Consiglio Nazionale delle Ricerche
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

DSCTM
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

ICCI CNR Istituto di Cristallografia

xmi l@b

Combining synchrotron radiation and Crystallography to decrypt the structure of materials impacting Energy, Environment and Health

Anna Moliterni

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Outlook

- How Crystallography can shed light on Materials Science;

- The Crystallography 'lens' to successfully characterize new materials:

why the need of synchrotron radiation?

The answer is in some cases of challenging characterization

(Synchrotron light makes the difference):

New materials of interest for Energy:

i.e., hybrid organic-inorganic perovskites and metal chalcohalides

New materials of interest for Environment and Health:

i.e., a new compound of possible pharmaceutical interest, an amosite amphibole asbestos fibre and an erionite fiber

- Conclusions

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- Conclusions and perspectives

How Crystallography can shed light on Materials Science

By determining the crystal structure of a new material, Crystallography can

- validate the expected crystal structure or reveal a completely unexpected structure
- identify the main intra- and inter-molecular interactions
- Identify the structure –property relationships

To answer to the following questions:

- Is the new crystal structure the expected/wanted one?
- Is the new 'recipe' correct or should it to be changed/further optimized?
- Why a new material shows unique physical properties?

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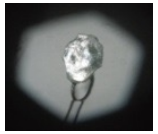
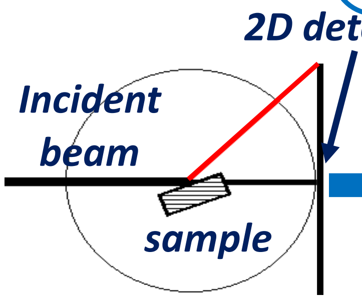
In the case of conventional X-ray sources

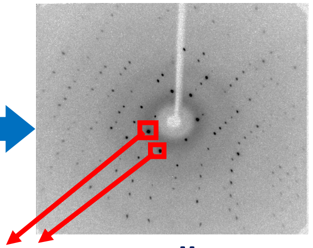
Single crystal

dimensions: fractions of mm



Individual information; Single phase

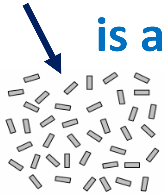




The diffraction effects are well separated
The experimental information is three-dimensional

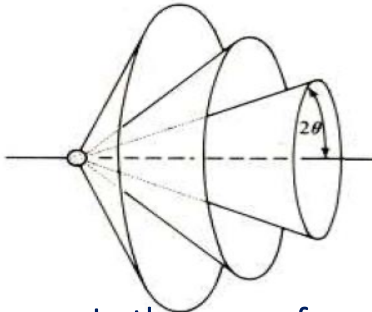
The *ab-initio* structure solution process is usually a routine and the structural details (e.g., bond lengths, positions of H atoms, …) are accurate.

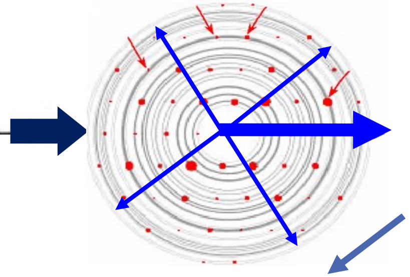
In case of micro/nanocrystals the powder crystallography is an obliged choice

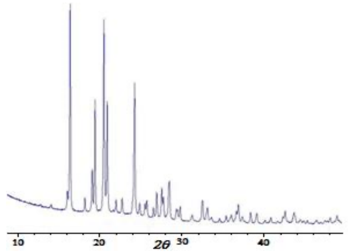


bulk information

Single phase or polyphase mixture







In the case of powder data the three-dimensional information is lost.

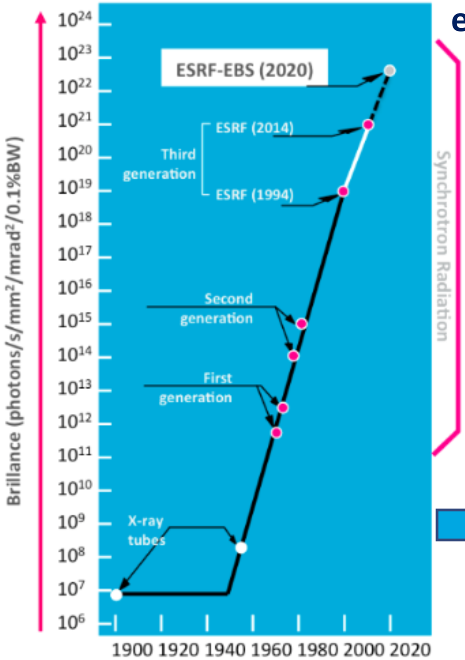
The experimental information is one-dimensional

The ab-initio structure solution process can be a challenge; the structural details are less accurate than those ones determined by single crystal data.

Why the need of synchrotron radiation?

In the case of single crystals, when the synchrotron radiation is an obliged choice?

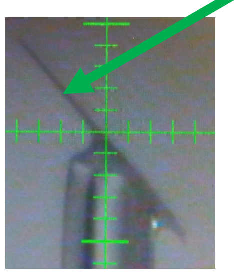
When the diffraction power of the single crystals is low, due to, for example, low crystallinity and/or small size (a few μm or ~ < 1 μm), as in the case of laminar or needle shaped samples

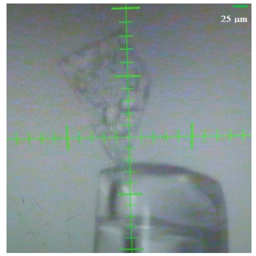


In these cases, if a conventional X-ray source is used, the data completeness is usually not reached.

A brighter X-ray source (synchrotron radiation) is needed for the success of the structure solution process by single crystal data.

Laminar samples a few μm thick





Needle shaped crystals

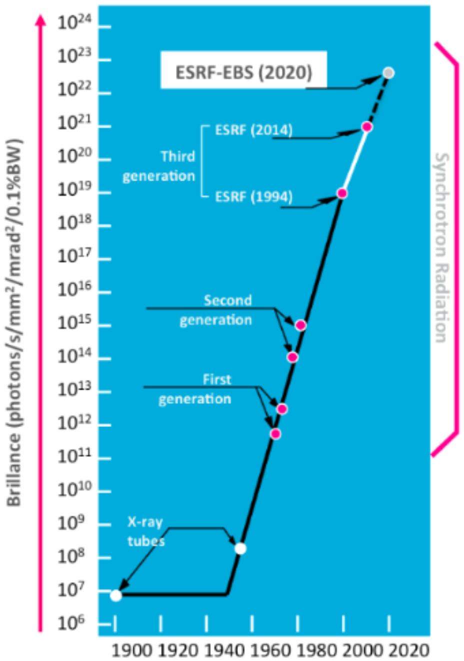
Crystal size: 0.09 x 0.01 x 0.01 mm

Why the need of synchrotron radiation?

If the size of crystals is very small (<μm or ~ nm)….

it may be impossible to carry out a successful structure solution process by synchrotron X-ray single-crystal microdiffraction data.

The structure solution by powder diffraction should be attempted.



Of course, if synchrotron sources (instead of conventional X-ray sources) are used, the higher quality and resolution of diffraction data will increase the probability of success of the structure solution process and will improve the results of the refinement step.

For challenging cases, a brighter X-ray source (synchrotron radiation) is needed for the success of the structure solution process by powder diffraction data.

Outlook

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- Conclusions

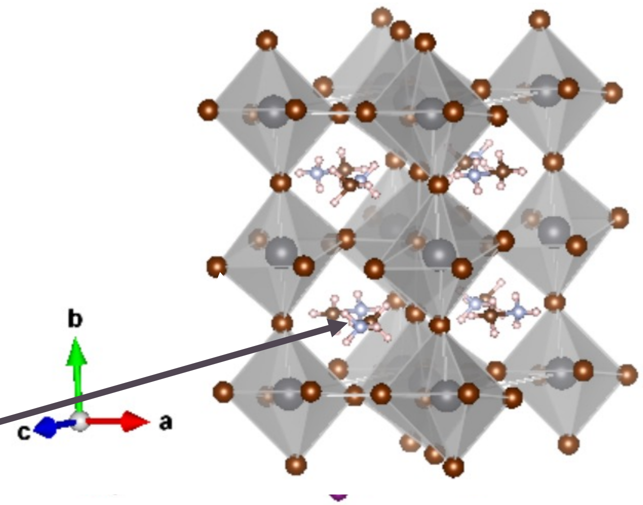
Perovskites and hybrid organic-inorganic perovskites: what are and their main application

The first Perovskite (*i.e.*, the mineral Calcium Titanate, $CaTiO_3$) was discovered by **Gustav Rose** in 1839 in Russia and was characterized for the first time by **Lev A. Perovski** (1792-1856), from which Perovskite derives its name.

The Perovskite name has been extended to all the compounds adopting the same general formula ABX_3 and a framework involving a corner-sharing network of BX_6 octahedra, where

- A is a monovalent cation (*e.g.*, Cs^+, MA^+, FA^+,...), with MA= methylammonium, FA= formamidinium
- B is a divalent metal cation (B site; *e.g.*, Sn^{2+} and Pb^{2+})
- X is a halide anion (*e.g.*, Cl^-, Br^-, or I^-)

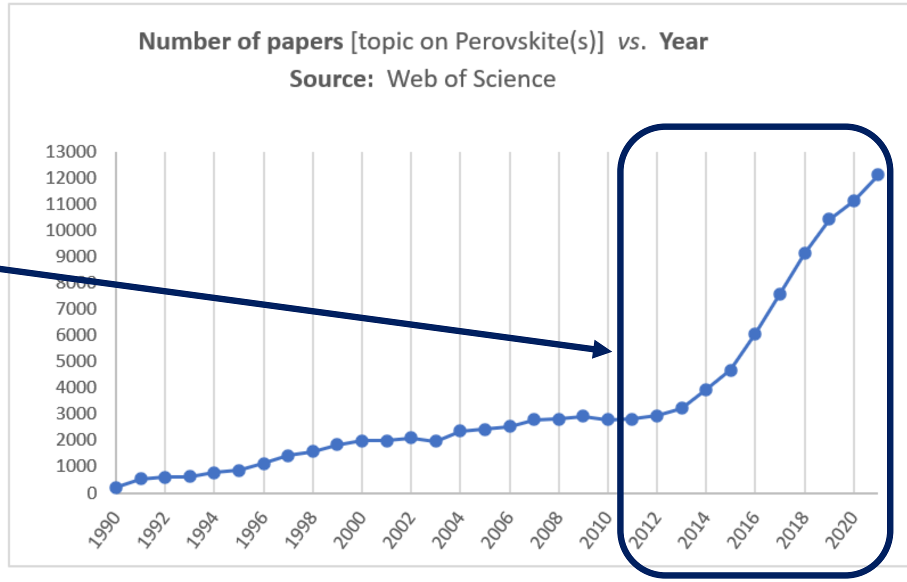
We will focus our attention on **hybrid organic-inorganic perovskites**, for which at least one of the "A", "B", or "X" ions is organic; typically, the "A" cation is organic, *e.g.*, $\mathbf{CH_3NH_3}PbI_3$ [where the "A" cation is methylammonium (MA)].



Perovskites and hybrid organic-inorganic perovskites: what are and their main application

The discovery in 1839, *i.e.*, an **ancient discovery,**

the recent explosion of the scientific interest.



