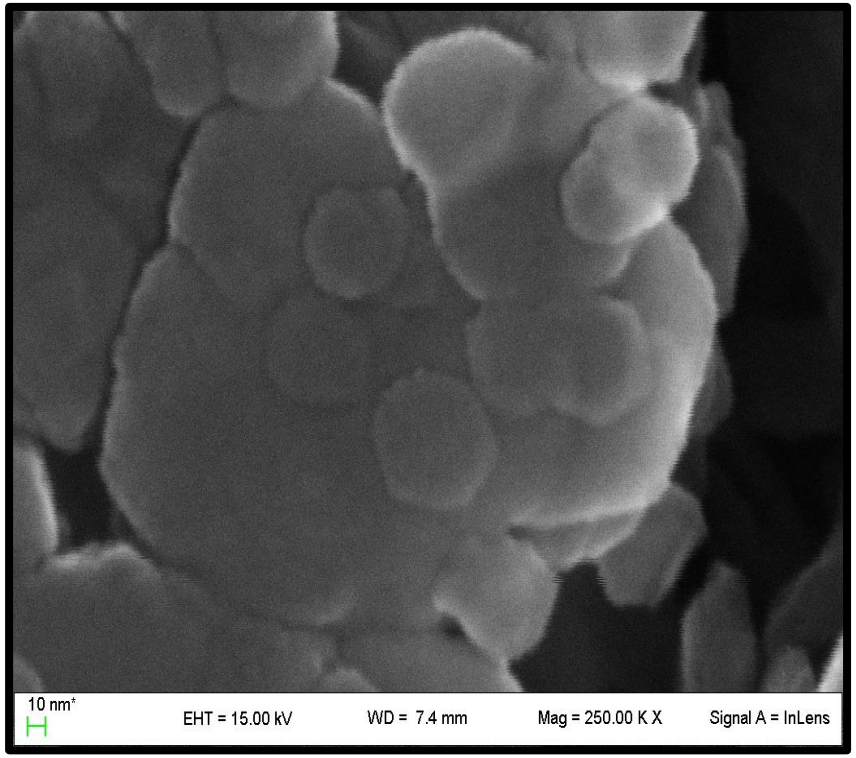

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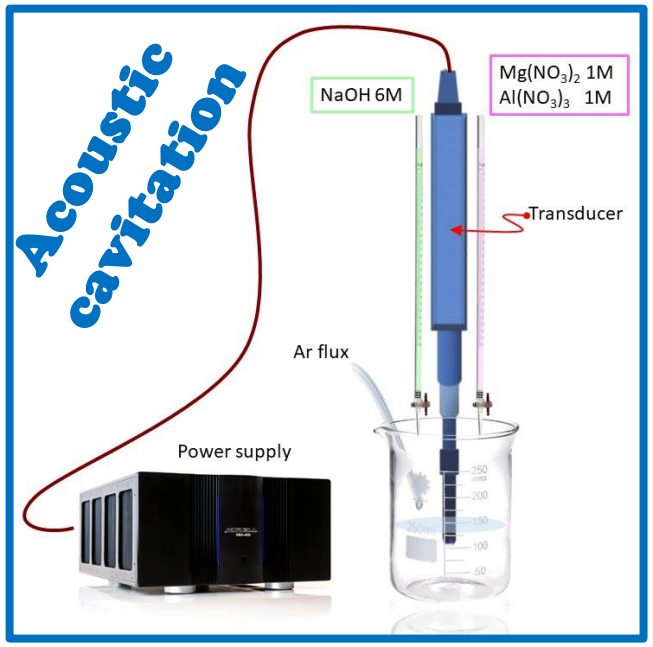
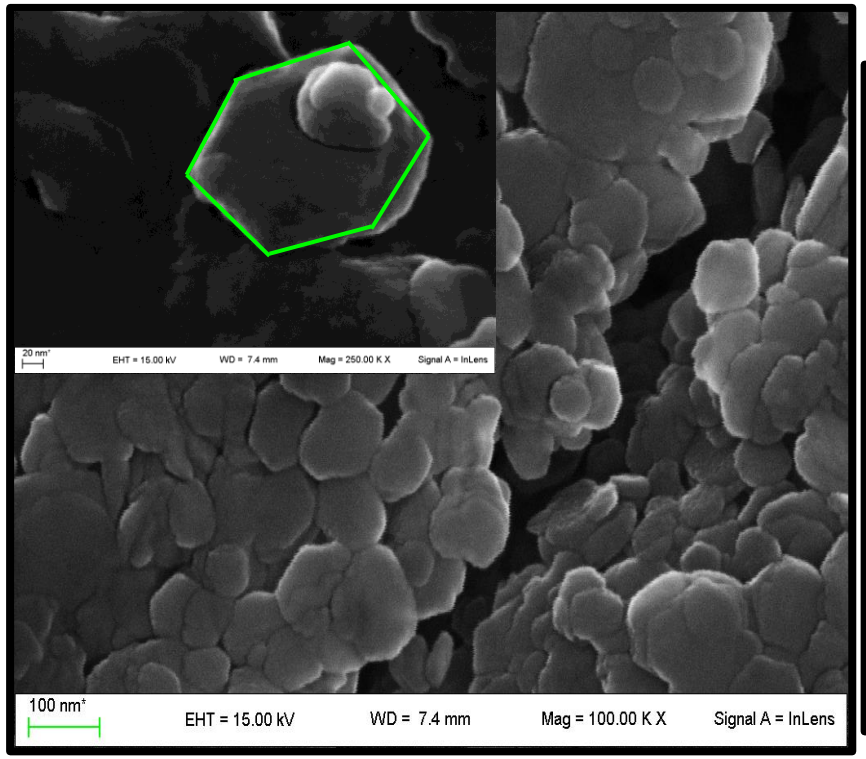
