Consiglio Nazionale delle Ricerche
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

DSCTM
Dipartimento Scienze Chimiche e Tecnologie dei Materiali

IC CNR Istituto di Cristallografia

xmi l@b

Crystallography sheds light on the fascinating world of perovskites

Anna Moliterni

CNR – ISTITUTO DI CRISTALLOGRAFIA

ANNAGRAZIA.MOLITERNI@IC.CNR.IT

Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main applications;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;

SECOND PART

- Crystallography and synchrotron radiation to study new lead-free compounds of interest for Energy: nanocrystalline bismuth chalcohalides;
- ***XMI-Lab@IC***, a first-generation-synchrotron-class X-ray microsource @home: a poweful tool for investigating crystalline materials by (grazing incidence) small- and wide-angle X-ray scattering [(GI)SAXS/WAXS];

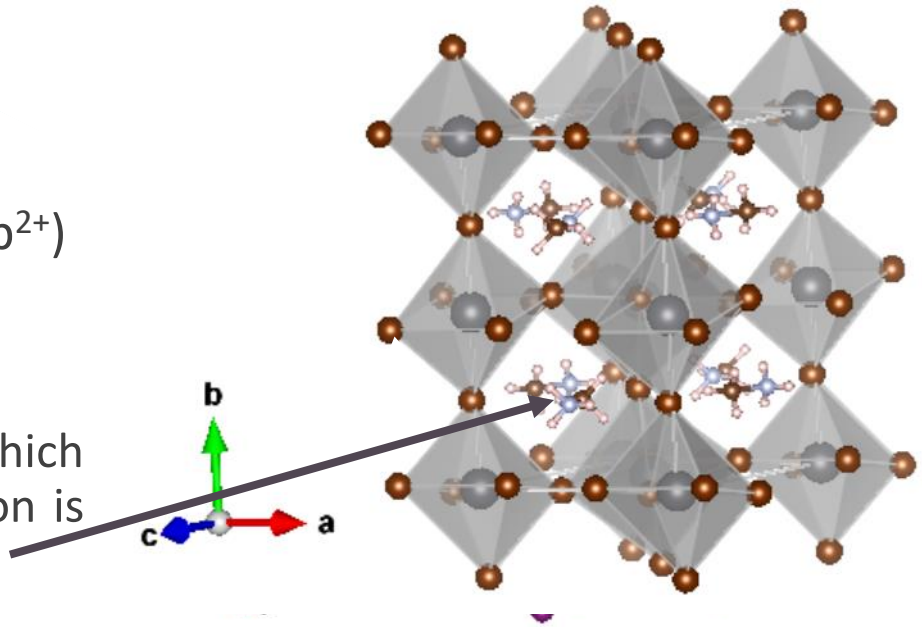
- Conclusions and perspectives

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^-)

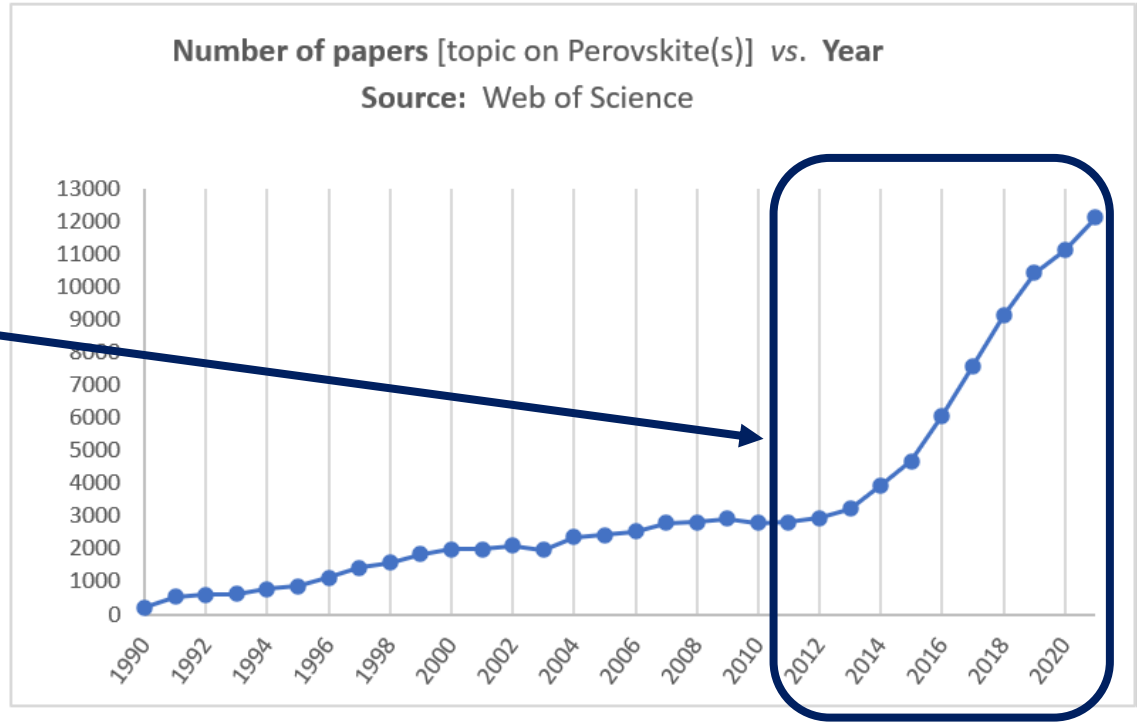


We will focus our attention on **hybrid organic-inorganic perovskites**, for which at least one of the "A", "B", or "X" ions are organic; typically, the "A" cation is organic, *e.g.*, **CH_3NH_3**PbI_3 [where the "A" cation is methylammonium (MA)].

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

First 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.*,

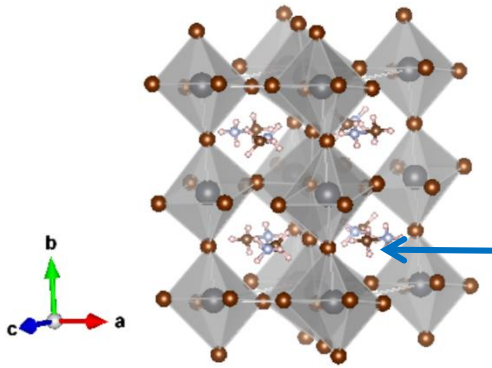
- Solar cells
- LEDs
- Lasers
- Photodetector devices

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

First debut of hybrid organic-inorganic perovskites in photovoltaics:

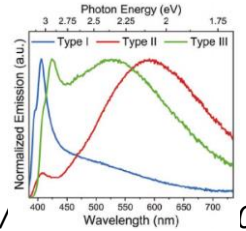
2006

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

Changing the 'ingredients' a large number of new perovskites can be created

Machine learning can help the creativity of scientists on the crystal engineering of perovskites

Journal of Energy Chemistry 66 (2022) 74–90

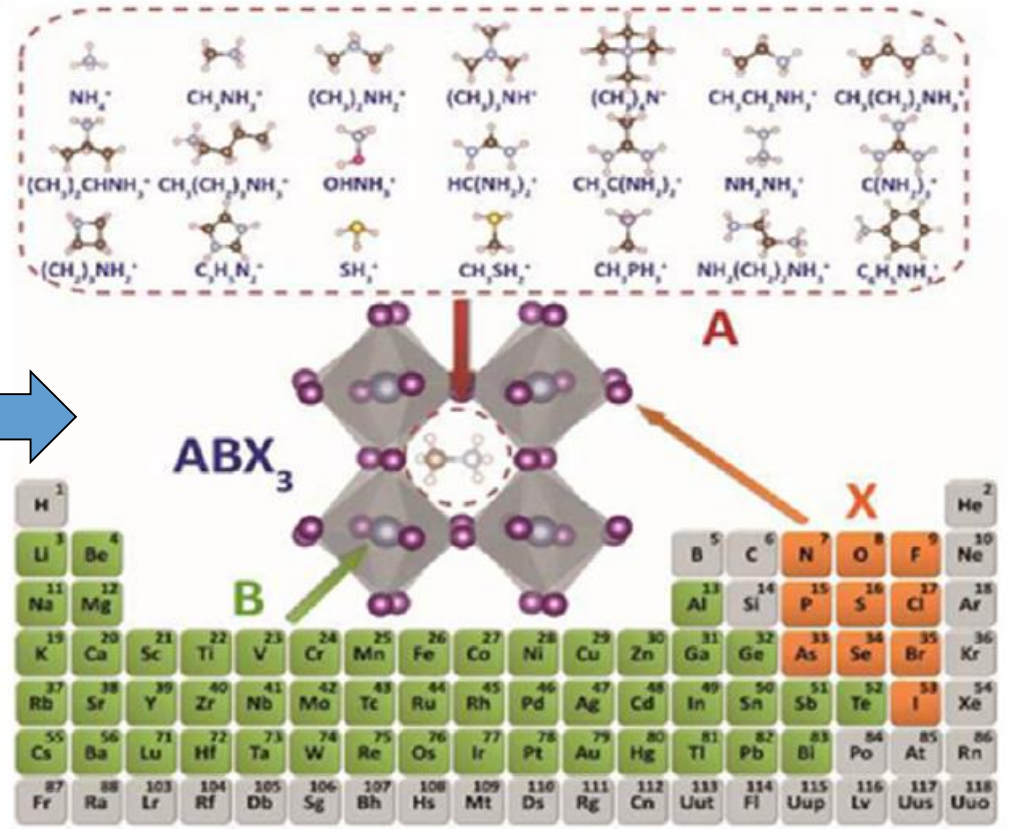
Contents lists available at ScienceDirect

Journal of Energy Chemistry

journal homepage: www.elsevier.com/locate/jechem

Is machine learning redefining the perovskite solar cells?