The reason:

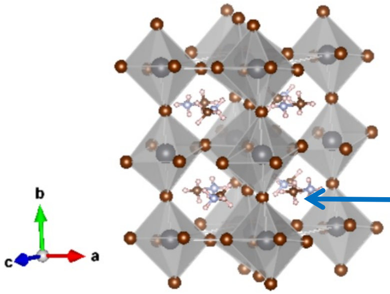
perovskites are fascinating materials, of growing interest because of their unique physical properties which make them promising candidates for technological applications, *e.g.*,

- Solar cells
- LEDs
- Lasers
- Photodetector devices

Hybrid organic-inorganic perovskite like a ‘millefoglie’ cake(**)

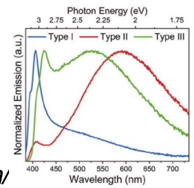
First debut of hybrid organic-inorganic perovskites in photovoltaics:
2006

High tunability of physical properties



Some ingredients

Kind of atoms of the inorganic chain	⟺	Kind of flour
Kind of organic component	⟺	Kind of cream
Number of carbon atoms in the organic chain	⟺	Number of eggs in the cream
Solvent	⟺	Milk



New recipes

To combine the building blocks (*i.e.*, the **perovskite ‘ingredients’**) in different ways:

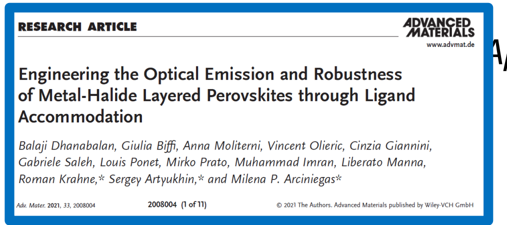
- to optimize and tune the optoelectronic properties of the new perovskites.
- to semplify and reduce the cost of the synthesis.

(**) *Nosengo, N., A recipe for perovskites, Nature Italy, Research highlight, Match 2021 https://www.nature.com/* 021-00025-6

Why the need of synchrotron radiation?

The answer is in some recent cases of challenging characterization:

Laminar single crystals (micrometric thickness) and powders


RESEARCH ARTICLE — ADVANCED MATERIALS — www.advmat.de

Engineering the Optical Emission and Robustness of Metal-Halide Layered Perovskites through Ligand Accommodation

Balaji Dhanabalan, Giulia Biffi, Anna Moliterni, Vincent Olieric, Cinzia Giannini, Gabriele Saleh, Louis Ponet, Mirko Prato, Muhammad Imran, Liberato Manna, Roman Krahne, Sergey Artyukhin,* and Milena P. Arciniegas**

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nature nanotechnology — ARTICLES — https://doi.org/10.1038/s41565-021-00977-2

Tuning of the Berry curvature in 2D perovskite polaritons

Laura Polimeno[1,2,3], Giovanni Lerario[2], Milena De Giorgi[2], Luisa De Marco[2], Lorenzo Dominici[2], Francesco Todisco[2], Annalisa Coriolano[1,2], Vincenzo Ardizzone[2], Marco Pugliese[1,2], Carmela T. Prontera[2], Vincenzo Maiorano[2], Anna Moliterni[4], Cinzia Giannini[4], Vincent Olieric[5], Giuseppe Gigli[1,2], Dario Ballarini[2], Qihua Xiong[6,7], Antonio Fieramosca[8], Dmitry D. Solnyshkov[9,10], Guillaume Malpuech[9] and Daniele Sanvitto[2,3]


RESEARCH ARTICLE — ADVANCED MATERIALS — www.advmat.de

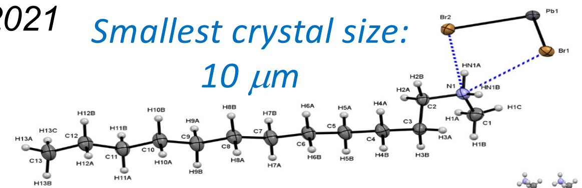
Managing Growth and Dimensionality of Quasi 2D Perovskite Single-Crystalline Flakes for Tunable Excitons Orientation

Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

Adv. Mater. 2021, 2102326 — 2102326 (1 of 9) — © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH

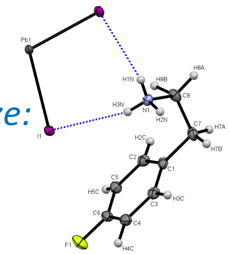
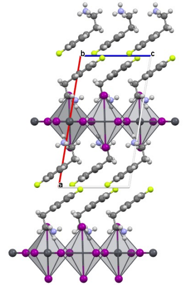
April 2021

Smallest crystal size: 10 μm



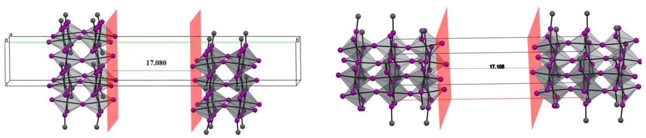
October 2021

Smallest crystal size: 50 μm

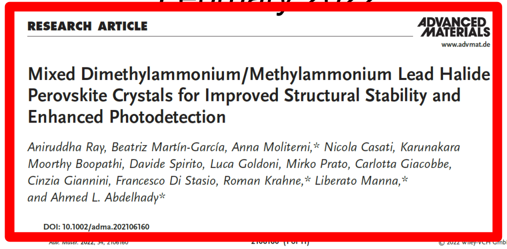
December 2021

Smallest crystal size 20 μm



Powders (phase transition vs. T)

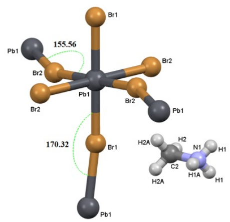
February 2022

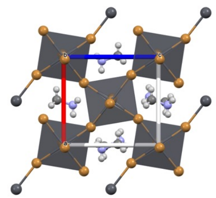

RESEARCH ARTICLE — ADVANCED MATERIALS — www.advmat.de

Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Crystals for Improved Structural Stability and Enhanced Photodetection

Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne,* Liberato Manna,* and Ahmed L. Abdelhady**

DOI: 10.1002/adma.202106160





Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 1

Case 1

RESEARCH ARTICLE

ADVANCED MATERIALS
www.advmat.de

Engineering the Optical Emission and Robustness of Metal-Halide Layered Perovskites through Ligand Accommodation

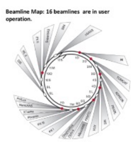
Balaji Dhanabalan, Giulia Biffi, Anna Moliterni, Vincent Olieric, Cinzia Giannini, Gabriele Saleh, Louis Ponet, Mirko Prato, Muhammad Imran, Liberato Manna, Roman Krahne, Sergey Artyukhin,* and Milena P. Arciniegas**

Adv. Mater. 2021, 33, 2008004 2008004 (1 of 11)

In collaboration with

Liberato Manna

Milena P. Arciniegas



Vincent Olieric

Main aim of the paper

- To explore different classes of organoamines to engineer the optical emission of new metal halide layered perovskites.

The exploration showed that

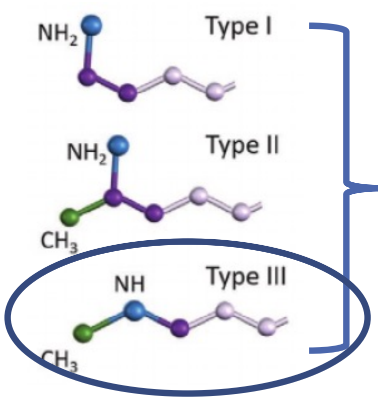
- The kind of organic molecules regulates the number of H-bonds with the edge sharing $[PbBr_6]^+$ octahedra layers and their distortion, leading to strong **differences in the wavelength of the emission** (from deep-blue to pure white);
- The **intensity of the emission** depends on the length of the organic molecules.

Main aims of the crystallographic study

- To solve the crystal structure of one of the new perovskites by single crystal synchrotron X-ray microdiffraction data.
- To identify the presence of H-bonds and estimate the degree of distortion of the inorganic chains.

Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 1

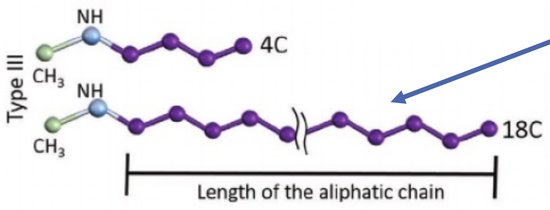
Explored amines used for the synthesis of new perovskites



Three different types of the terminal group of the amines have been considered.

The crystallographic study was carried out in the case of an amine with terminal group of **Type III** and a **12 C** aliphatic chain:

$(N\text{-}MDDA)_2PbBr_4$



Different lengths of the aliphatic chain have been explored.

Crystallographic study

Small size of single crystals (laminar samples, third dimension of a few μm)

Synchrotron radiation was an obliged choice for ensuring to reach the data completeness.

Low temperature experiment (T=100 K).

- Structure solution carried out by *SIR2019*

JAC COMPUTER PROGRAMS

J. Appl. Cryst. (2015). 48, 306-309
https://doi.org/10.1107/S1600576715001132

Crystal structure determination and refinement *via SIR2014*

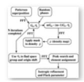
M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori

The program *SIR2014* for crystal structure solution is described.

- Structure refinement carried out by *SHELXL2014*

A RESEARCH PAPERS

Acta Cryst. (2015). A71, 3-8
https://doi.org/10.1107/S2053273314026370



***SHELXT* - Integrated space-group and crystal-structure determination**

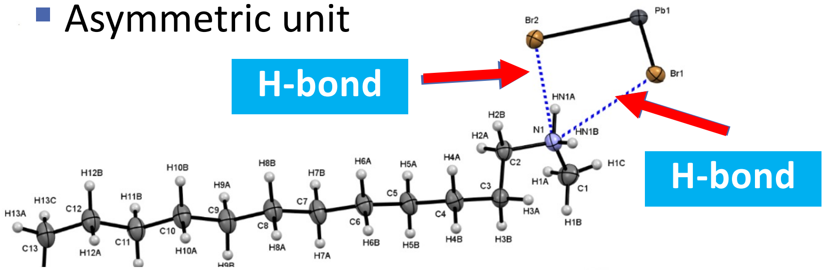
G. M. Sheldrick

SHELXT automates routine small-molecule structure determination starting from single-crystal reflection data, the Laue group and a reasonable guess as to which elements might be present.

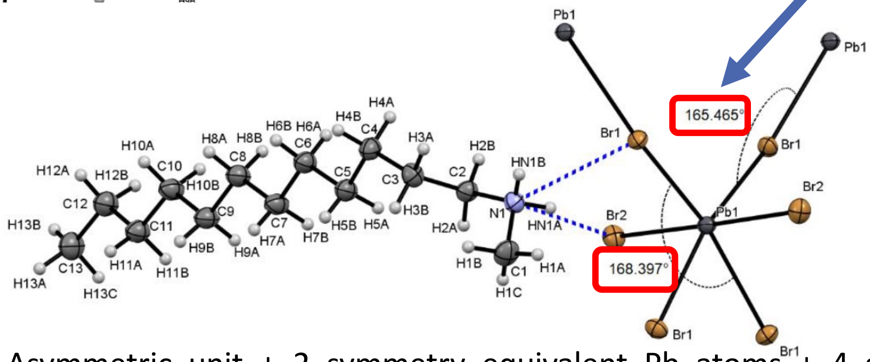
Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 1

The crystallographic study confirmed the expected structure:

- Asymmetric unit



Distortions of the inorganic layers due to the interactions between the halides of the inorganic layers and the hydrogens of the ammonium functional group (180° for undistorted layers).



- Asymmetric unit + 2 symmetry equivalent Pb atoms + 4 symmetry equivalent Br atoms to show the inorganic chain distortion.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C3—H3*B*···Br2^{i}	0.99 (5)	3.08 (5)	3.844 (4)	134 (3)
N1—H*N*1*A*···Br2	0.99 (6)	2.31 (6)	3.265 (4)	162 (4)
N1—H*N*1*B*···Br1	0.81 (6)	3.02 (5)	3.488 (3)	120 (4)
N1—H*N*1*B*···Br1^{ii}	0.81 (6)	2.97 (5)	3.624 (3)	139 (4)
C2—H2*B*···Br2^{iii}	0.96 (5)	2.92 (5)	3.564 (4)	126 (3)

Symmetry codes: (i) $x+1, y, z$; (ii) $-x+1, y, -z+1/2$; (iii) $-x+1/2, y-1/2, z$.