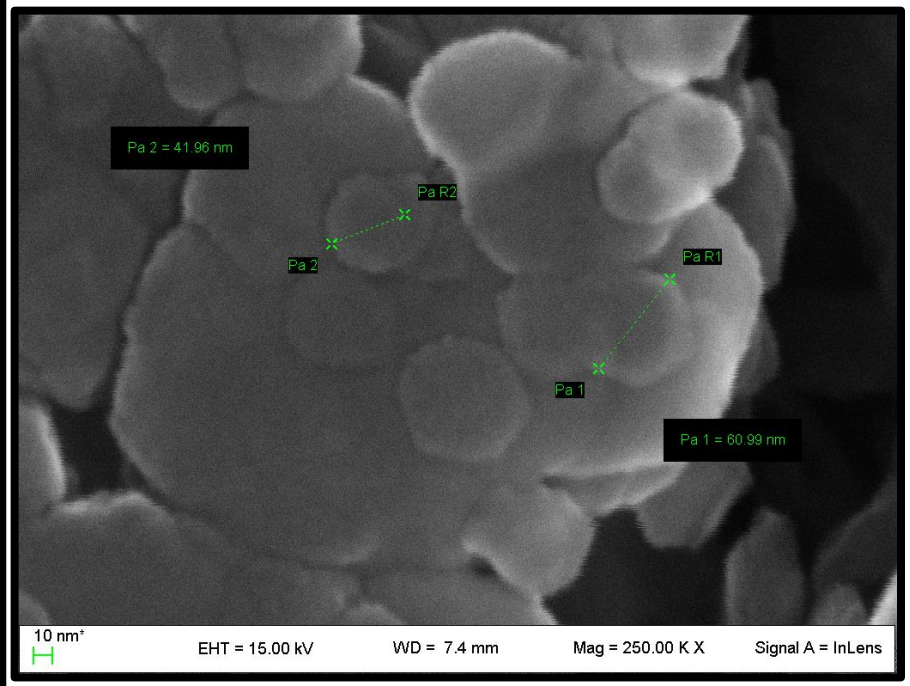






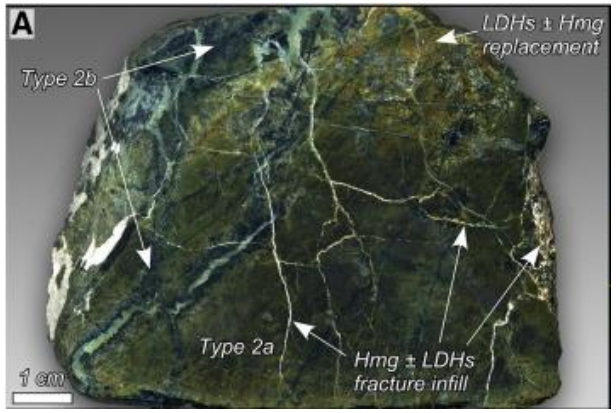
3

Preliminary study of the **HIGH-PRESSURE** powder diffraction behaviour of **LDH-CO_3^{2-}**