Nishi Parikh [a], Meera Karamta [b], Neha Yadav [c], Mohammad Mahdi Tavakoli [d], Daniel Prochowicz [e], Seckin Akin [f], Abul Kalam [g], Soumitra Satapathi [h], Pankaj Yadav [i,*]



Possible A, B and X-site ions used to create the database.

Changing the ‘ingredients’ a large number of new perovskites can be created

Many pages of the ‘recipes book’ of perovskites
can be still written with new recipes

Today we will analyse the structural characterization concerning the results of four perovskites ‘recipes’ published in 2021-2022:

February 2022

December 2021

October 2021

April 2021

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)

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)

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[3✉], 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

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)

Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main applications;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;

How Crystallography can shed light on the perovskites world

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 the new materials, *via* an optoelectronic characterization, show some unique properties?

Outlook

FIRST PART

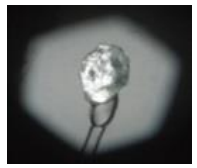
- Perovskites and hybrid organic-inorganic perovskites: what are and their main applications;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;

Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?

Single crystal and/or powder diffraction?

It depends on the crystal size and on the kind of wanted structural information

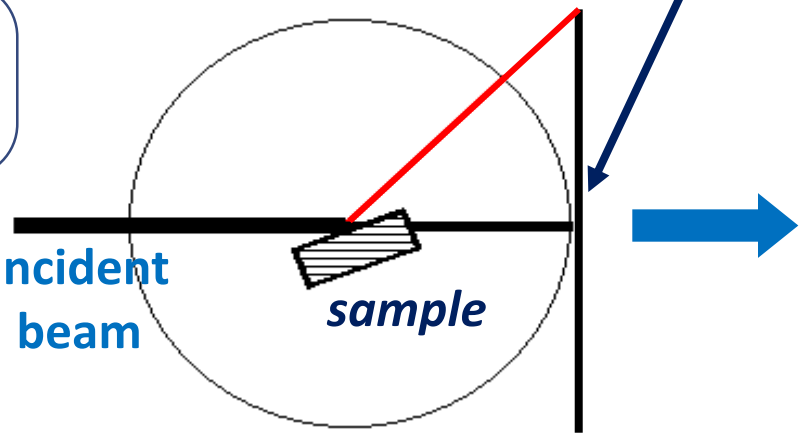
In case of conventional X-ray sources

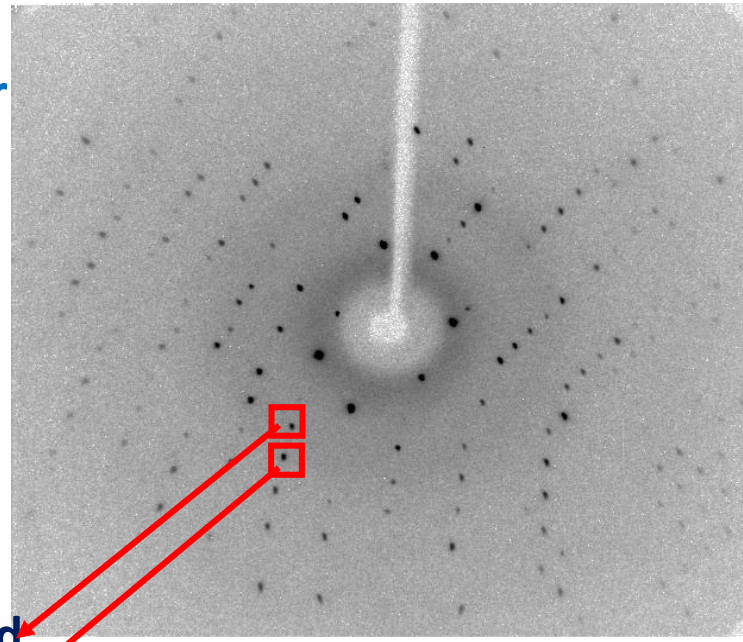


Single crystal

(dimensions: fractions of mm)

Individual information; Single phase



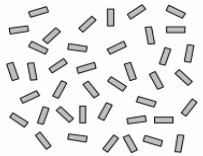


The diffraction effects are well separated

The experimental information is three-dimensional

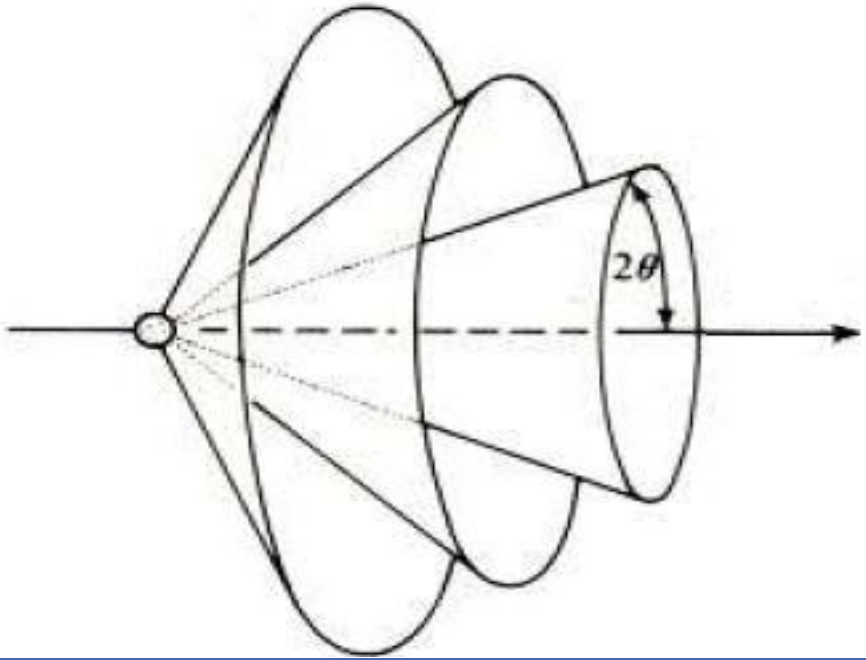
Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?

In case of powders

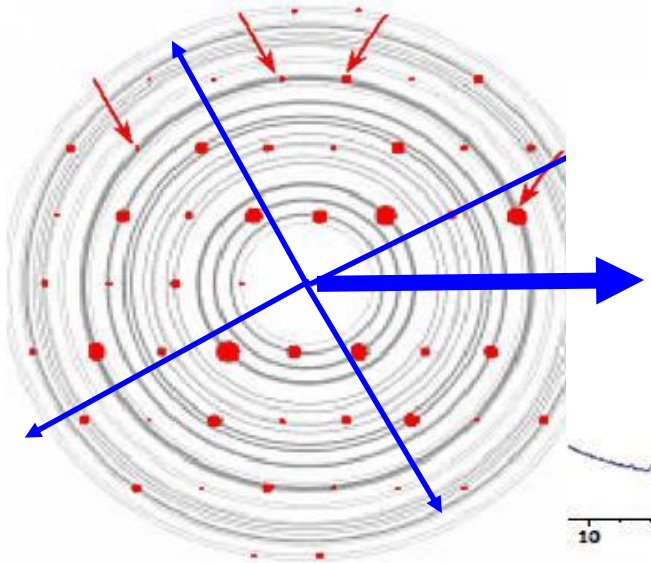


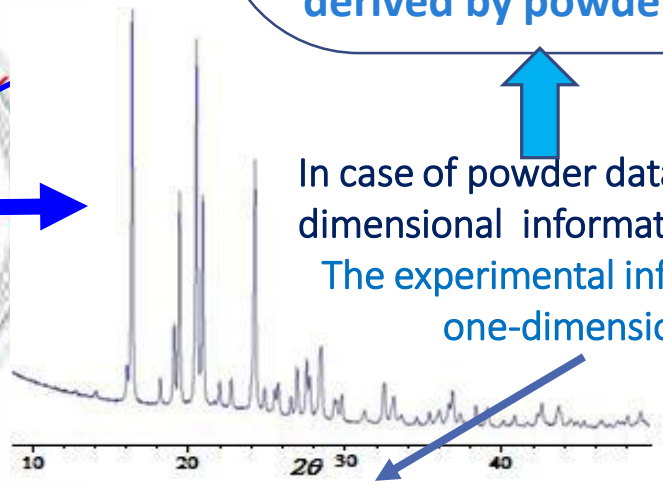
bulk information

Single phase or polyphase mixture



The corresponding single crystal pattern is superimposed (red spots)