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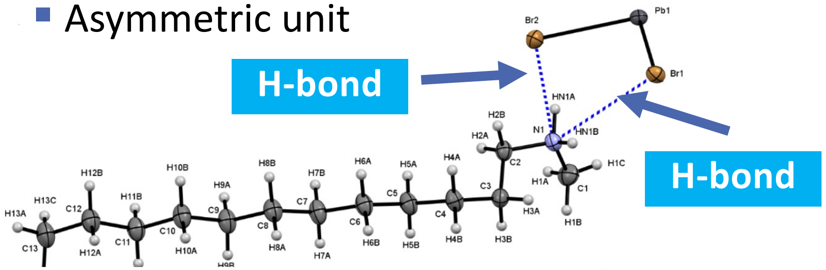

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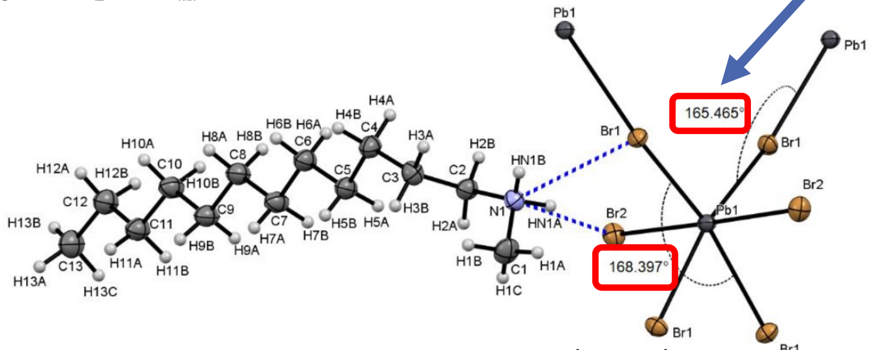
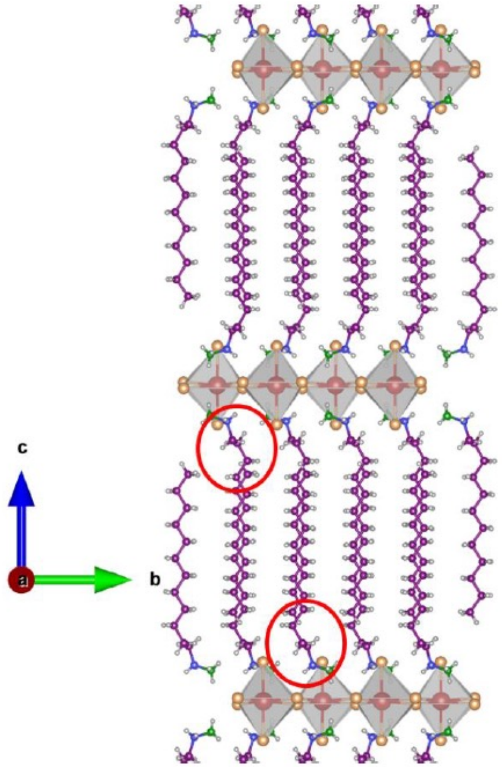


- Asymmetric unit + 2 symmetry equivalent Pb atoms + 4 symmetry equivalent Br atoms to show the inorganic chain distortion.

A view of the crystal packing of the $(N\text{-}MDDA)_2PbBr_4$ crystal showing the bending of the chains (framed in red) near to the anchor site.



Why the need of synchrotron radiation?

The answer is in some cases of challenging cases of successful recent study:

Laminar single crystals (micrometric thickness) and powders

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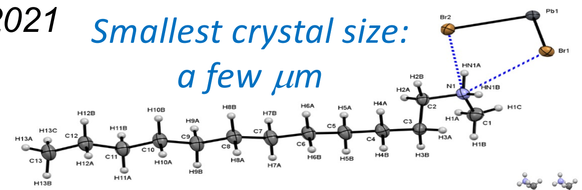
Adv. Mater. 2021, 33, 2008004 — 2008004 (1 of 11) — © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH

April 2021

Smallest crystal size: a few μm



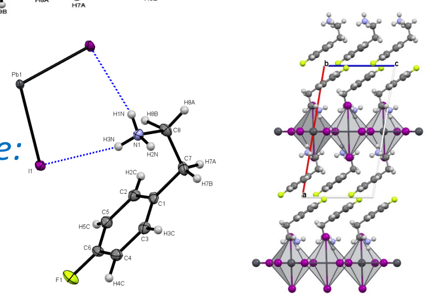
nature nanotechnology — ARTICLES — https://doi.org/10.1038/s41565-021-00977-2

Tuning of the Berry curvature in 2D perovskite polaritons

Laura Polimeno[1,2,3], Giovanni Lerario[2], Milena De Giorgi[2], Luisa De Marco[2], Lorenzo Dominici[2], Francesco Todisco[2], Annalisa Coriolano[1,2], Vincenzo Ardizzone[2], Marco Pugliese[1,2], Carmela T. Prontera[2], Vincenzo Maiorano[2], Anna Moliterni[4], Cinzia Giannini[4], Vincent Olieric[5], Giuseppe Gigli[1,2], Dario Ballarini[2], Qihua Xiong[6,7], Antonio Fieramosca[8], Dmitry D. Solnyshkov[9,10],

October 2021

Smallest crystal size: 50 μm



RESEARCH ARTICLE — ADVANCED MATERIALS www.advmat.de

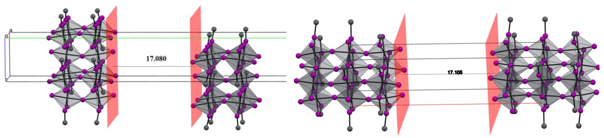
Managing Growth and Dimensionality of Quasi 2D Perovskite Single-Crystalline Flakes for Tunable Excitons Orientation

Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

Adv. Mater. 2021, 2102326 — 2102326 (1 of 9) — © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH

December 2021

Smallest crystal size: 20 μm



Powders (phase transition vs. T)

February 2022

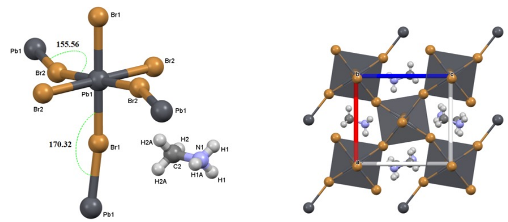
RESEARCH ARTICLE — ADVANCED MATERIALS www.advmat.de

Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Crystals for Improved Structural Stability and Enhanced Photodetection

Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne,* Liberato Manna,* and Ahmed L. Abdelhady**

DOI: 10.1002/adma.202106160

Adv. Mater. 2022, 34, 2106160 — 2106160 (1 of 11) — © 2022 Wiley-VCH GmbH



Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 3

Case 3

RESEARCH ARTICLE — ADVANCED MATERIALS www.advmat.de

Managing Growth and Dimensionality of Quasi 2D Perovskite Single-Crystalline Flakes for Tunable Excitons Orientation

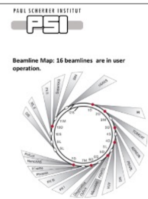
Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

Adv. Mater. 2021, 2102326 2102326 (1 of 9)

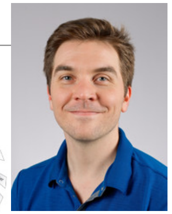
In collaboration with

CNRNANOTEC INSTITUTE OF NANOTECHNOLOGY

Luisa De Marco



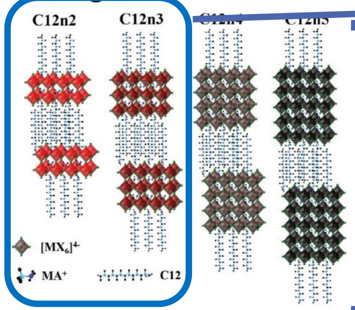
Photon Factory
Institute of Materials Structure Science
High Energy Accelerator Research Organization,KEK



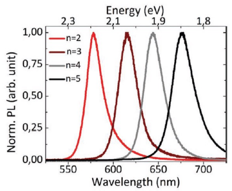
Vincent Olieric

Main aims of the paper

- To face a big challenge: to propose an efficient synthesis protocol able to prepare new hybrid organic-inorganic 2D perovskites with a number of inorganic layers ***n* > 1** and finely control and tune the thickness of the inorganic slabs.



- The optoelectronic properties depend also on the **number *n* of the inorganic layers in the slabs** and on the distortion of the inorganic chains.
  - The combination of synthesis and optical characterization paves the way to the design of new materials with optimized optoelectronic properties.



Main aims of the crystallographic study

- To prove the validity of the synthesis protocol by solving the crystal structure of two new hybrid organic-inorganic perovskites **$(C12)_2(MA)_{n-1}Pb_nI_{3n+1}$ ($C12=C_{12}H_{25}NH_3^+$; cases *n*= 2,3)** by single-crystal synchrotron X-ray microdiffraction data.
  Structure solution carried out by *SIR2019.*
  Structure refinement carried out by *SHELXL2014.*
- To determine the degree of distortion of the inorganic chains.

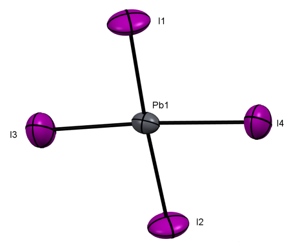
Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 3

The crystallographic study confirmed the expected structure (the inorganic component only is shown):

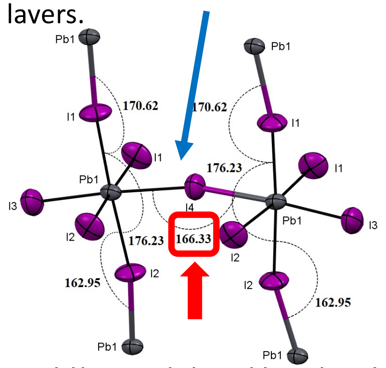
n=2 $(C12)_2(MA)Pb_2I_7$

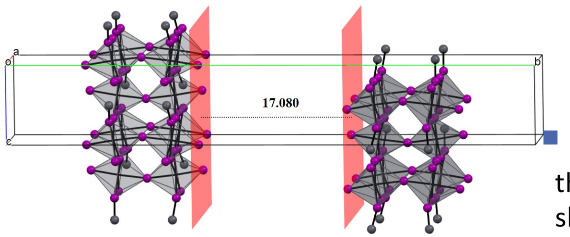
Very small crystal size: 0.04 x 0.03 x 0.02 mm

- Asymmetric unit



- A view of the local environment of the asymmetric unit showing the polyhedral coordination of the Pb atoms and the distortion angles of the inorganic layers.



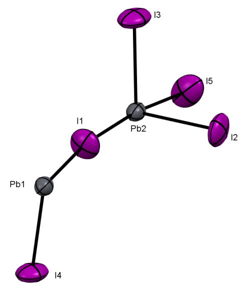


- A view of the crystal packing showing the distance between two nearest slabs of inorganic layers.