@ ESRF beamline ID 15b

Science.org

Grenoble, France



Modified from Boschi et al., 2017

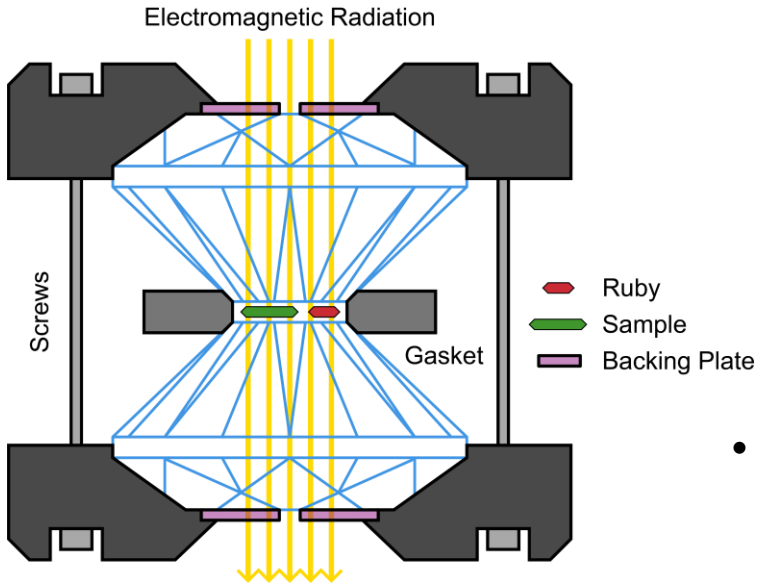
MgAl-CO_3

$[Mg_{0.67}Al_{0.33}(OH)_2](CO_3)_{0.165}$

From Urea Synthesis method

Results: LDH-CO_3 HP XRPD @ ESRF

High Pressure (**HP**) X-ray powder diffraction using Diamond Anvil Cell (**DAC**)



schematic representation of a **DAC**

https://en.wikipedia.org/wiki/Diamond_anvil_cell#/media/File:Diamond_Anvil_Cell_-_Cross_Section.svg

Experiment set-up:

- Beamline ID-15b @ESRF
- Detector EIGER2 X 9M CdTe
- X-ray wavelength 0.410371 Å
- Ne transmitting medium
- Ruby and Au pressure calibrants
- 300 µm coulet diamond

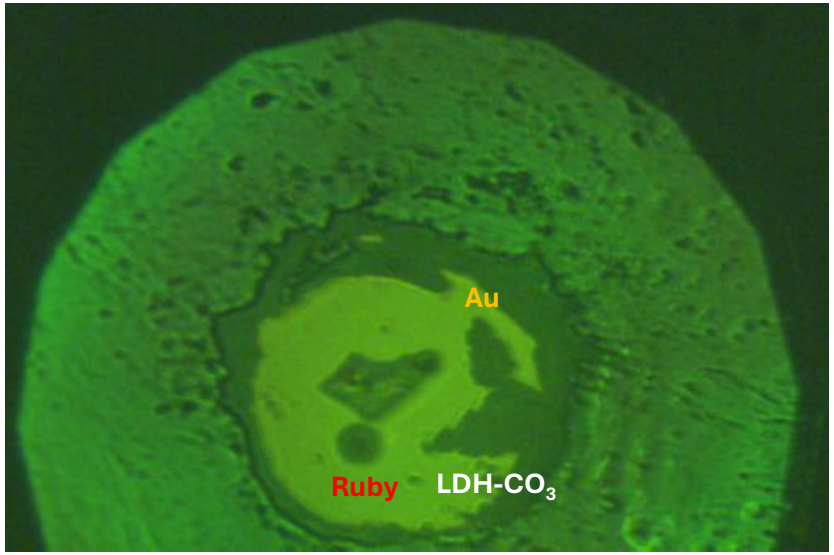
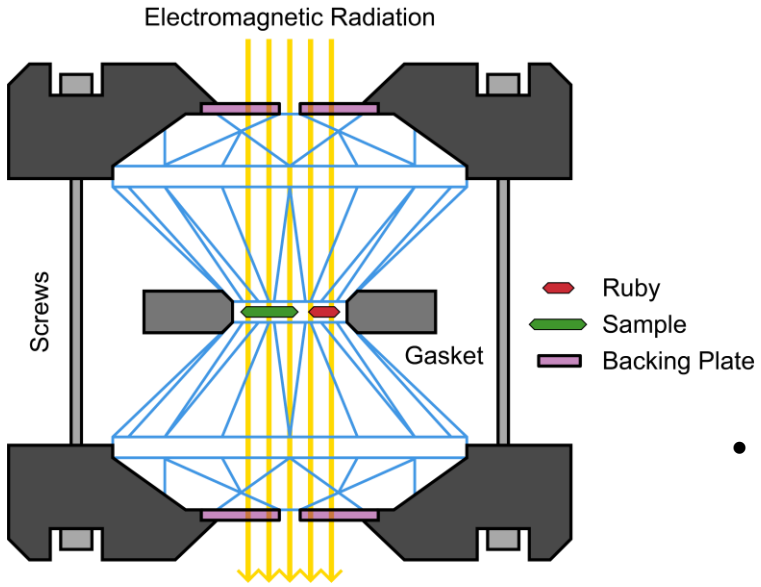