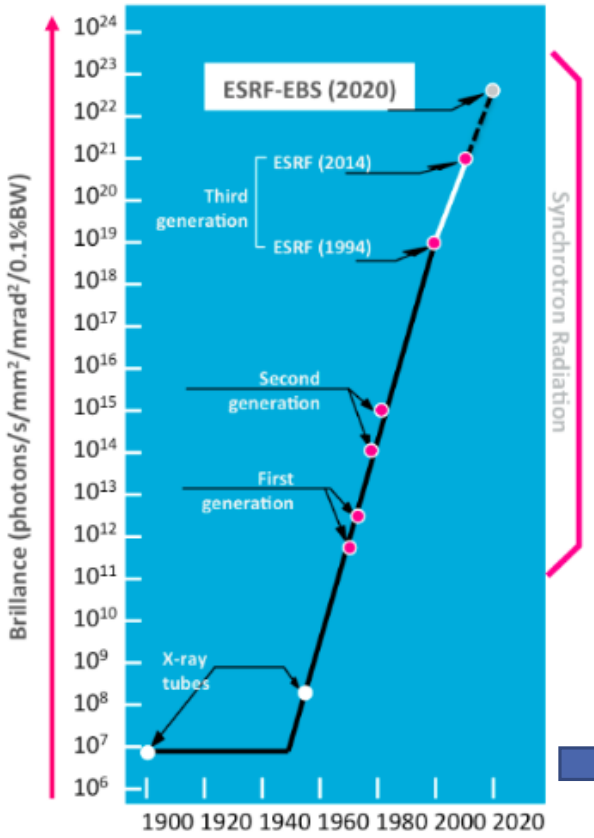


In case of single crystal diffraction, thanks to the usual greater quality and resolution of data, the obtained structure details are more reliable and accurate than those ones derived by powder data

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

Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?

Why in case of hybrid organic-inorganic perovskites the use of synchrotron radiation could be an obliged choice?

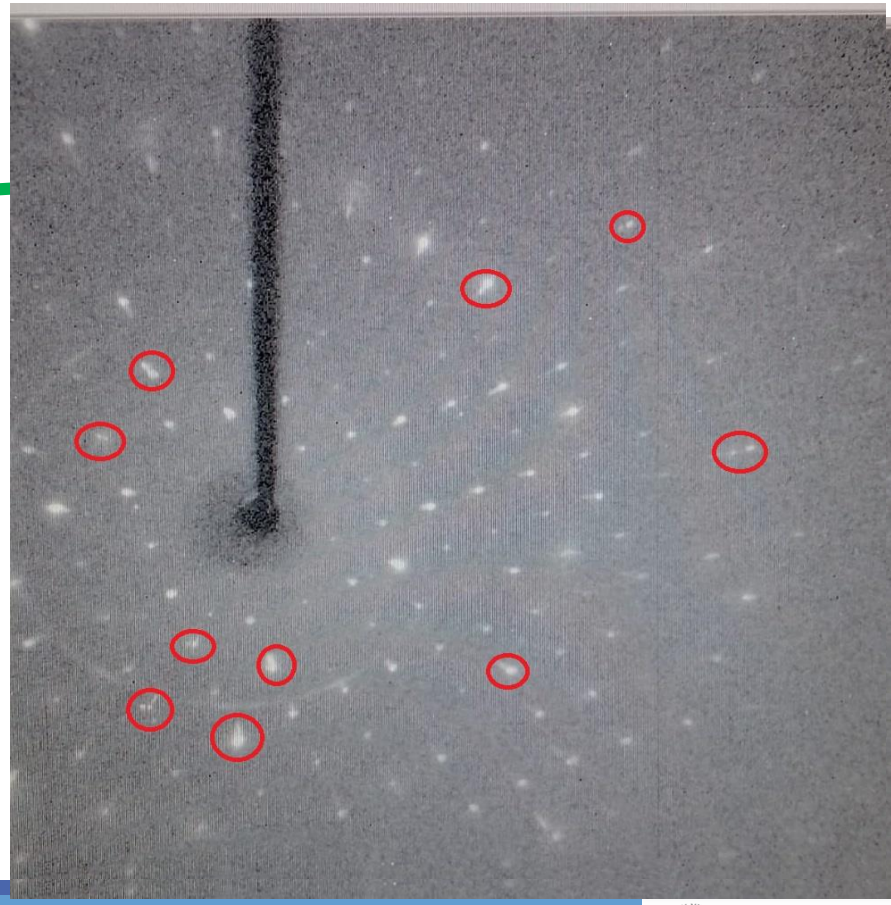


In case of hybrid organic-inorganic perovskites, the available single crystals are often laminar samples a few μm thick

If a conventional X-ray source is used, to measure not negligible diffraction effects the sample should consist of more than one crystal (a single crystal will diffract weakly)

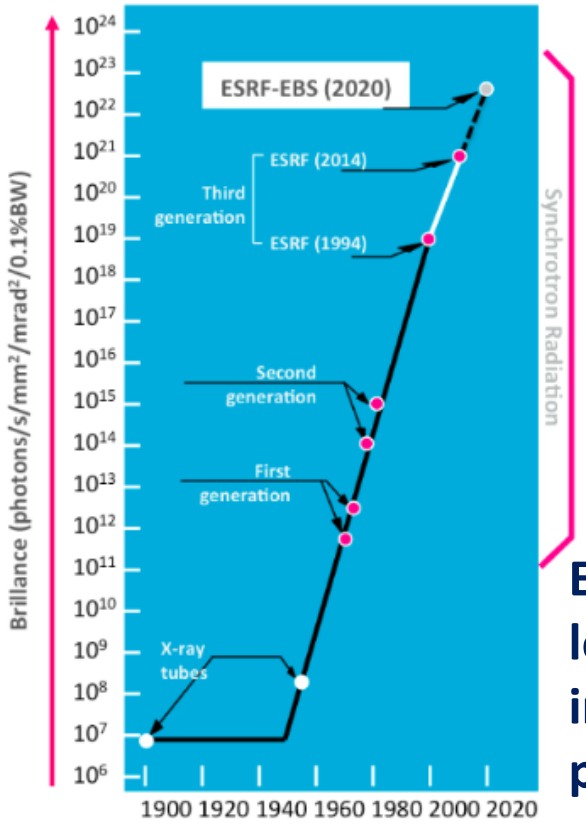
The integrated intensities will be affected by errors and data completeness usually not reached.

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



Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?

Why in case of hybrid organic-inorganic perovskites the use of synchrotron radiation could be an obliged choice?