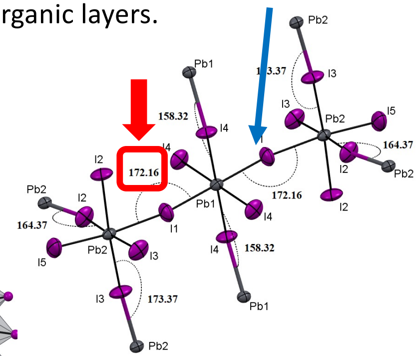
n=3 $(C12)_2(MA)_2Pb_3I_{10}$

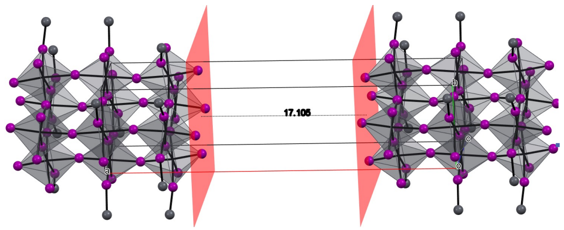
Very small crystal size: 0.08 x 0.04 x 0.02 mm

- Asymmetric unit



- A view of the local environment of the asymmetric unit showing the polyhedral coordination of the Pb atoms and the distortion angles of the inorganic layers.





- A view of the crystal packing showing the distance between two nearest slabs of inorganic layers.

Why the need of synchrotron radiation?

The answer is in some cases of challenging cases of successful recent study:

Laminar single crystals (micrometric thickness) and powders

RESEARCH ARTICLE — ADVANCED MATERIALS www.advmat.de

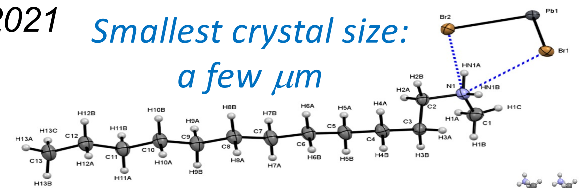
Engineering the Optical Emission and Robustness of Metal-Halide Layered Perovskites through Ligand Accommodation

Balaji Dhanabalan, Giulia Biffi, Anna Moliterni, Vincent Olieric, Cinzia Giannini, Gabriele Saleh, Louis Ponet, Mirko Prato, Muhammad Imran, Liberato Manna, Roman Krahne, Sergey Artyukhin,* and Milena P. Arciniegas**

Adv. Mater. 2021, 33, 2008004 — 2008004 (1 of 11) — © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH

April 2021

Smallest crystal size: a few μm



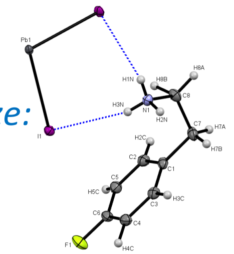
nature nanotechnology — ARTICLES — https://doi.org/10.1038/s41565-021-00977-2

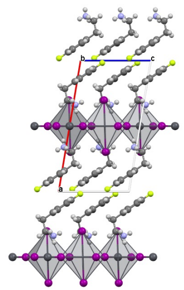
Tuning of the Berry curvature in 2D perovskite polaritons

Laura Polimeno[1,2,3], Giovanni Lerario[2], Milena De Giorgi[2], Luisa De Marco[2], Lorenzo Dominici[2], Francesco Todisco[2], Annalisa Coriolano[1,2], Vincenzo Ardizzone[2], Marco Pugliese[1,2], Carmela T. Prontera[2], Vincenzo Maiorano[2], Anna Moliterni[4], Cinzia Giannini[4], Vincent Olieric[5], Giuseppe Gigli[1,2], Dario Ballarini[2], Qihua Xiong[6,7], Antonio Fieramosca[8], Dmitry D. Solnyshkov[9,10], Guillaume Malpuech[9] and Daniele Sanvitto[2,3]

October 2021

Smallest crystal size: 50 μm





RESEARCH ARTICLE — ADVANCED MATERIALS www.advmat.de

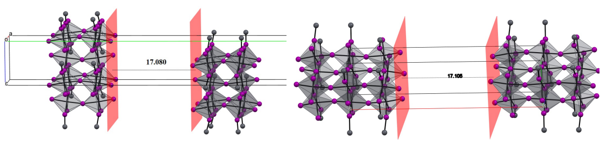
Managing Growth and Dimensionality of Quasi 2D Perovskite Single-Crystalline Flakes for Tunable Excitons Orientation

Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

Adv. Mater. 2021, 2102326 — 2102326 (1 of 9) — © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH

December 2021

Smallest crystal size: 20 μm



Powders (phase transition vs. T)

February 2022

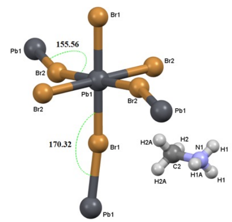
ADVANCED MATERIALS

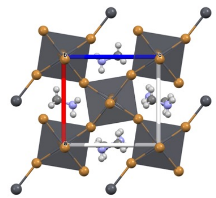
Research Article | Full Access

Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Single Crystals for Improved Structural Stability and Enhanced Photodetection

Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors

First published: 01 December 2021 | https://biblioproxy.cnr.it:2481/10.1002/adma.202106160





Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 4

Case 4

ADVANCED MATERIALS

Research Article | Full Access

Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Single Crystals for Improved Structural Stability and Enhanced Photodetection

Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors

First published: 01 December 2021 | https://biblioproxy.cnr.it:2481/10.1002/adma.202106160

In collaboration with

PAUL SCHERRER INSTITUT PSI

IIT ISTITUTO ITALIANO DI TECNOLOGIA

Liberato Manna

ESRF The European Synchrotron

Ahmed L. Abdelhady

Aniruddha Ray

Carlotta Giacobbe

Nicola P.M. Casati

Main aims of the paper

- Methylammonium lead tribromide ($MAPbBr_3$) and mixed dimethylammonium/methylammonium lead tribromide ($DMA/MAPbBr_3$) perovskites were synthesized, reaching for $DMA/MAPbBr_3$ the highest incorporation of DMA (i.e., 44%).
- The mixed $DMA/MAPbBr_3$ perovskite showed improved temperature-dependent photoluminescence properties and higher detectivity (if used for photodetector devices) with respect to $MAPbBr_3$.
- The enhancement in detectivity both at room temperature and at low temperature proved the potential use of the mixed $DMA/MAPbBr_3$ in visible light communication and space application.

Main aims of the crystallographic study

- To confirm the crystal structure of $MAPbBr_3$ (already characterized in literature) and to determine the crystal structure of the new mixed perovskite ($DMA/MAPbBr_3$) by temperature-dependent synchrotron powder diffraction data (range of the temperature: 80-300K).

The *ab-initio* crystal structure solution was carried out by *EXPO2014*:

JAC COMPUTER PROGRAMS

J. Appl. Cryst. (2013). **46**, 1231-1235
https://doi.org/10.1107/S0021889813013113

***EXPO2013*: a kit of tools for phasing crystal structures from powder data**

A. Altomare, C. Cuocci, C. Giacovazzo, A. Moliterni, R. Rizzi, N. Corriero and A. Falcicchio

- To understand why the two componds ($MAPbBr_3$ and $DMA/MAPbBr_3$) showed different optoelectronic properties.

Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 4

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Case 4

ADVANCED MATERIALS

Research Article | Full Access

Mixed Dimethylammonium/Methylammonium Lead Halide Perovskite Single Crystals for Improved Structural Stability and Enhanced Photodetection

Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors ^

First published: 01 December 2021 | https://biblioproxy.cnr.it:2481/10.1002/adma.202106160

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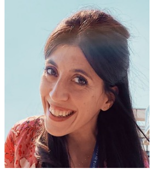
Liberato Manna

Ahmed L. Abdelhady

Anir

ESRF The European Synchrotron



Carlotta

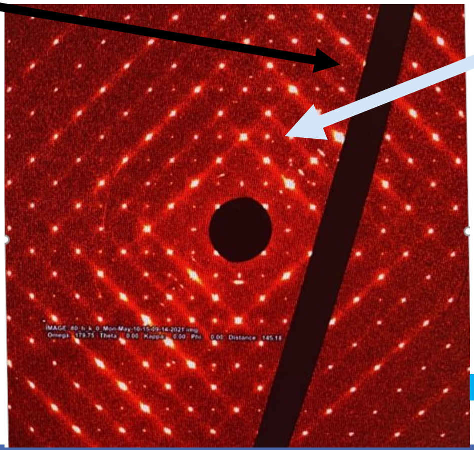
Nicola P.M. Casati

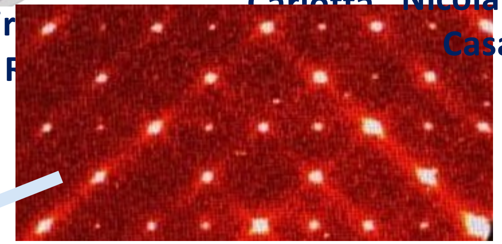
Main aims of the crystallographic study

First attempts:

Ab-initio structure solution by single-crystal synchrotron X-ray microdiffraction (dimensions of crystals: a few μm)

Detector gap (no signal)





The samples consist of more than one single crystal. The quality of the integrated intensities is not high (due to overlap of reflections)

We tried the *ab-initio* structure solution by powder diffraction data.

Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 4

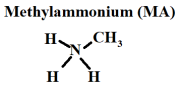
The crystallographic study by powder diffraction data revealed the following results in the range 80-300K:

The different optoelectronic properties of $MAPbBr_3$ and DMA/$MAPbBr_3$ are related to the difference in the organic component.

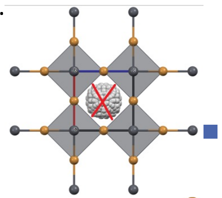
Our proposal:

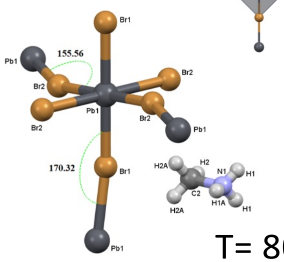
due to the probable greater disorder of the organic cations in the 44% DMA sample, a higher symmetry and less distorted inorganic framework is observed compared to the pure $MAPbBr_3$ sample.

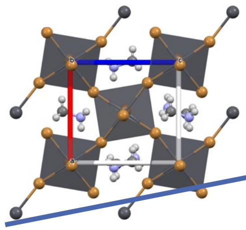
$MAPbBr_3$



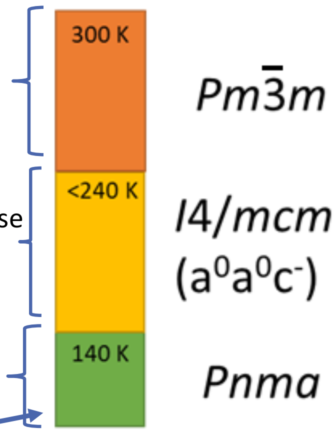
- The literature results were confirmed:
- At larger temperature the disorder of the organic component increased and only the heavy atoms were reliably located.



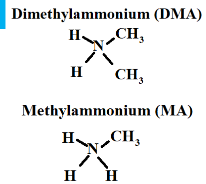


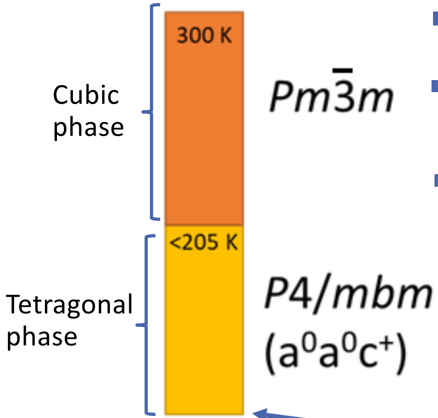


T= 80 K



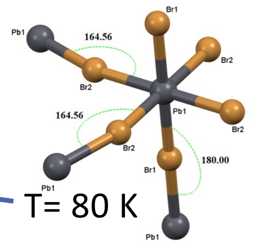
DMA/$MAPbBr_3$

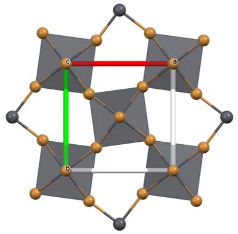




- Only two phase transitions occured (no orthorhombic phase was observed);
- The temperature corresponding to the transition from tetragonal to cubic phase was lower than that one observed for $MAPbBr_3$ (*i.e.*, 205 K instead of 240 K);
- Due to the greater disorder of the organic component (compared to the case of $MAPbBr_3$) only the heavy atoms were reliably located, also at low T values.