Photo of the inside of the **DAC**

Results: LDH-CO_3 HP XRPD @ ESRF

High Pressure (**HP**) X-ray powder diffraction using Diamond Anvil Cell (**DAC**)



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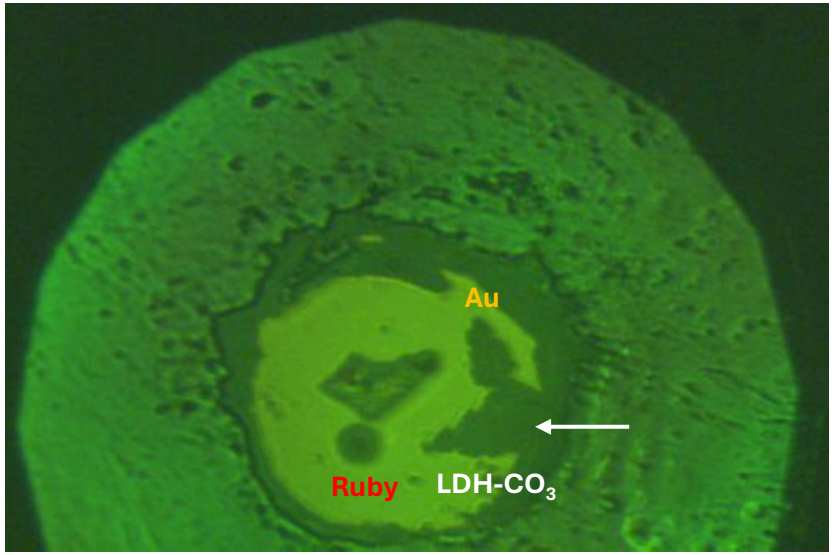

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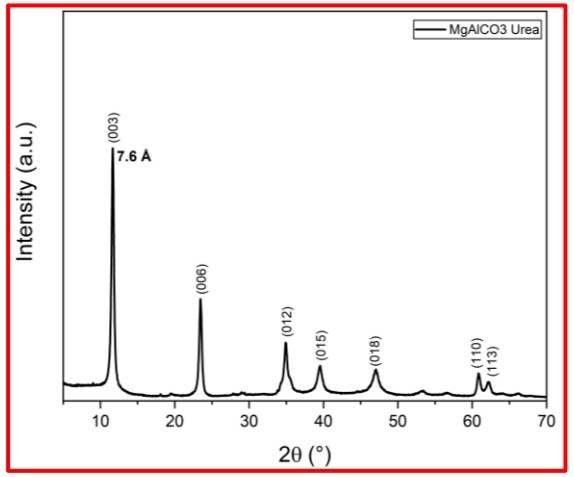