High-quality and high-resolution diffraction data can be measured by single crystal diffraction

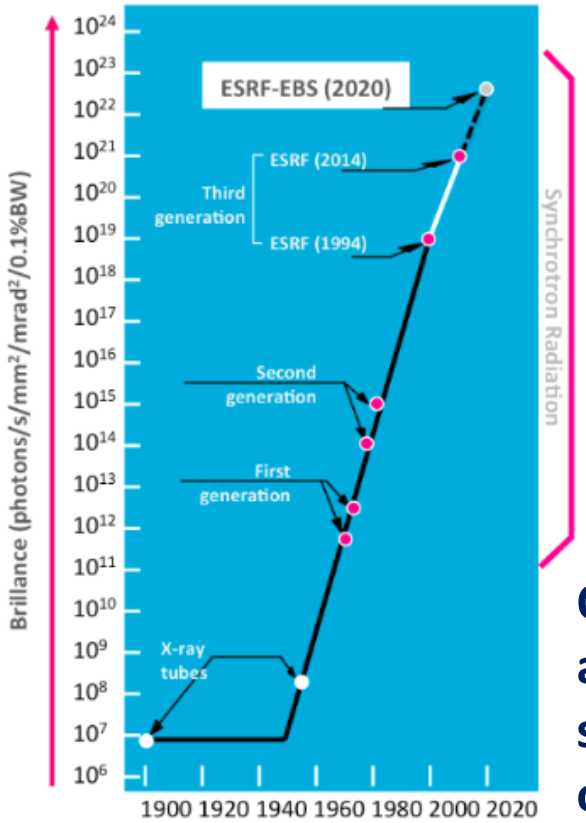
High-resolution diffraction data → **To reduce the Fourier truncation errors, *i.e.*, the ripples in the electron density map, due to the limited number of measured reflections used in the Fourier synthesis**

High-quality and high-resolution diffraction data →

Effective difference Fourier synthesis (F_o-F_c), allowing to reliably and accurately locate light atoms (also H atoms) by the observed F_o values, by searching for maxima in the difference Fourier map and contrasting the effects of the heavy atoms presence, whose contribution tends to dominate and hinder that one of light atoms.

Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?

Why in case of hybrid organic-inorganic the use of synchrotron radiation could be an obliged choice?



In the case of very small size of crystallites (<μm or nm) it may be not possible to carry out a successful structure solution process by synchrotron X-ray single-crystal microdiffraction data

The structure solution by powder diffraction data should be attempted.

Of course, also in the case of synchrotron X-ray powder diffraction data, the availability of high-resolution data will increase the probability of success of the structure solution process with respect to the case of powder diffraction data obtained by using conventional X-ray sources.

Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main application;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;


RESEARCH ARTICLE

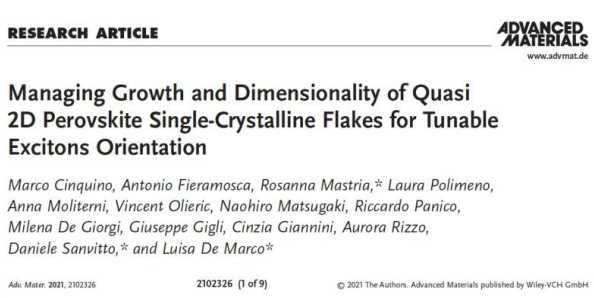
ADVANCED MATERIALS
www.advmat.de

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


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

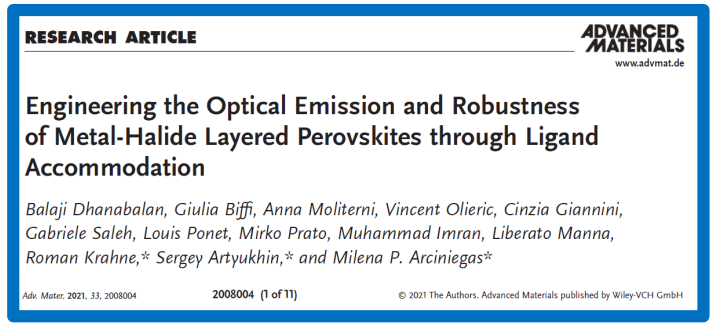

nature nanotechnology ARTICLES

https://doi.org/10.1038/s41565-021-00977-2

Check for updates

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[4,7], Antonio Fieramosca[8], Dmitry D. Solnyshkov[9,10✉], Guillaume Malpuech[9] and Daniele Sanvitto[2,3]


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

Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study

Case 1

RESEARCH ARTICLE

ADVANCED MATERIALS
www.advmat.de

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

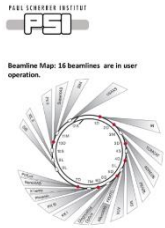
Balaji Dhanabalan, Giulia Biffi, Anna Moliterni, Vincent Olieric, Cinzia Giannini, Gabriele Saleh, Louis Ponet, Mirko Prato, Muhammad Imran, Liberato Manna, Roman Krahne, Sergey Artyukhin,* and Milena P. Arciniegas**

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

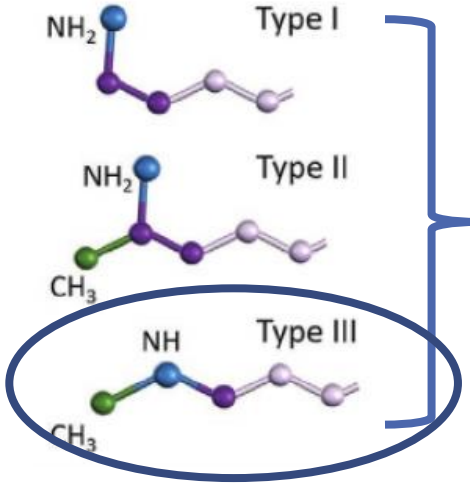
- The kind of organic molecules regulates the number of H-bonds with the edge sharing $[PbBr_6]^+$ octahedra layers and their distortion, leading to strong **differences in the wavelength of the emission** (from deep-blue to pure white);
- The **intensity of the emission** depends on the length of the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

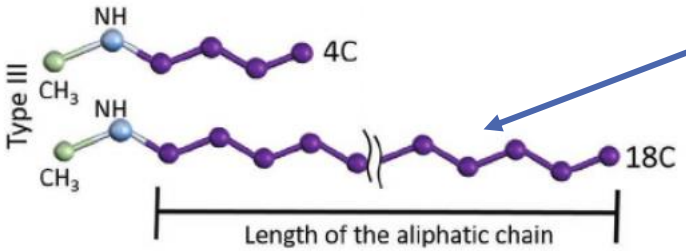
Explored amines used for the synthesis of new perovskites



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.

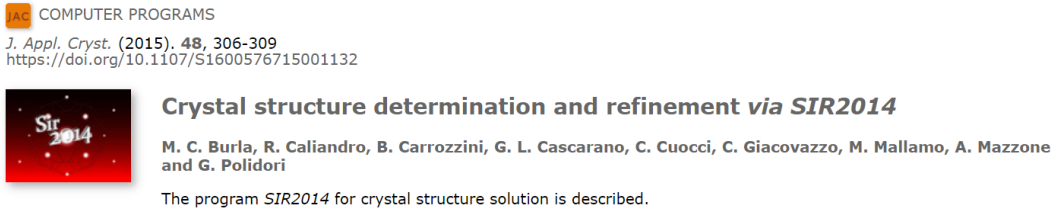
Crystallographic study

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*


COMPUTER PROGRAMS

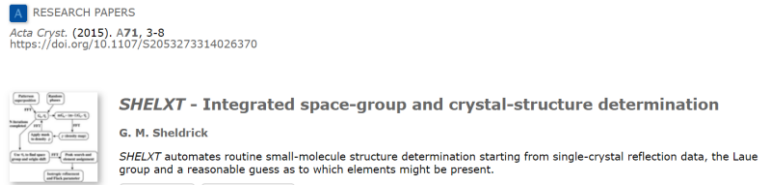
J. Appl. Cryst. (2015). **48**, 306-309
https://doi.org/10.1107/S1600576715001132