T= 80 K





Outlook

- How Crystallography can shed light on Materials Science;

- The Crystallography 'lens' to successfully characterize new materials:
  why the need of synchrotron radiation?

The answer is in some cases of challenging characterization
(Synchotron light makes the difference):

New materials of interest for Energy:

i.e., hybrid organic-inorganic perovskites and metal chalcohalides

New materials of interest for Environment and Health:

i.e., a new compound of possible pharmaceutical interest, an amosite amphibole asbestos fibre and an erionite fiber

- Conclusions

Why the need of synchrotron radiation?

The answer is in some cases of challenging cases of successful recent study:

- nanocrystalline bismuth chalcohalides;

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How to cite: *Angew. Chem. Int. Ed.* **2022**, *61*, e202201747
International Edition: doi.org/10.1002/anie.202201747
German Edition: doi.org/10.1002/ange.202201747

Nanocrystals *Hot Paper*

Colloidal Bismuth Chalcohalide Nanocrystals

Danila Quarta+, Stefano Toso+, Roberto Giannuzzi, Rocco Caliandro, Anna Moliterni, Gabriele Saleh, Agostina-Lina Capodilupo, Doriana Debellis, Mirko Prato, Concetta Nobile, Vincenzo Maiorano, Ivan Infante, Giuseppe Gigli, Cinzia Giannini, Liberato Manna, and Carlo Giansante**

Angew. Chem. Int. Ed. **2022**, 61, e202201747 (1 of 8)

March 2022

- the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides;

ARTICLE

https://doi.org/10.1038/s41467-022-31699-1 OPEN

Check for updates

Halide perovskites as disposable epitaxial templates for the phase-selective synthesis of lead sulfochloride nanocrystals

Stefano Toso[1,2,8], Muhammad Imran[1,8✉], Enrico Mugnaioli[3], Anna Moliterni[4✉], Rocco Caliandro[4], Nadine J. Schrenker[5], Andrea Pianetti[6], Juliette Zito[1,7], Francesco Zaccaria[1], Ye Wu[1], Mauro Gemmi[3✉], Cinzia Giannini[4], Sergio Brovelli[6✉], Ivan Infante[1✉], Sara Bals[5✉] & Liberato Manna[1✉]

NATURE COMMUNICATIONS | (2022)13:3976 | https://doi.org/10.1038/s41467-022-31699-1 | www.nature.com/naturecommunications

July 2022

Crystallography and synchrotron radiation to study new lead-free compounds of interest for Energy: nanocrystalline bismuth chalcohalides

GDCh Research Articles Angewandte Chemie International Edition www.angewandte.org

Nanocrystals Hot Paper

How to cite: *Angew. Chem. Int. Ed.* **2022**, *61*, e202201747
International Edition: doi.org/10.1002/anie.202201747
German Edition: doi.org/10.1002/ange.202201747

Colloidal Bismuth Chalcohalide Nanocrystals

Danila Quarta[+], Stefano Toso[+], Roberto Giannuzzi, Rocco Caliandro, Anna Moliterni, Gabriele Saleh, Agostina-Lina Capodilupo, Doriana Debellis, Mirko Prato, Concetta Nobile, Vincenzo Maiorano, Ivan Infante, Giuseppe Gigli, Cinzia Giannini, Liberato Manna, and Carlo Giansante**

Angew. Chem. Int. Ed. **2022**, *61*, e202201747 (1 of 8)

In collaboration with

IIT Istituto Italiano di Tecnologia

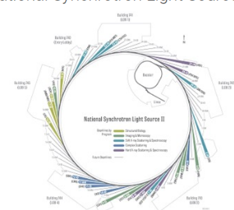

Liberato Manna **Stefano Toso**

CNR NANOTEC Institute of Nanotechnology

Carlo Giansante

Brookhaven National Laboratory

National Synchrotron Light Source II



Hybrid organic-inorganic perovskites

General formula: **ABX_3**, where

- **A** is a monovalent organic cation (*e.g.*, MA^+, FA^+,...), with MA= methylammonium, FA= formamidinium;
- **B** is a divalent metal cation (B site; *e.g.*, Sn^{2+} and Pb^{2+});
- **X** is a halide anion (*e.g.*, Cl^-, Br^-, or I^-).

Metal chalcohalides:

General formula: **$M_nE_pX_q$**, where

- **M** is a metal;
- **E** is S, Se;
- **X** is a halogen (*e.g.*, Cl, Br, or I).

Crystallography and synchrotron radiation to study new lead-free compounds of interest for Energy: nanocrystalline bismuth chalcohalides

GDCh Research Articles Angewandte Chemie www.angewandte.org

Nanocrystals Hot Paper

How to cite: Angew. Chem. Int. Ed. 2022, 61, e202201747
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German Edition: doi.org/10.1002/ange.202201747

Colloidal Bismuth Chalcohalide Nanocrystals

Danila Quarta[+], Stefano Toso[+], Roberto Giannuzzi, Rocco Caliandro, Anna Moliterni, Gabriele Saleh, Agostina-Lina Capodilupo, Doriana Debellis, Mirko Prato, Concetta Nobile, Vincenzo Maiorano, Ivan Infante, Giuseppe Gigli, Cinzia Giannini, Liberato Manna, and Carlo Giansante**

Angew. Chem. Int. Ed. 2022, 61, e202201747 (1 of 8)

Main aims of the paper

- To develop a new and versatile colloidal approach to synthesize bismuth chalcohalide nanocrystals (**BiEX** NCs, where **E** = S, Se and **X** = Cl, Br, I);
- The proposed method allowed to obtain nanocrystals displaying a composition-dependent band gap spanning the visible spectral range;
- The **BiEX** NCs were non-toxic and chemically stable at standard laboratory conditions and formed colloidal inks in different solvents;
- The bismuth chalcohalide nanocrystals were used in photoactive inks applied for producing electrodes able to convert sunlight into electric current, **giving new opportunities for the manufacturing of photovoltaic and optoelectronic devices in a simple and relatively low-cost way.**

In collaboration with

ISTITUTO ITALIANO DI TECNOLOGIA

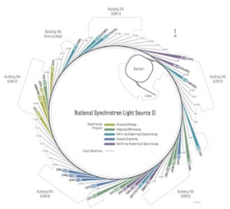
Liberato Manna

Stefano Toso

CNRNANOTEC INSTITUTE OF NANOTECHNOLOGY

Carlo Giansante

Brookhaven National Laboratory
National Synchrotron Light Source II



Main aims of the crystallographic study

- To carry out a crystallographic characterization for a set of **BiEX** NCs **(BiSCl, BISBr, BiSI** and **BiSeBr)** by synchrotron X-ray powder diffraction data and Pair Distribution Function (PDF) data;
- **This study allowed to discover a new phase, a polymorph of BiSCl, that has been solved *ab-initio* by synchrotron X-ray powder diffraction data by *EXPO2014.***

Crystallography and synchrotron radiation to study new lead-free compounds of interest for Energy: nanocrystalline bismuth chalcohalides

Main results of the crystallographic study

- A qualitative phase analysis carried out by the software ***QUALX2.0*** on the synchrotron X-ray powder diffraction patterns measured in the case of BiSCl, BiSBr and BiSI NCs, revealed that BiSCl was unknown;

J. Appl. Cryst. (2015). **48**, 598-603 [doi:10.1107/S1600576715002319]

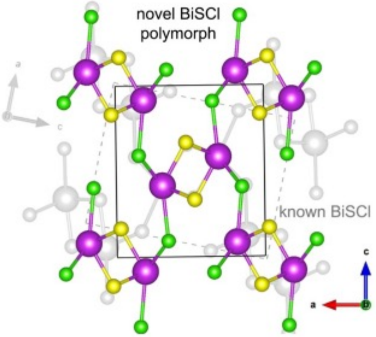
***QUALX2.0*: a qualitative phase analysis software using the freely available database POW_COD**

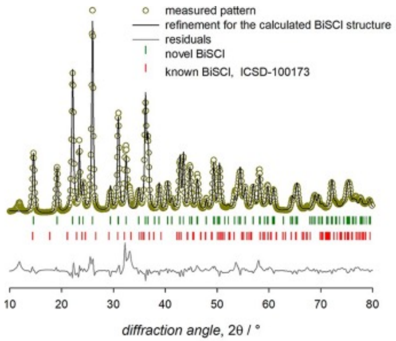
A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni and R. Rizzi

A daylight picture of toluene colloidal dispersions of BiSCl, BiSBr, and BiSI NCs

- In the case of BiSCl, the *ab-initio* structure solution process by ***EXPO2014*** allowed to successfully determine the crystal structure of a new polymorph of BiSCl;

The crystal structure located by *EXPO2014* was refined by FullProf (**)





- The structure model determined by ***EXPO2014*** was refined also in the direct space by PDF data *via* the software **PDFGUI** (***).

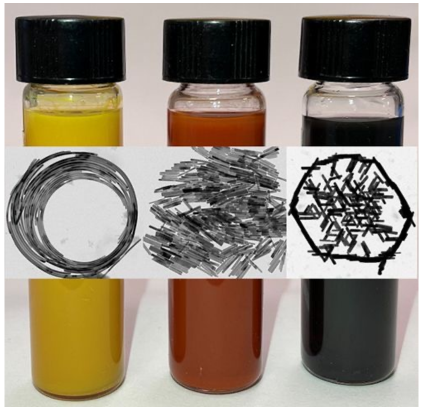
***** C. L. Farrow, P. Juhás, J. W. Liu, D. Bryndin, E. S. Božin, J. Bloch, T. Proffen S. J. L. Billinge (2007). *J. Phys. Condens. Matter*, 19, 335219.**

The structure models obtained by the refinement in direct space (PDF) and reciprocal space (FullProf) were overlapping, giving confidence in the reliability of the structural results.

**** Rodriguez-Carvajal, *J.Abstracts of the Satellite Meeting on Powder Diffraction of the XV Congress of the IUCr*. *In* A Program for Rietveld Refinement and Pattern Matching Analysis. (1990). 127–128.**

Crystallography and synchrotron radiation to study new lead-free compounds of interest for Energy: nanocrystalline bismuth chalcohalides

Remarks



- In our knowledge, **for the first time** a family of bismuth chalcohalides compounds has been characterized **at the nanoscale** by powder diffraction (thanks to the use of **synchrotron light**);
- The proposed new protocol of synthesis revealed efficient and reliable;
- The nanocrystalline compounds were stable (*i.e.*, an advantageous feature with respect to hybrid organic-inorganic perovskites) and the optoelectronic applications very promising for the applied nanotechnology;
- The new method opened the door to the amazing exploration of new materials of interest for Energy, to be discovered thanks to the necessary help of Crystallography.

Why the need of synchrotron radiation?