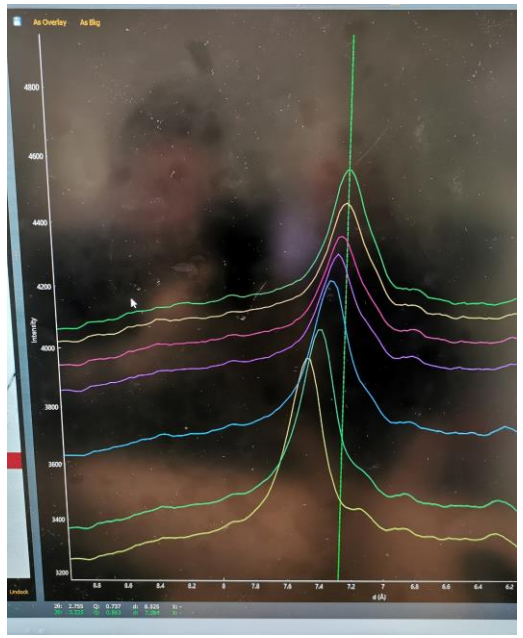

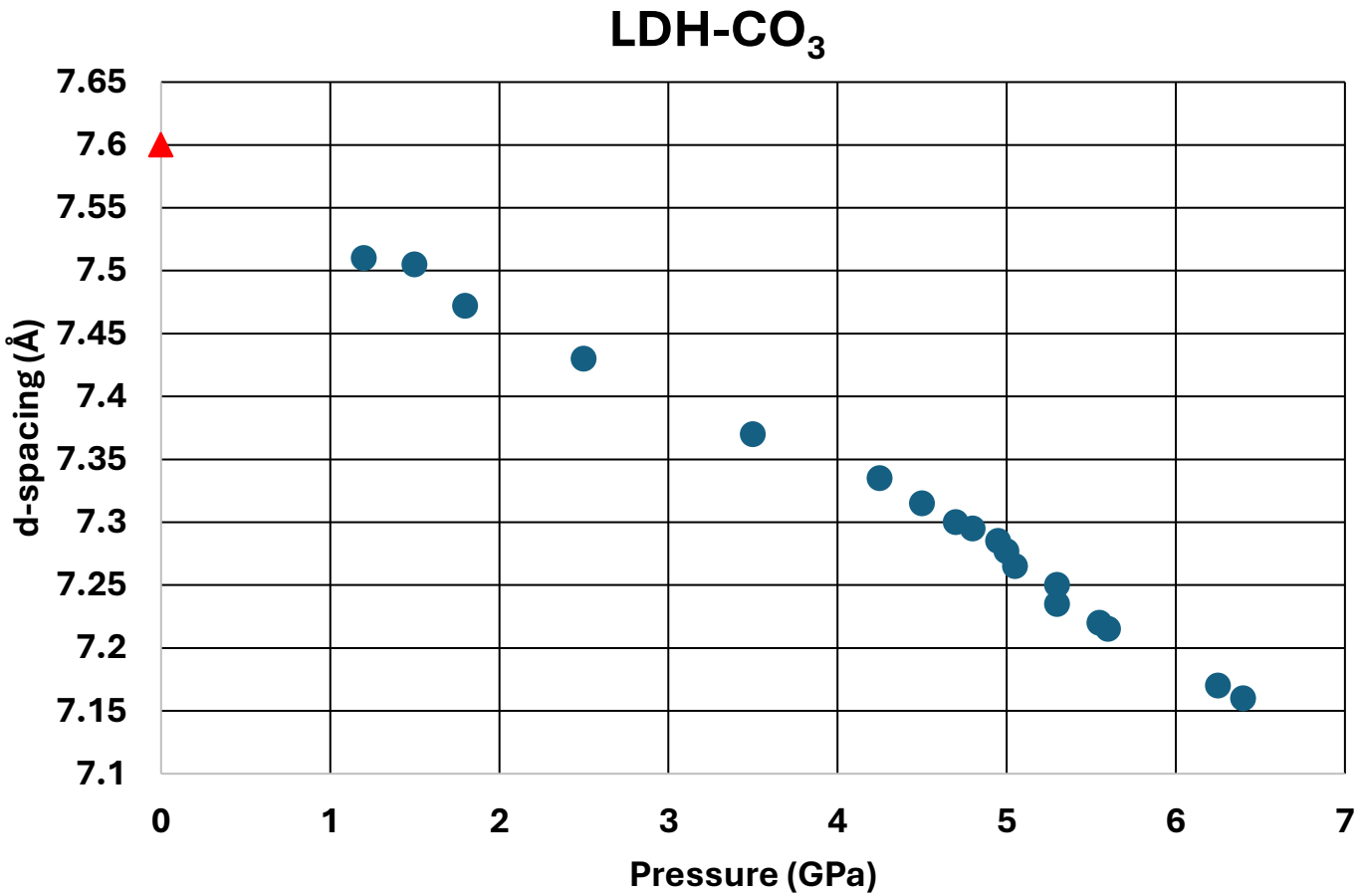

No amorphisation until **6.4 GPa**

Fastelli, M. et al.