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*


RESEARCH PAPERS

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

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

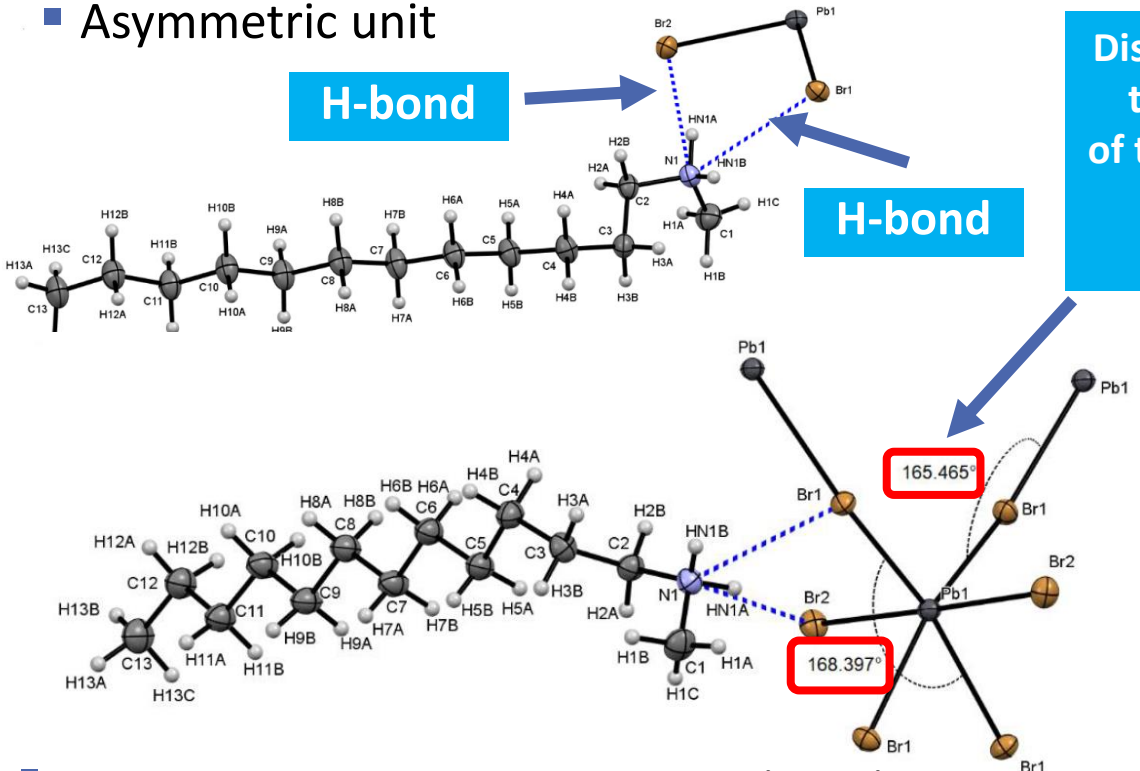
G. M. Sheldrick

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.

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

The crystallographic study confirmed the expected structure:

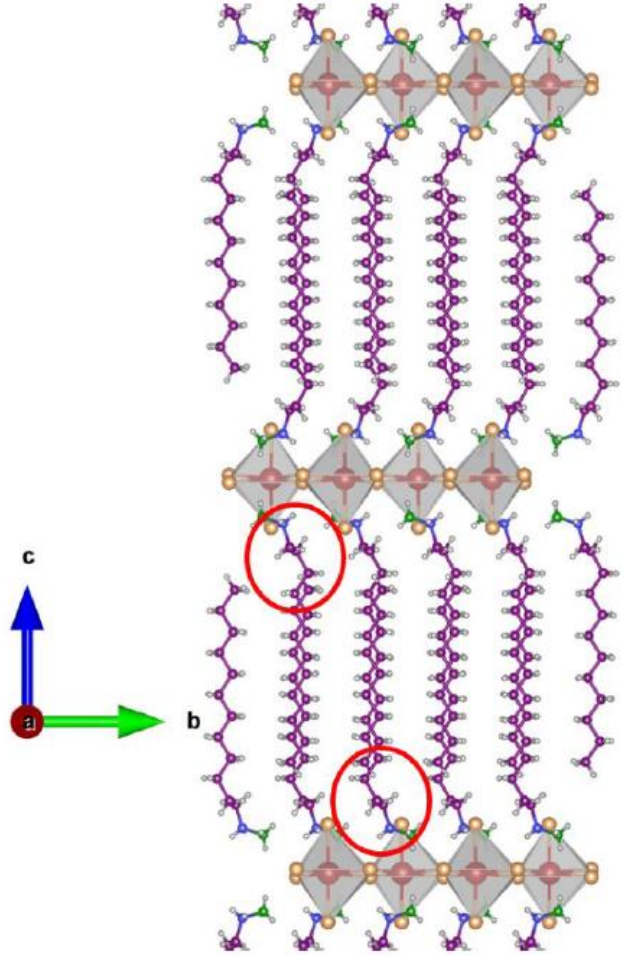
- Asymmetric unit



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.

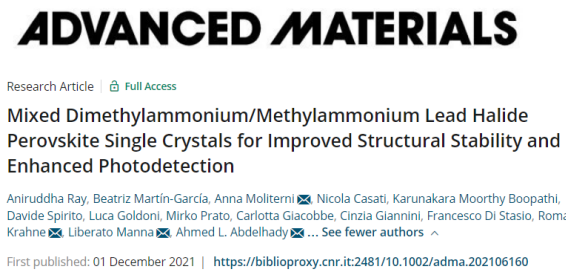
A view of the crystal packing of the $(N\text{-}MDDA)_2PbBr_4$ crystal showing the bending of the chains (framed in red) near to the anchor site.



Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main application;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;

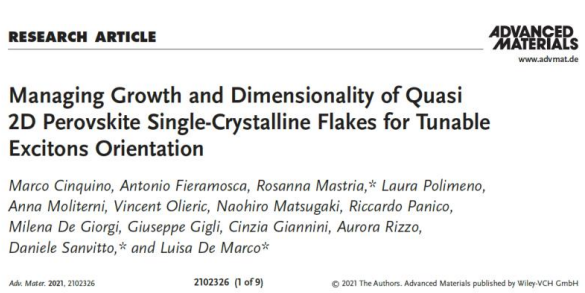

ADVANCED MATERIALS

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, Roma Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors

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


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**

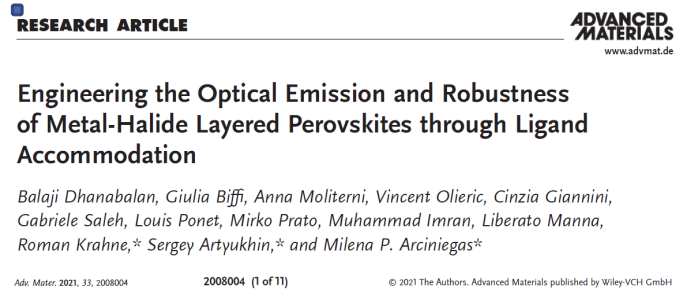
Adv. Mater. 2021, 2102326 2102326 (1 of 9) © 2021 The Authors. Advanced Materials published by Wiley-VCH GmbH


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

Check for updates

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

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

Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 2

Case 2

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

Tuning of the Berry curvature in 2D perovskite polaritons

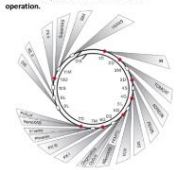
Laura Polimeno[1,2,3], Giovanni Lerario[2], Milena De Giorgi[2✉], Luisa De Marco[2✉], Lorenzo Dominici[2], Francesco Todisco[2], Annalisa Coriolano[1,2], Vincenzo Ardizzone[2], Marco Pugliese[1,2], Carmela T. Prontera[2], Vincenzo Maiorano[2], Anna Moliterni[4], Cinzia Giannini[4], Vincent Olieric[5], 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]

In collaboration with

CNRNANOTEC INSTITUTE OF NANOTECHNOLOGY

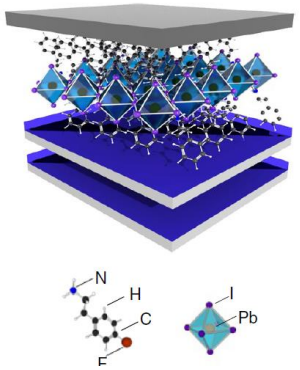
Luisa De Marco

PAUL SCHERRER INSTITUT PSI



Vincent Olieric

- A new hybrid organic-inorganic 2D perovskite $F(C_6H_5(CH_2)_2NH_3)_2PbI_4$) (code name: PEAI-F) was synthetized.



- The new crystalline material revealed promising for optoelectronic devices such as transistors based on the anomalous Hall effect.

Main aims of the crystallographic study

- To solve the crystal structure of the new hybrid organic-inorganic perovskite PEAI-F by single crystal synchrotron X-ray microdiffraction data.