The answer is in some cases of challenging cases of successful recent study:

- nanocrystalline bismuth chalcohalides;

GDCh Research Articles Angewandte Chemie

Nanocrystals Hot Paper

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Angew. Chem. Int. Ed. 2022, 61, e202201747 (1 of 8)

March 2022

- the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides;

ARTICLE

https://doi.org/10.1038/s41467-022-31699-1 OPEN

Check for updates

Halide perovskites as disposable epitaxial templates for the phase-selective synthesis of lead sulfochloride nanocrystals

Stefano Toso[1,2,8], Muhammad Imran[1,8], Enrico Mugnaioli[3], Anna Moliterni[4], Rocco Caliandro[4], Nadine J. Schrenker[5], Andrea Pianetti[6], Juliette Zito[1,7], Francesco Zaccaria[1], Ye Wu[1], Mauro Gemmi[3], Cinzia Giannini[4], Sergio Brovelli[6], Ivan Infante[1], Sara Bals[5] & Liberato Manna[1]

NATURE COMMUNICATIONS | (2022)13:3976 | https://doi.org/10.1038/s41467-022-31699-1 | www.nature.com/naturecommunications

July 2022

Crystallography and synchrotron radiation to study new compounds of interest for Energy: the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides

ARTICLE

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Halide perovskites as disposable epitaxial templates for the phase-selective synthesis of lead sulfochloride nanocrystals

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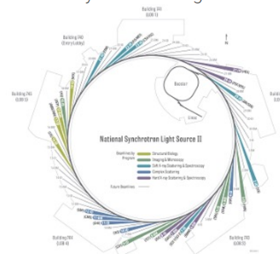

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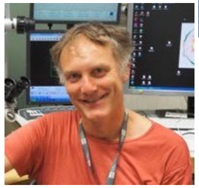

Mauro Gemmi

Enrico Mugnaioli

Inorganic perovskites

General formula: **ABX_3**, where

- **A** is a monovalent inorganic cation (*e.g.*, Cs^+);
- **B** is a divalent metal cation (B site; *e.g.*, Sn^{2+} and Pb^{2+});
- **X** is a halide anion (*e.g.*, Cl^-, Br^-, or I^-).

Lead chalcohalides:

General formula: **$Pb_nE_pX_q$**, where

- **E** is S, Se;
- **X** is a halogen (*e.g.*, Cl, Br, I).

Crystallography and synchrotron radiation to study new compounds of interest for Energy: the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides

ARTICLE

https://doi.org/10.1038/s41467-022-31699-1 OPEN

Halide perovskites as disposable epitaxial templates for the phase-selective synthesis of lead sulfochloride nanocrystals

Stefano Toso[1,2,8], Muhammad Imran[1,8], Enrico Mugnaioli[3], Anna Moliterni[4], Rocco Caliandro[4], Nadine J. Schrenker[5], Andrea Pianetti[6], Juliette Zito[1,7], Francesco Zaccaria[1], Ye Wu[1], Mauro Gemmi[3], Cinzia Giannini[4], Sergio Brovelli[6], Ivan Infante[1], Sara Bals[5] & Liberato Manna[1]

NATURE COMMUNICATIONS | (2022)13:3976 | https://doi.org/10.1038/s41467-022-31699-1 | www.nature.com/naturecommunications

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Mauro Gemmi

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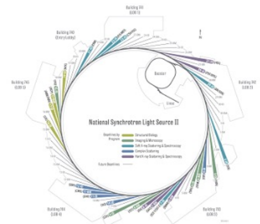


Main aims of the paper

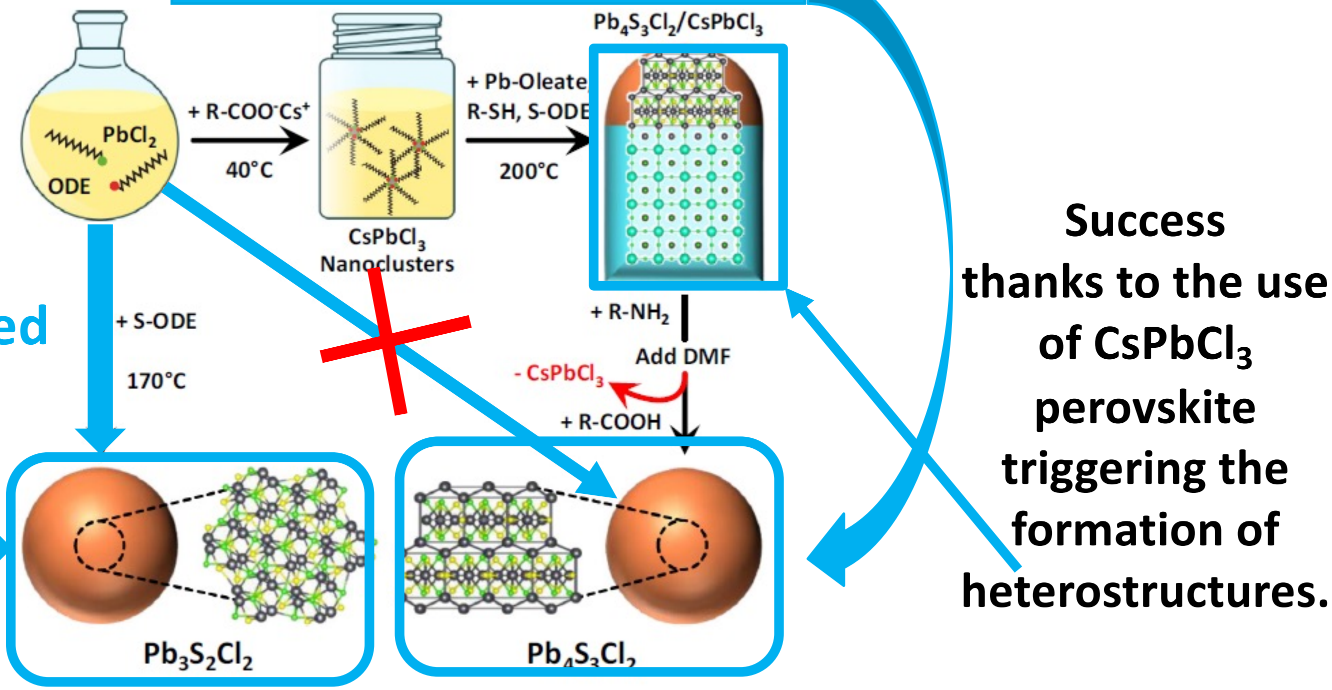
- To propose a new powerful method for crystallizing new lead chalcohalides by using $CsPbCl_3$ perovskite nanocrystals to drive the synthesis;
- The proposed method exploited the epitaxial templating effect of $CsPbCl_3$ to control the synthesis of lead sulfohalide NCs through the formation of heterostructures (*e.g.*, $Pb_4S_3Cl_2/CsPbCl_3$);
- The etching of the perovskite domain in the $Pb_4S_3Cl_2/CsPbCl_3$ heterostructure enabled to easily recover the stand-alone new $Pb_4S_3Cl_2$ NCs.

Main aims of the crystallographic study

- To carry out a crystallographic characterization for a set of lead sulfohalides NCs (**$Pb_4S_3Cl_2$, $Pb_3S_2Cl_2$, $Pb_4S_3Br_2$**, and **$Pb_4S_3I_2$**) by synchrotron X-ray powder diffraction (SXRPD), Pair Distribution Function (PDF) and electron diffraction (ED) data;
- To successfully solve the crystal structure by SXRPD it was necessary to supply to *EXPO2014* the information on the cell parameters and space group determined by ED data. The crystal structure located by *EXPO2014* was optimized by alternating the refinement in the reciprocal space (SXRPD) and in the direct space (PDF).

Crystallography and synchrotron radiation to study new compounds of interest for Energy: the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides

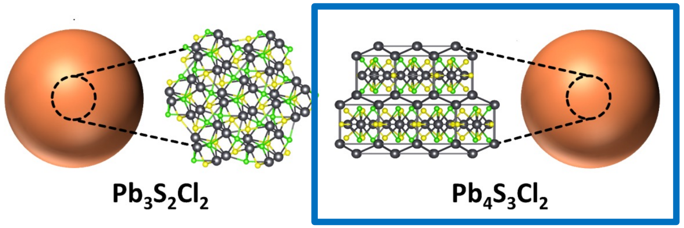
- **phase-selective templating approach**



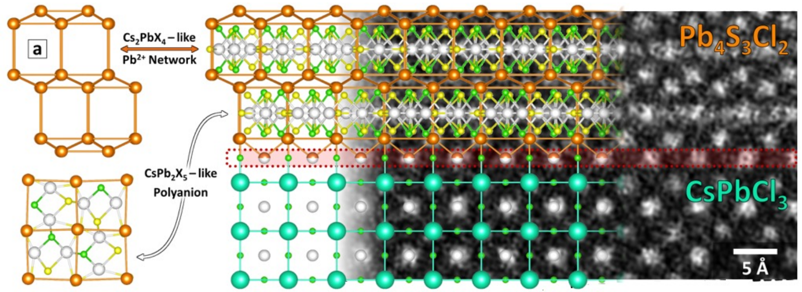
- **Direct synthesis**

Crystallography and synchrotron radiation to study new compounds of interest for Energy: the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides

Main results of the crystallographic study on $Pb_4S_3Cl_2$

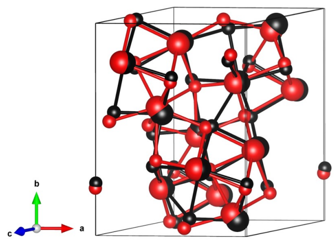


Chalcohalide and perovskite share a plane of Pb^{2+}, ensuring stability of the interface.



$Pb_4S_3Cl_2$ was obtained only by the formation of **$Pb_4S_3Cl_2$/$CsPbCl_3$** heterostructures.

- First of all, the **$Pb_4S_3Cl_2$** NCs were characterized by electron diffraction (ED) data. Due to the low quality of ED data the structure solution needed to be confirmed by other techniques, *i.e.*, using **synchrotron X-ray powder diffraction (SXRPD)** and Pair Distribution Function (PDF).
- The low quality of SXRPD data and, in particular, the great overlap of reflections prevented the correct determination of the cell parameters and space group by SXRPD data. To be able to solve the structure, ***EXPO2014*** needed the information on the cell parameters and space group determined by ED.
- The structure model located by ***EXPO2014*** was refined in both reciprocal (***EXPO2014***) and direct (**PDFGUI**) spaces on data collected at the Brookhaven National Laboratory synchrotron.



- The structure model refined by SXRPD/PDF data (red) was strongly overlapping with that one obtained by ED data (black) confirming the reliability of the structural results.

Crystallography and synchrotron radiation to study new compounds of interest for Energy: the use of $CsPbCl_3$ perovskite nanocrystals to drive the crystallization of yet unexplored lead chalcohalides

Remarks

- The proposed phase-selective templating approach will open a new door to the synthesis of new nanomaterials showing appealing optoelectronic properties;

- In the case of NCs, the use of a **multitechnique approach** can reveal itself fundamental for the success of the structure solution by X-ray powder diffraction; **it can be the obliged way to successfully solve unknown challenging nanostructured compounds.**

Outlook

- How Crystallography can shed light on Materials Science;

- The Crystallography 'lens' to successfully characterize new materials:

why the need of synchrotron radiation?

The answer is in some cases of challenging characterization
(Synchotron light makes the difference):

New materials of interest for Energy:
i.e., hybrid organic-inorganic perovskites and metal chalcohalides

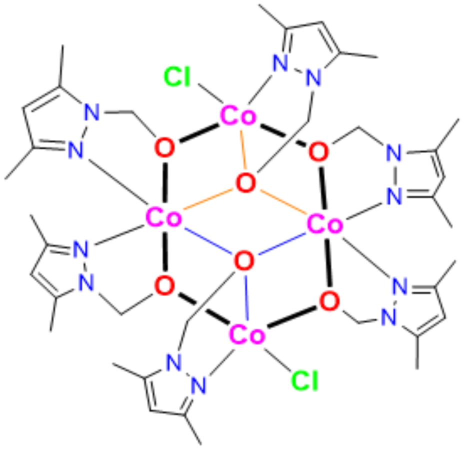
New materials of interest for Environment and Health:
i.e., a new compound of possible pharmaceutical interest, an amosite amphibole asbestos fibre and an erionite fiber

- Conclusions and perspectives

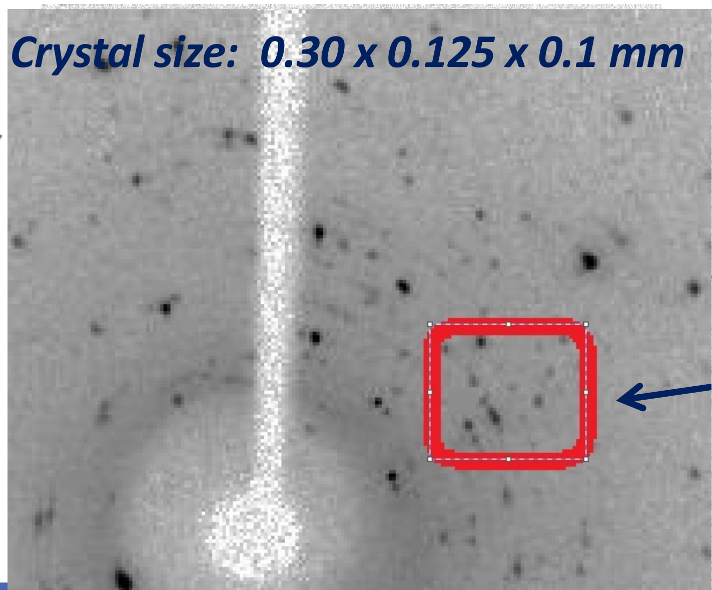
Why the need of synchrotron radiation?