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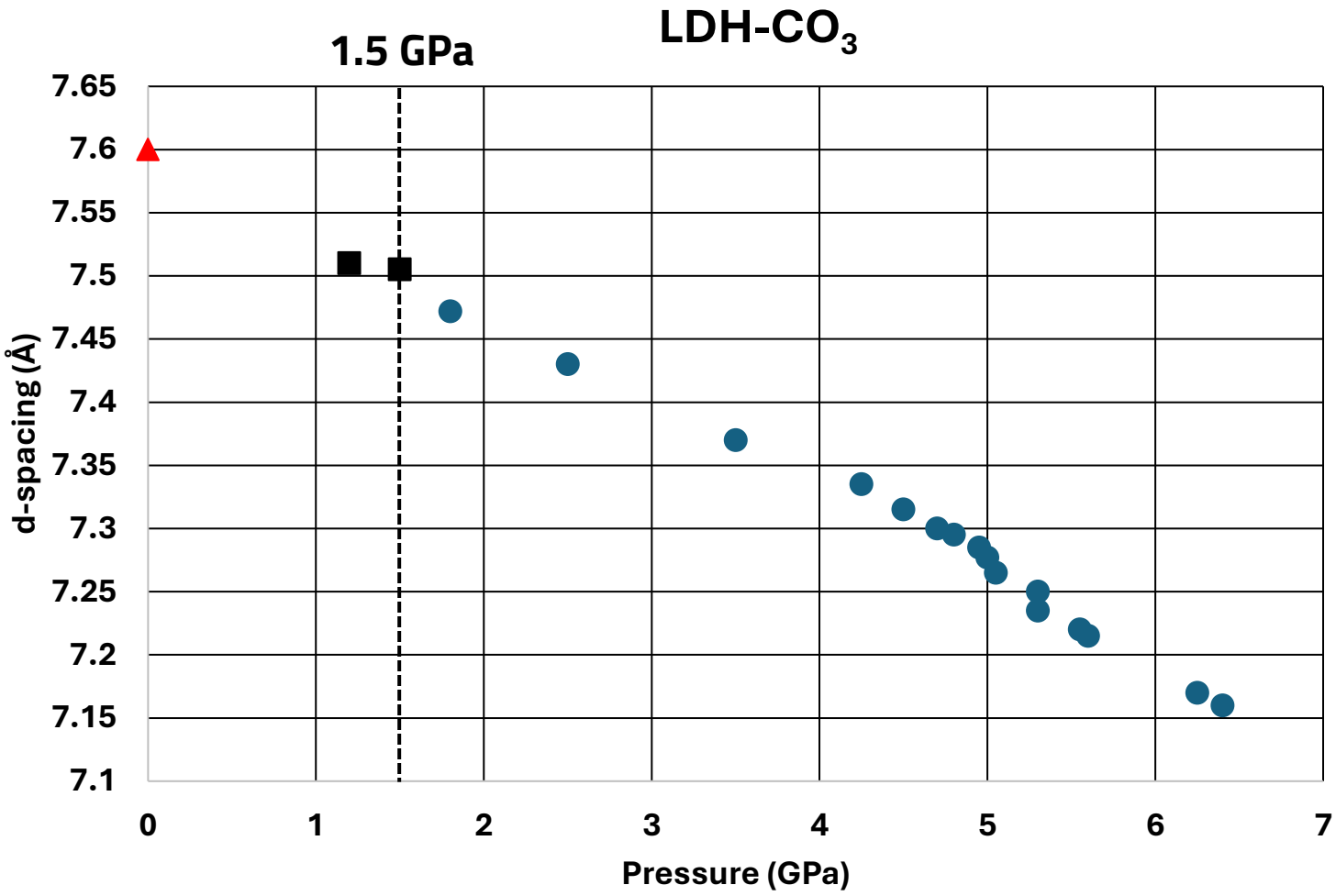
Results: LDH-CO_3 HP XRPD @ ESRF

1.5 Gpa: First transition as reported in Parthasarathy et al., 2002 where were observed a decrease of electrical resistivity

Conversion to **hydrotalcite** (3-layer rhombohedral polytype)

to

(Manasseite) polytype 2H (2-layer hexagonal polytype)