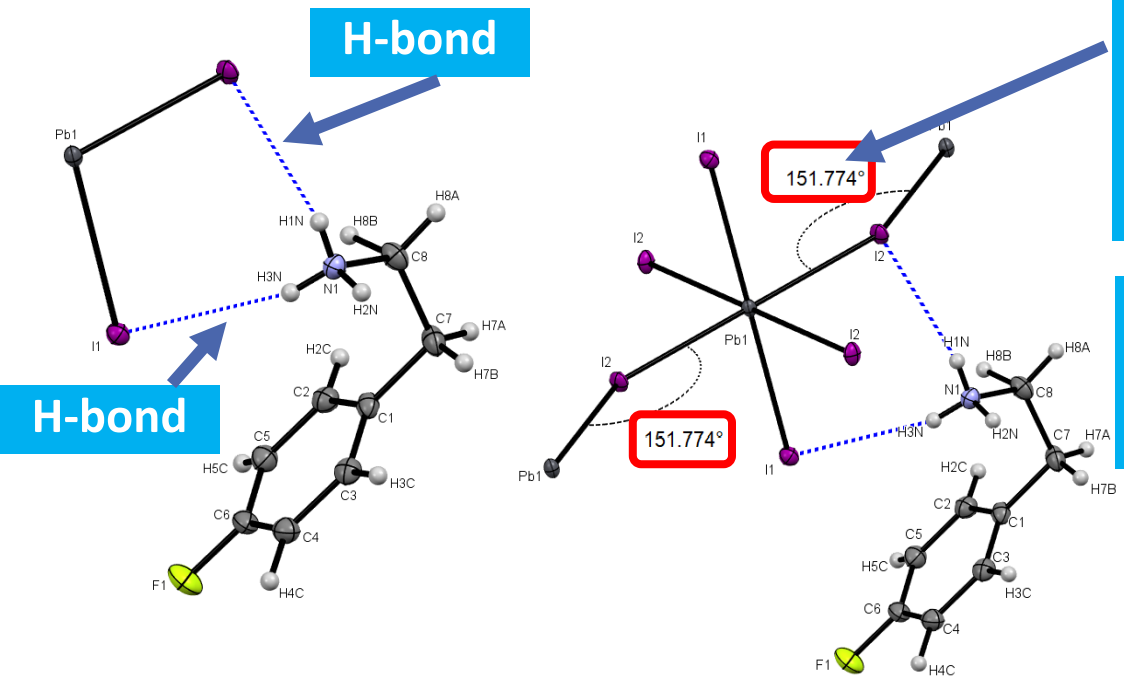
Structure solution carried out by *SIR2019.*
Structure refinement carried out by *SHELXL2014.*

- 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 2

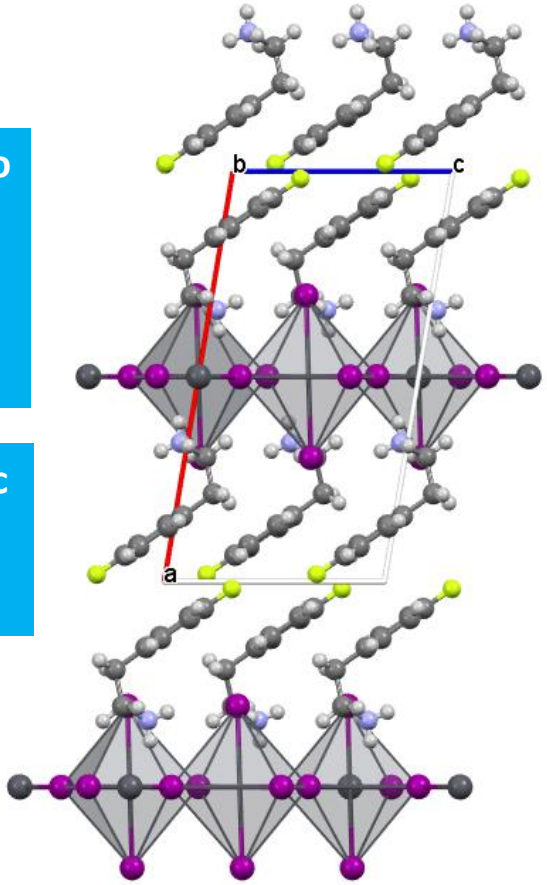
The crystallographic study confirmed the expected structure:

- Asymmetric unit



Strong 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).

The strong in-plane distortions of the inorganic layers with octahedral tilting could favour the optical birifrangency property of the material.

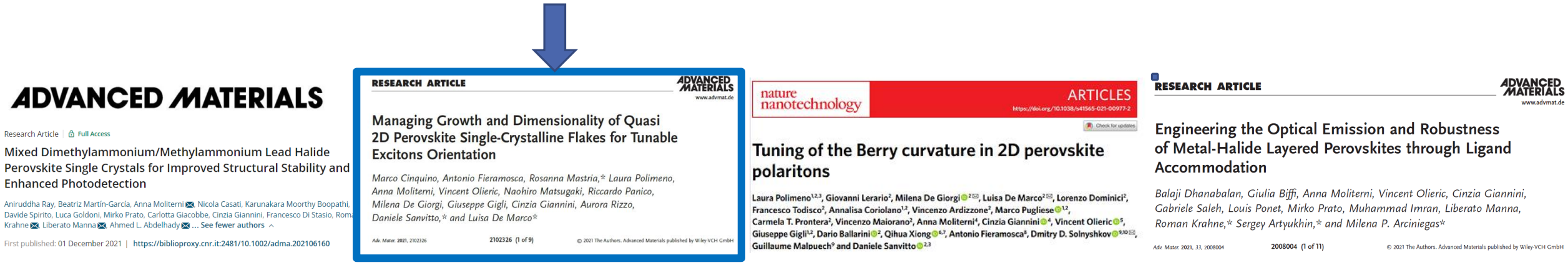


- Asymmetric unit + 2 symmetry equivalent Pb atoms + 4 symmetry equivalent I atoms to show the inorganic chain distortion:

Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main application;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchtrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;



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, Rom... Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors

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

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

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

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

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

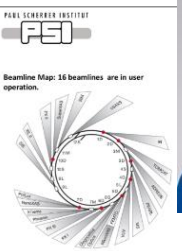
Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

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

In collaboration with

CNR NANOTEC INSTITUTE OF NANOTECHNOLOGY

Luisa De Marco



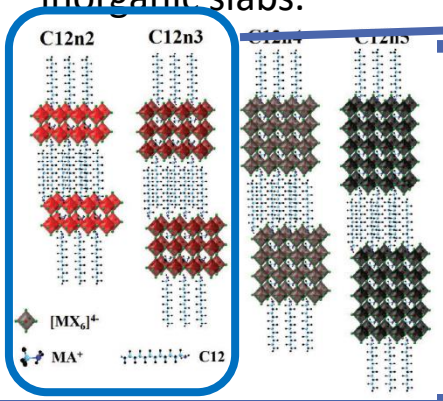
PSI Beamline Map: 16 beamlines are in user operation.

Vincent Olieric

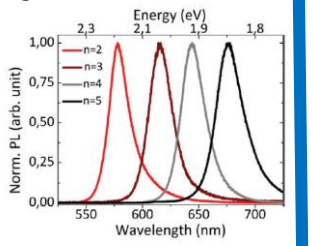
Photon Factory
Institute of Materials Structure Science
High Energy Accelerator Research Organization,KEK

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.

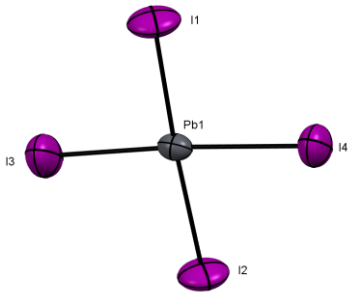
Crystallography and synchrotron X-ray diffraction to characterize new perovskites: Case 3

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

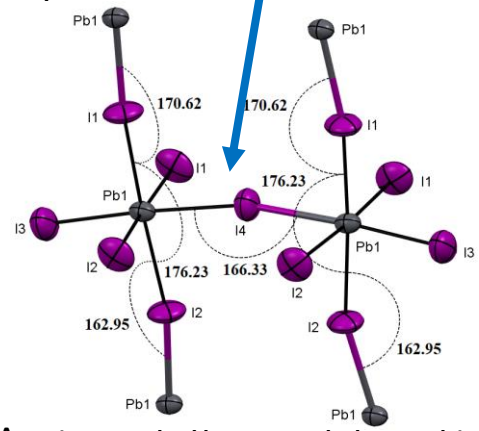
n=2 $(C12)_2(MA)Pb_2I_7$

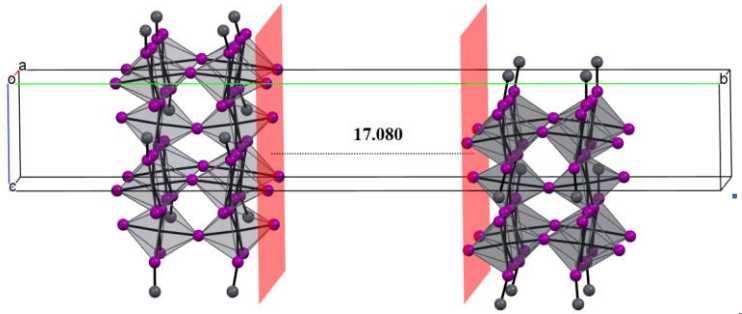
Very small crystal size: 0.04 x 0.03 x 0.02 μm

- 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.