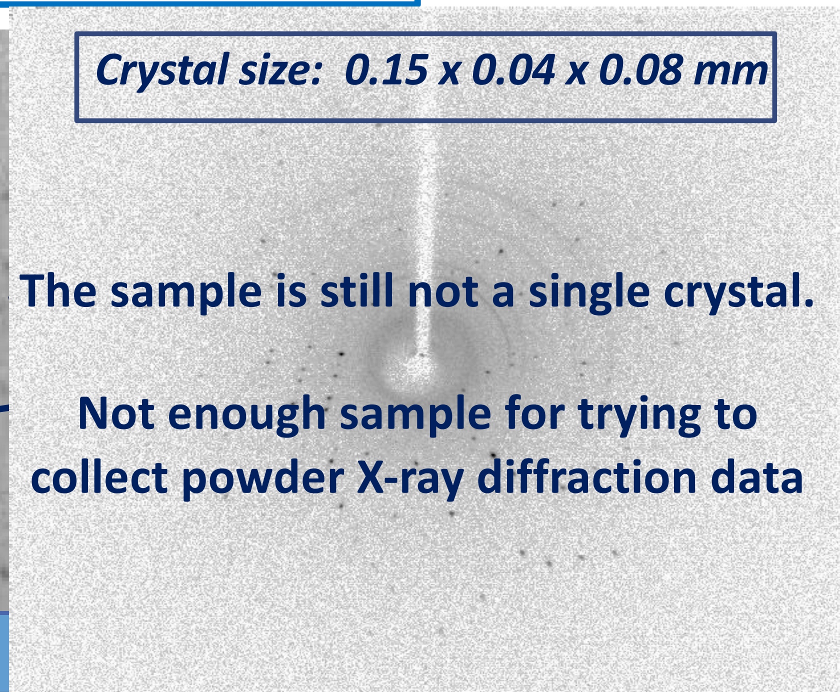
Case n. 1: a new compound of pharmaceutical interest, based an a double-open-Co_4O_6 cubane cluster

Single crystal X-Ray diffraction (laboratory data; λ= 0.71073 Å)



$(NNCO)_6Co_4Cl_2$

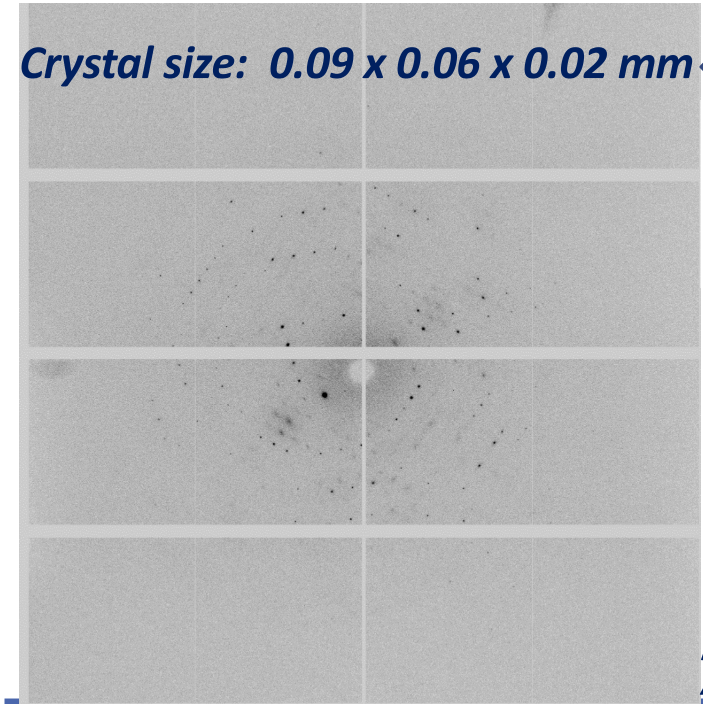




When the crystal size is extremely small…Synchrotron light can make the difference!

As a last trial, we selected a very small crystal to be analysed by synchrotron X-ray microdiffraction data

ESRF
The European Synchrotron



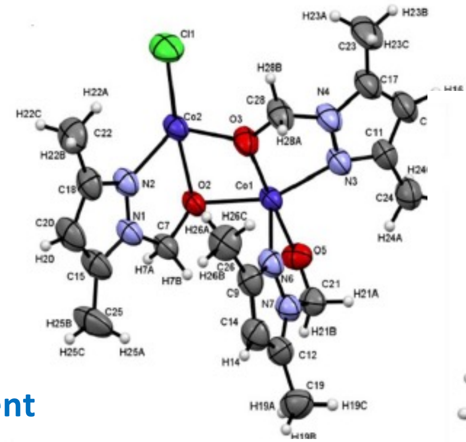
Crystal size: 0.09 x 0.06 x 0.02 mm

- **R_{int} = 5.9%**
- **Res(Å) = 0.75**
- **λ= 0.29339 Å**

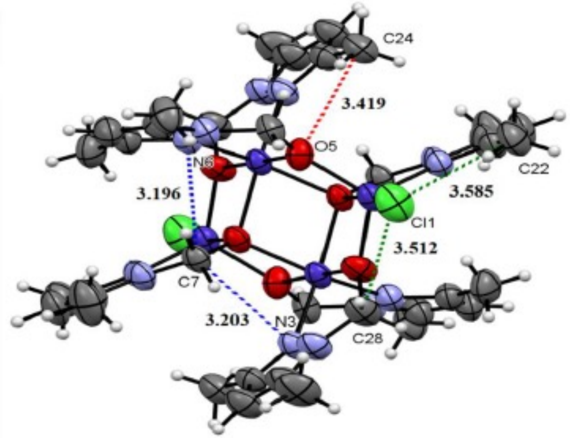
Structure solution By *SIR2019*

Structure refinement By *SHELXL2014*

A view of the asymmetric unit



- **R_F = 5.1%**

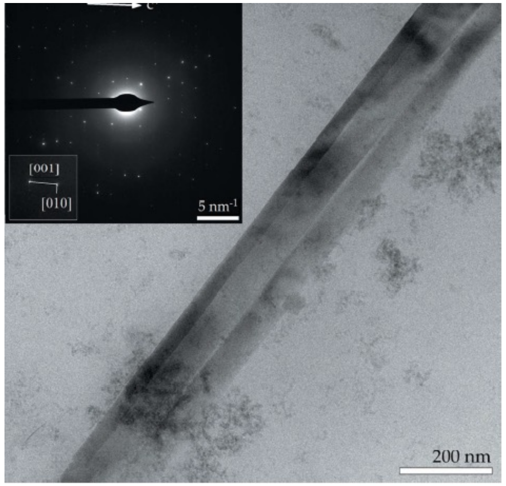


A view of the asymmetric unit and its local environment

A. Titi,R. Touzani, A. Moliterni, C. Giacobbe, F. Baldassarre, M. Taleb, N. Al-Zaqri, A. Zarrouk, I. Warad (2022). *ACS Omega 7, 32949-32958.*

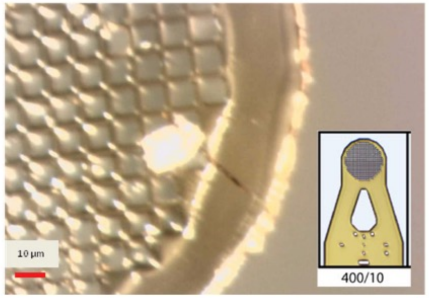
Why the need of synchrotron radiation?

Case n. 2: *ab-initio* structure solution of an amosite amphibole asbestos fibre that had remained, for ≈ 40 years, in the lung of a patient dead of malignant mesothelioma, in order to verify its stability *in vivo*



TEM image and selected-area electron diffraction (SAED) pattern of the asbestos fiber

A 30 μm long amosite fibre, diameter ≈ 1 μm, was investigated for the first time by single crystal synchrotron X-ray microdiffraction



The amosite fibre mounted on a MiTeGen microloops^{TM} of 400 μm diameter and 10 μm mesh size.

Experimental details:

ID11 beamline
Energy: 40 keV
Wavelength ≈ 0.3 Å
Beam size: 800 nm x 500 nm
Investigated volume: < 1μm^3

ESRF
The European Synchrotron

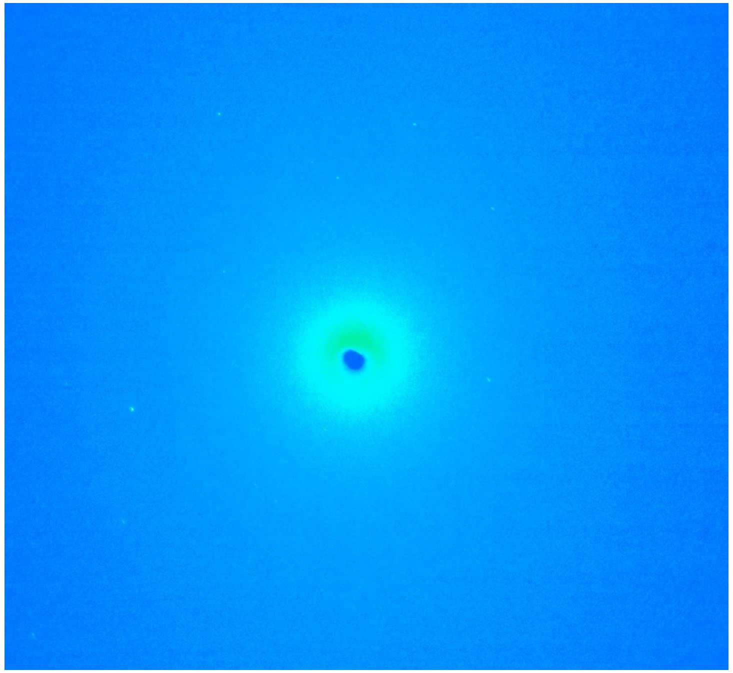
https://doi.org/10.1107/S2052252520015079
IUCrJ
ISSN 2052-2525
NEUTRON | SYNCHROTRON
IUCrJ (2021). 8, 76–86

Crystal structure determination of a lifelong biopersistent asbestos fibre using single-crystal synchrotron X-ray micro-diffraction