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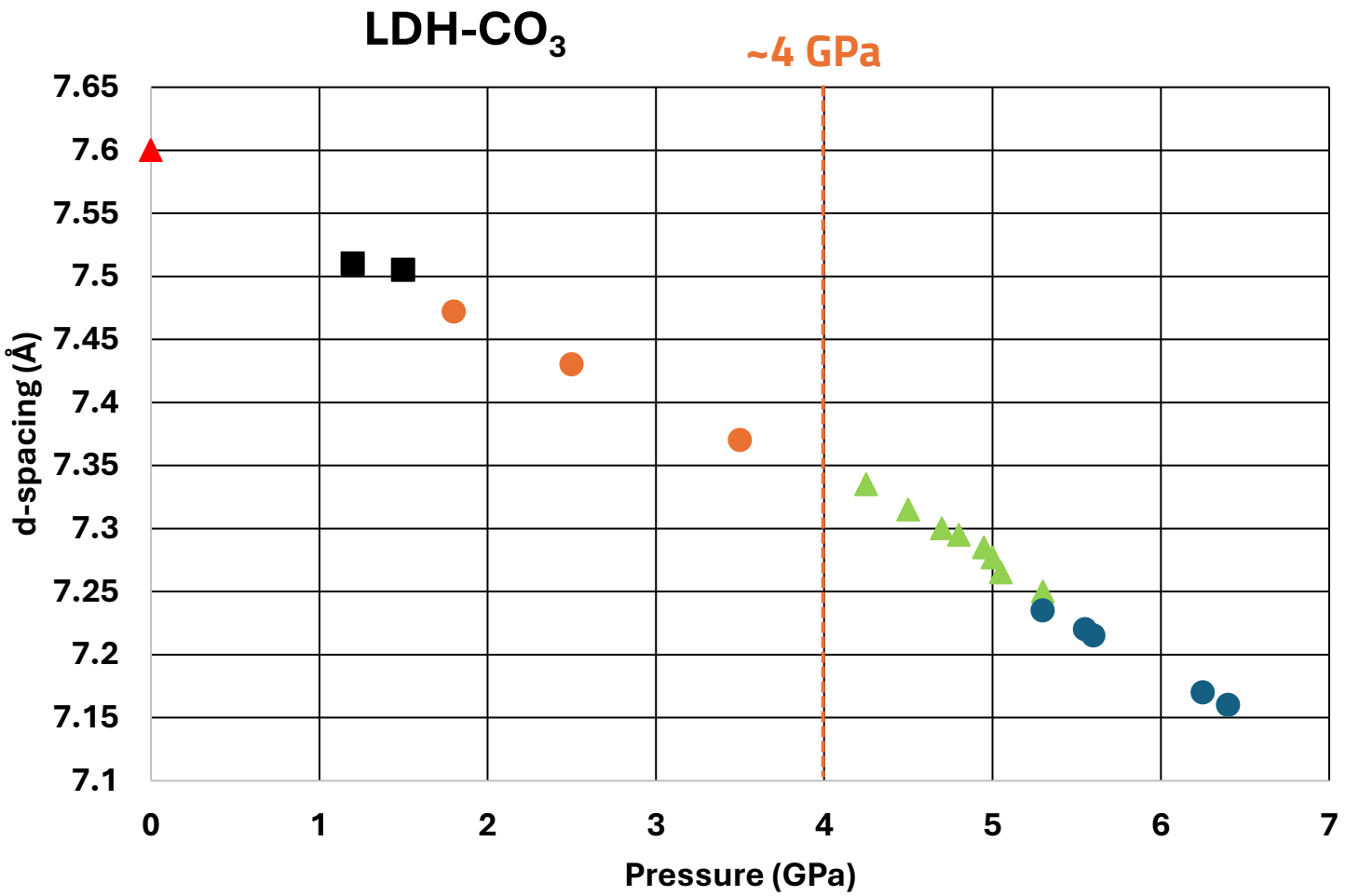