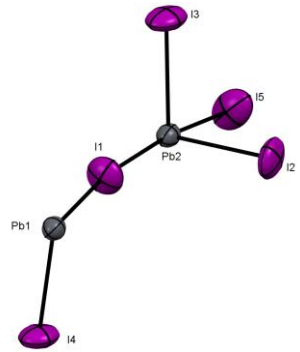


A view of the crystal packing showing the distance between two nearest slabs of inorganic layers.

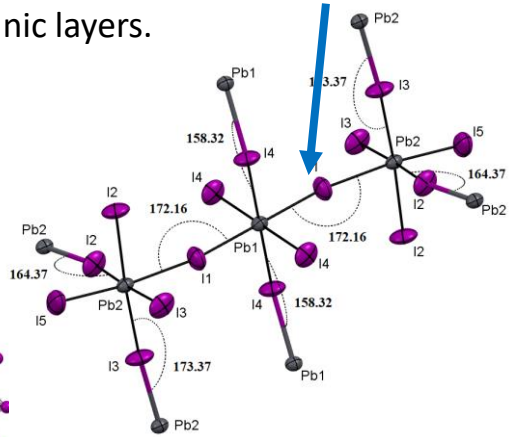
n=3 $(C12)_2(MA)_2Pb_3I_{10}$

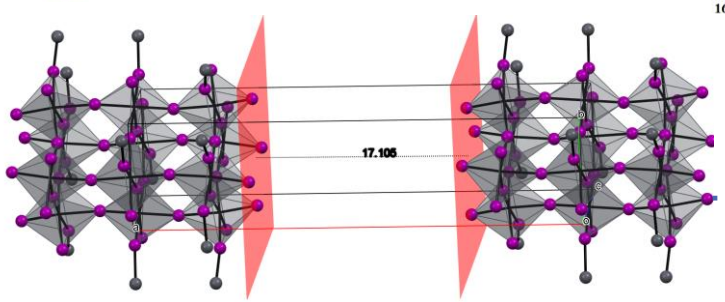
Very small crystal size: 0.08 x 0.04 x 0.02 μm

- 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.



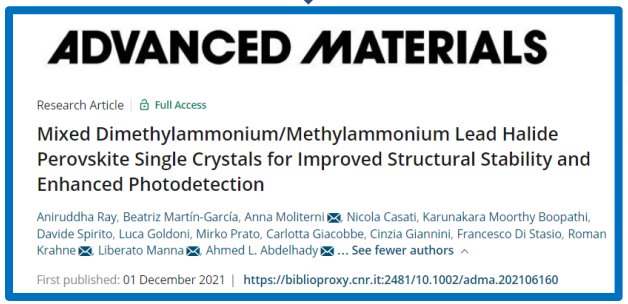


A view of the crystal packing showing the distance between two nearest slabs of inorganic layers.

Outlook

FIRST PART

- Perovskites and hybrid organic-inorganic perovskites: what are and their main application;
- How Crystallography can shed light on the perovskites world;
- Crystallography to characterize new hybrid perovskites: why use synchrotron radiation?
- Crystallography and synchrotron X-ray diffraction to characterize new perovskites: four cases of successful recent study;


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


RESEARCH ARTICLE

ADVANCED MATERIALS www.advmat.de

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

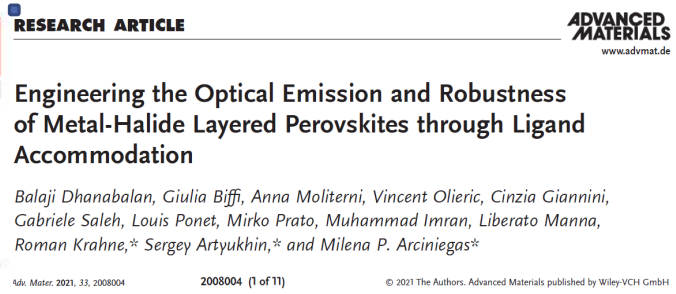
Marco Cinquino, Antonio Fieramosca, Rosanna Mastria, Laura Polimeno, Anna Moliterni, Vincent Olieric, Naohiro Matsugaki, Riccardo Panico, Milena De Giorgi, Giuseppe Gigli, Cinzia Giannini, Aurora Rizzo, Daniele Sanvitto,* and Luisa De Marco**

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


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

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

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

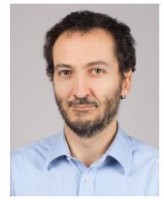
Aniruddha Ray, Beatriz Martín-García, Anna Moliterni, Nicola Casati, Karunakara Moorthy Boopathi, Davide Spirito, Luca Goldoni, Mirko Prato, Carlotta Giacobbe, Cinzia Giannini, Francesco Di Stasio, Roman Krahne, Liberato Manna, Ahmed L. Abdelhady ... See fewer authors

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

In collaboration with

Liberato Manna

Carlotta Giacobbe



Nicola P.M. Casati

Ahmed L. Abdelhady

Aniruddha Ray

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*:

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 compounds ($MAPbBr_3$ and $DMA/MAPbBr_3$) showed different optoelectronic properties.

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

Liberato Manna

Ahmed L. Abdelhady

Anir

Carlotta

Nicola P.M. Casati

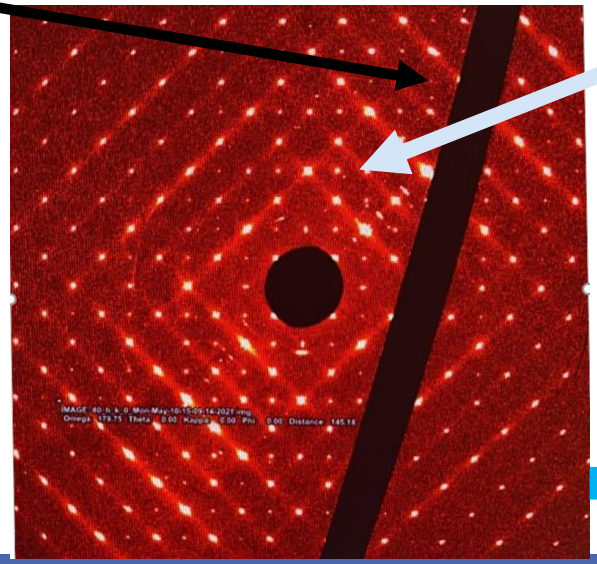
Main aims of the crystallographic study

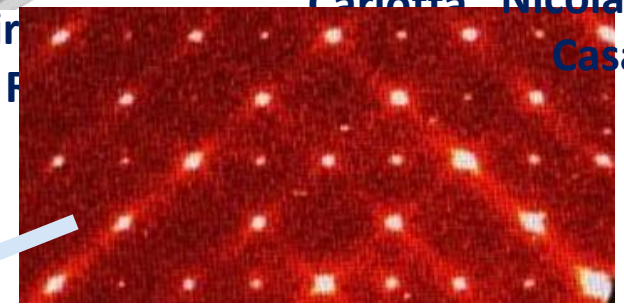
- To confirm the crystal structure of $MAPbBr_3$ (already characterized in literature) and to determine the crystal structure of the new mixed perovskite ($DMA/MAPbBr_3$) by temperature-dependent synchrotron powder diffraction data (range of the temperature: 80-300K).

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 synchtrotron 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:

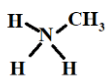
The different optoelectronic properties of $MAPbBr_3$ and $DMA/MAPbBr_3$ are related to the difference in the organic component.

Our proposal:

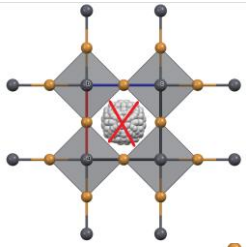
due to the probable greater disorder of the organic cations in the 44% DMA sample, a higher symmetry and less distorted inorganic framework is realized compared to the pure $MAPbBr_3$ sample.