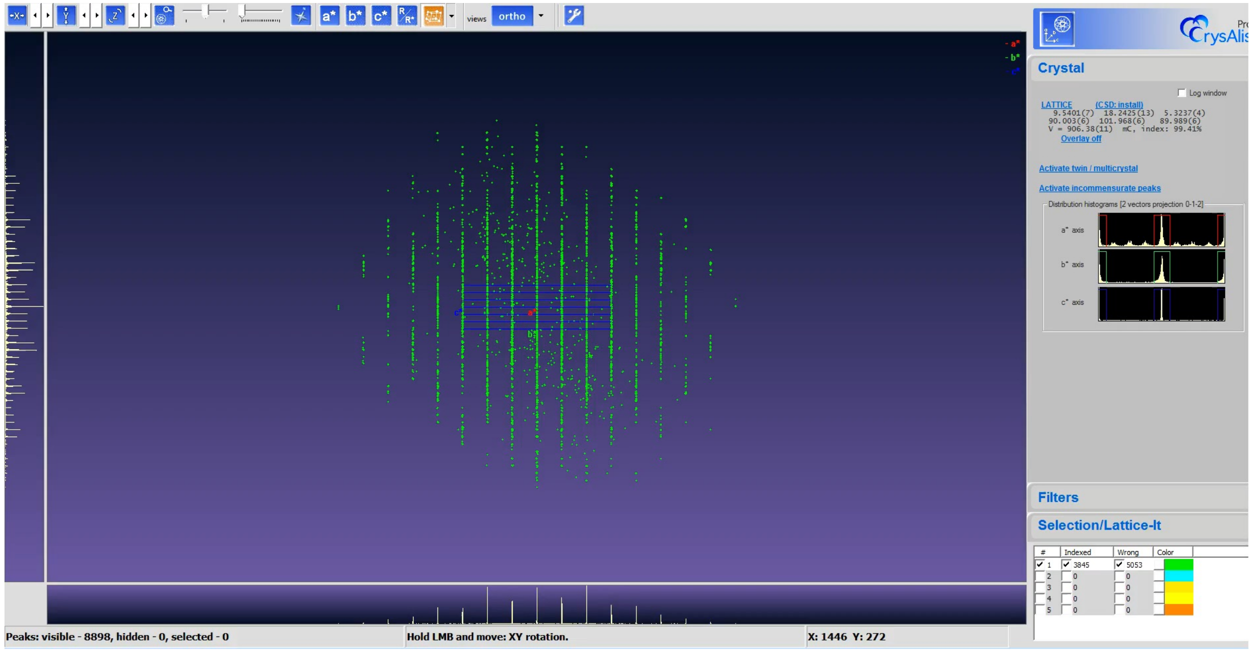
Carlotta Giacobbe,[a] Dario Di Giuseppe,[b,c] Alessandro Zoboli,[b] Magdalena Lassinantti Gualtieri,[d] Paola Bonasoni,[e] Anna Moliterni,[f*] Nicola Corriero,[f] Angela Altomare,[f] Jonathan Wright[a] and Alessandro F. Gualtieri[b*]

When the crystal size is extremely small…Synchrotron light can make the difference!

Data collection step:



3D reciprocal space:



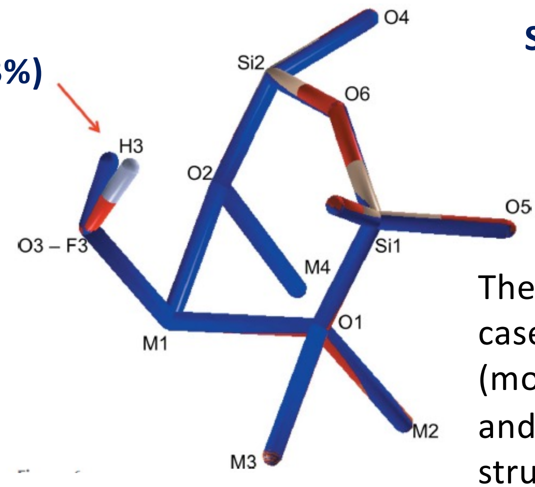
When the crystal size is extremely small… Synchrotron light can make the difference!

Case n. 2: *ab-initio* structure solution of an amosite amphibole asbestos fibre

Two sets of data were collected by investigating two different zones (volume < 1μm^3) of the amosite fibre, *i.e.*, the top (fibre_T) and the center (fibre_C).
For each of them the *ab-initio* structure solution process was successfully carried out (structure solution by *SIR2019* and structure refinement by *SHELXL2014*)

High resolution data (Res = 0.75 Å), for fibre_T: R_{int}=3%)

An inspection of the electron-density map calculated by difference Fourier synthesis allowed to position a hydrogen atom bonded to the O3 atom.



Substitutional disorder:

M1 ⟶ (Fe, Mg)
M2 ⟶ (Fe, Mg)
M3 ⟶ (Fe, Al)
M4 ⟶ (Fe, Ca)

The two refined structure models in the case of fibre_T (in colour) and fibre_C (monochromatic blu) strongly overlap and are in agreement with the literature structure model.

JAC COMPUTER PROGRAMS
J. Appl. Cryst. (2015). **48**, 306-309
https://doi.org/10.1107/S1600576715001132

Crystal structure determination and refinement *via SIR2014*
M. C. Burla, R. Caliandro, B. Carrozzini, G. L. Cascarano, C. Cuocci, C. Giacovazzo, M. Mallamo, A. Mazzone and G. Polidori

A RESEARCH PAPERS
Acta Cryst. (2015). A**71**, 3-8
https://doi.org/10.1107/S2053273314026370

***SHELXT* - Integrated space-group and crystal-structure determination**
G. M. Sheldrick
SHELXT automates routine small-molecule structure determination starting from single-crystal reflection data, the Laue group and a reasonable guess as to which elements might be present.

When the crystal size is extremely small… Synchrotron light can make the difference!

Case n. 2: *ab-initio* structure solution of an amosite amphibole asbestos fibre

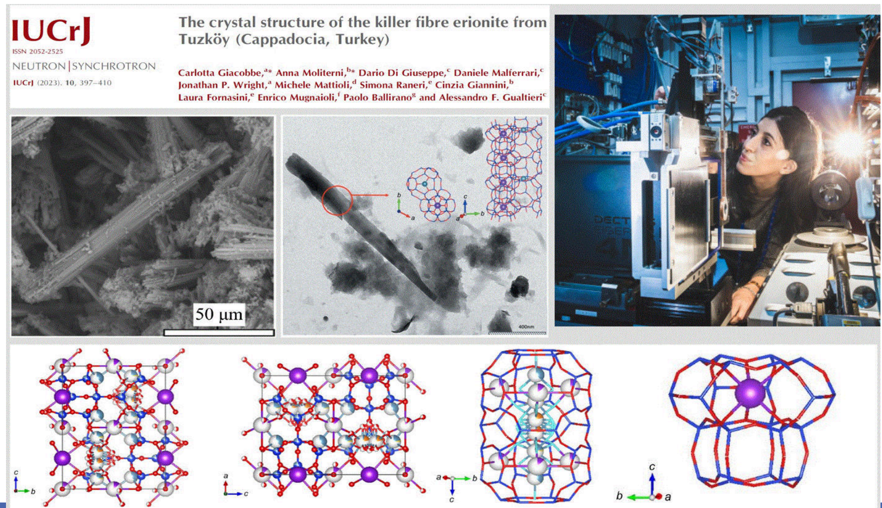
By SCXRD Crystallography and **the help of synchrotron** radiation we concluded the following:

- Amosite asbestos fibres can be chemically stable at the atomic scale in the lungs for 40 years;
- The structure refinements showed that the amosite fibres are not iron depleted.
- The obtained results have a paramount importance for the understanding of the asbestos toxicity/carcinogenicity mechanisms as they show that **the atomic structure of amphibole asbestos fibres remains stable in the lungs for a lifetime, during which they can cause chronic inflammation and other adverse effects that are responsible for the carcinogenesis.**

Why the need of synchrotron radiation?

Case n. 3: *ab-initio* structure solution of an erionite fiber from Tuzköy (Cappadocia, Turkey)

Erionite is a non asbestos fibrous zeolite classified by the International Agency for Research on Cancer (IARC) as a Group 1 carcinogen; similarly to asbestos minerals is responsible for malignant mesothelioma (MM) and is considered even more carcinogenic than asbestos minerals.



A 20 µm long erionite fibre, section =350 nm x 540 nm, was investigated for the first time by single crystal synchrotron X-ray microdiffraction

Experimental details:

ID11 beamline
Energy: 38 keV
Wavelength = 0.3257 Å
Fiber size: 350 nm x 540 nm x 20 µm

Why the need of synchrotron radiation? Some not routinary cases of study

In Cappadocia, tuff rocks contain erionite; unfortunately they were used for building three villages (Karain Tuzköy and Sarihidir). The erionite caused epidemics of malignant mesothelioma (MM).

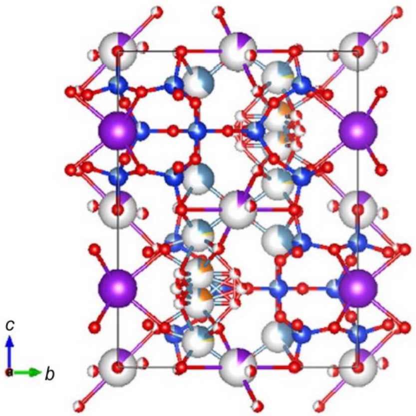
Cappadocia: A view of the 'fairy chimneys', rocks containing erionite. (photo by courtesy of Mangano D.)

Cappadocia: A view of the abandoned houses of the Turkish village of Tuzköy (photo: source https://www.trt.net.tr/italiano/arte-cultura/2017/01/24/capadocia-ospita-oltre-1-milione-turisti-658094).

Why the need of synchrotron radiation? Some not routinary cases of study

Erionite is a natural zeolite, characterized by a framework of tetrahedra (with Si and/or Al as central atom, and oxygen atoms at the vertices), channels and cavities (micropores) that host, in variable quantities, exchangeable water molecules and extra-framework cations (*e.g.*, Na^+, Ca^{2+}, Mg^{2+}, K^+).

The knowledge of the crystal structure of erionite is fundamental for the comprehension of the carcinogenic process caused by the inhalation of the erionite fibers.



The crystal structure of erionite was successfully solved by ***SIR2019*** and refined by ***SHELXL2014*** **(R_F=3.8%)**.

The high quality of diffraction data and the applied special refinement protocols allowed to overcome the difficulties due to the substitutional disorder typical of this material and to locate also the extra-framework cations, positioned *via* a careful inspection of the electron-density map calculated by difference Fourier synthesis.

Substitutional disorder

***Tetrahedra*:**

- **T1 → (Si1, Al1)**
- **T2 → (Si2,Al2)**

Cations

- **C1 → (Ca2, Na2)**
- **C2 → (Ca3, Mg3)**

Why the need of synchrotron radiation? Some not routinary cases of study

Case n. 3: *ab-initio* structure solution of an erionite fiber from Tuzkoy (Cappadocia, Turkey)

By SCXRD Crystallography and **the help of synchrotron radiation** we

- Verified the similarity of the crystal structure of erionite and asbestos fibres;
- Determined in details the crystal structure of erionite, extra-framework cations included.

The detailed structural knowledge of erionite represents a first important and crucial step on the path towards the construction of a carcinogenicity model of the fibrous erionite and the full understanding of the biochemical mechanisms responsible for the onset of MM.

Conclusions

Crystallography, with the help of synchrotron radiation,

- sheds light on the fascinating world of Materials Science;

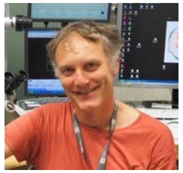
- is the key for opening the door to new explorations, helping crystal engineering in the project and synthesis of new materials with optimized optoelectronic properties;

- can provide effective tools for studying **also at the nanoscale** yet unexplored materials of interest for Energy (*e.g.*, metal chalcohalides) and characterize challenging materials of interest for Environment and Health (*e.g.*, fibers).

Acknowledgments

Thank you for your kind attention!

Liberato Manna and his team



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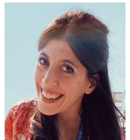
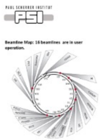
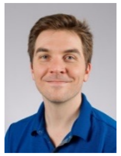


Carlotta Giacobbe





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