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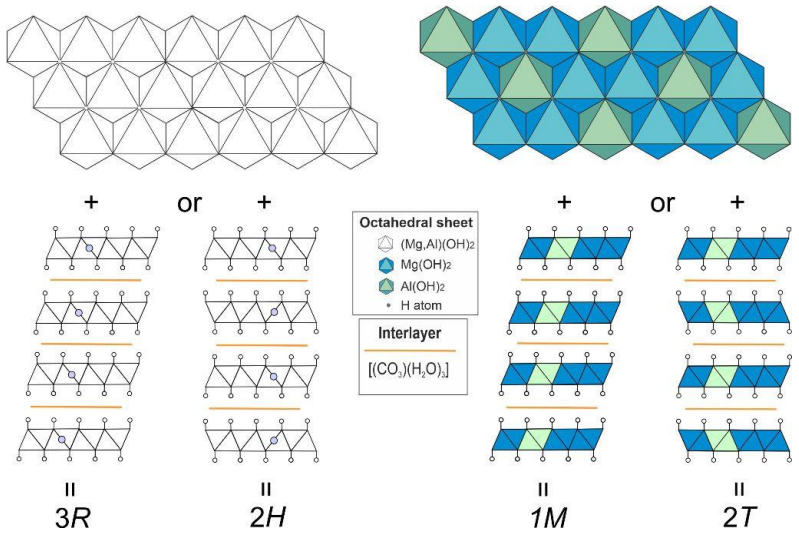
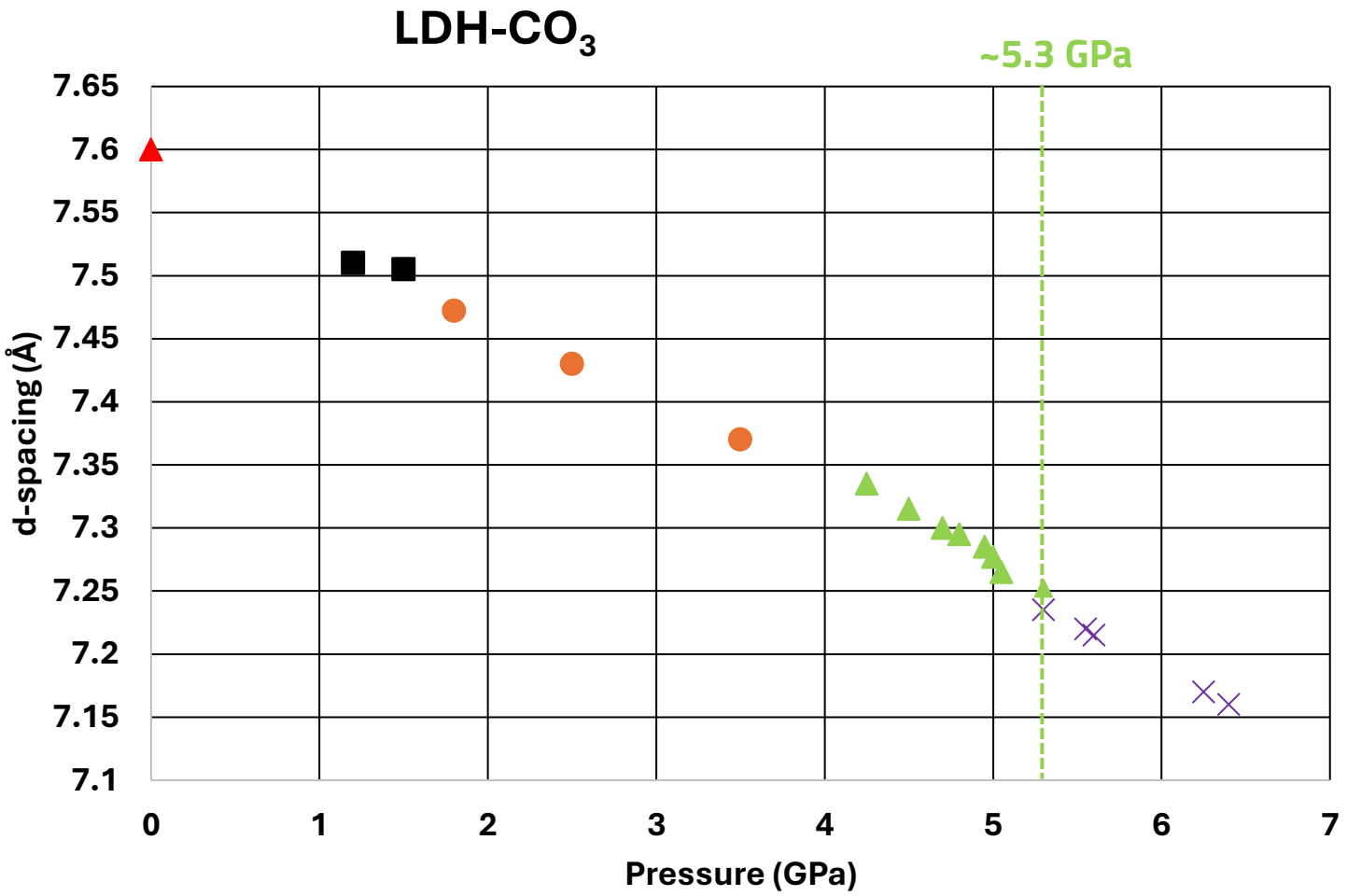


Zhitova et al., 2023



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Discussions and conclusions

- **No amosphisation** of the sample were observed up to **6.4 GPa**

A reduction of the peak intensity and broadening were observed

- Given the **high quality of the data and resolution,** the observed **discontinuities could be significative** due to small error

Discontinuity can be associated to a possible transition to polytype of hydrotalcite like materials or approach of the lamellas

Future perspective

- Collection of a new dataset with a different set up

Using the DAC with diamond with a larger coulet and using a differentiated pressure medium that can be intercalated within the structure.

- Studying the effect of pressure not only by diffraction technique but also by *in situ* **Raman spectroscopy**

Raman spectroscopy could provide important information on possible phase transitions and intercalation of the pressure medium.

- Studying the contribution of pressure on the **memory effect** of LDH

Indeed, temperature does not affect the memory effect but the effect of pressure on this property is not known

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Thank you for your attention!

...and thanks to the whole research team

Comodi P.

Di Michele A.

Mortaro F.

Zucchini A.

Vivani R.

Schoubben A.

ESRF
The European Synchrotron

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The joint virtual event of the
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and the
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AfPS