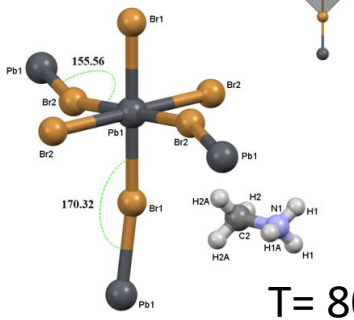
$MAPbBr_3$

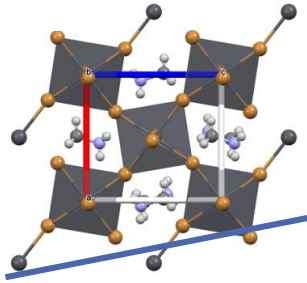
Methylammonium (MA)



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

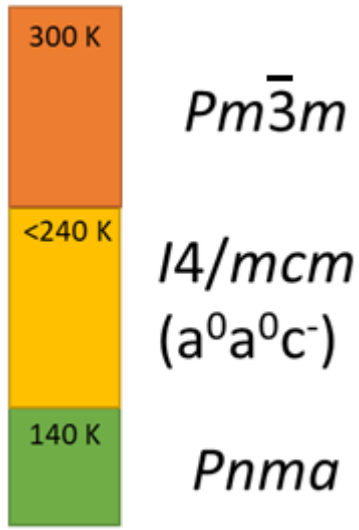






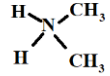
T= 80 K

- Cubic phase
- Tetragonal phase
- Orhorhombic phase

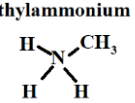


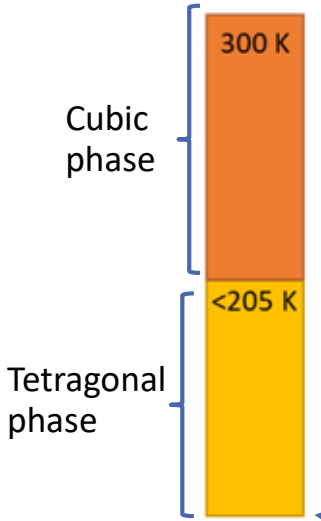
$DMA/MAPbBr_3$

Dimethylammonium (DMA)

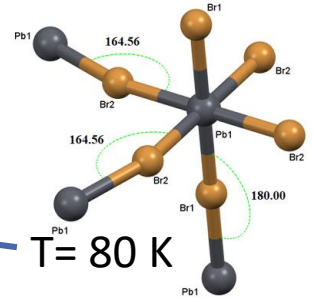


Methylammonium (MA)

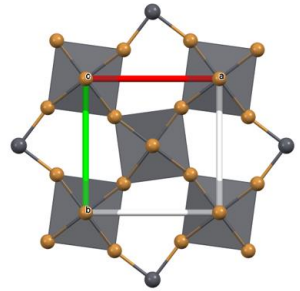




- Only two phase transitions occured (no orthorhombic phase was observed);
- The temperature transition from cubic to tetragonal phase was lower than that one observed for $MAPbBr_3$ (*i.e.*, 205 K instead of 240 K);
- Due to the greater disorder of the organic component (compared to the case of $MAPbBr_3$)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



T= 80 K



Outlook

SECOND PART

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

- ***XMI-Lab@IC***, a first-generation-synchrotron-class X-ray microsource @home: a powerful tool for investigating crystalline materials by (grazing incidence) small- and wide-angle X-ray scattering [(GI)SAXS/WAXS];

- Conclusions and perspectives

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

GDCh Research Articles Angewandte International Edition Chemie 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

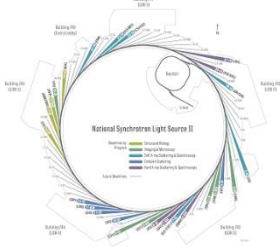
Stefano Toso

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 International Edition Chemie 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)

Main aims of the paper

- To develop a new and versatile colloidal approach to synthesize bismuth chalcohalide orthorhombic 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 nontoxic 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

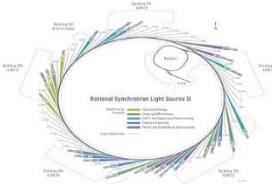
CNRNANOTEC INSTITUTE OF NANOTECHNOLOGY

Brookhaven National Laboratory
National Synchrotron Light Source II

Liberato Manna

Stefano Toso

Carlo Giansante



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 PDF data;
- **This study allowed to discover a new phase, a polymorph of BiSCl, that has been solved *ab-initio* by X-ray 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]

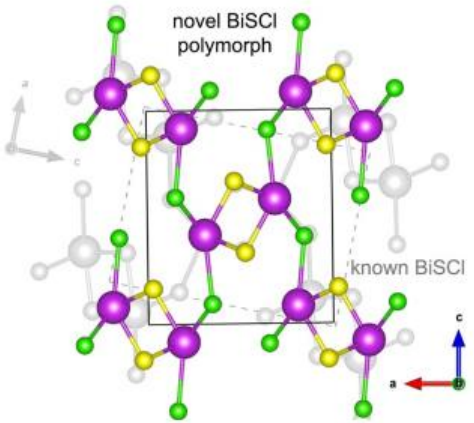
***QUALX2.0*: a qualitative phase analysis software using the freely available database POW_COD**

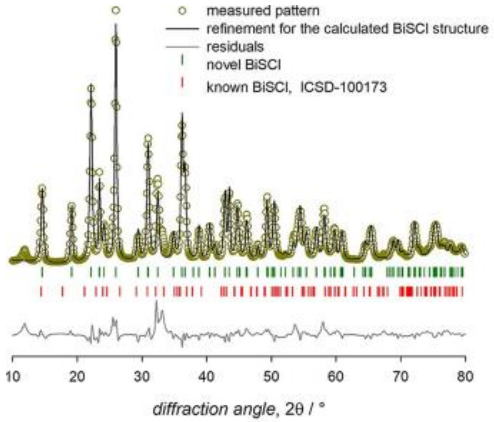
A. Altomare, N. Corriero, C. Cuocci, A. Falcicchio, A. Moliterni and R. Rizzi

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

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

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

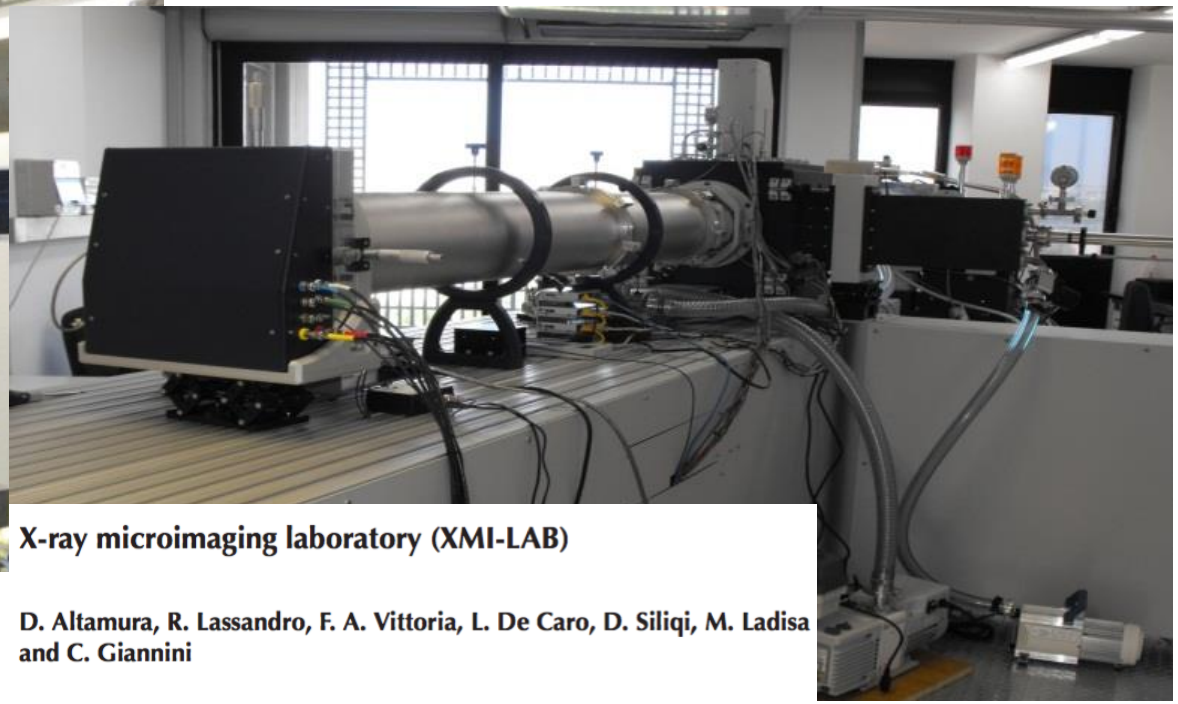
Remarks

- In our knowledge, **for the first time** a family of bismuth chalcohalides compounds has been characterized at the nanoscale by powder diffraction;
- The proposed new protocol of synthesis revealed efficient and reliable;
- The nanocrystalline compounds were stable (*i.e.*, an advantageous feature with respect to hybrid 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.

Outlook

SECOND PART

- Crystallography and synchrotron light to study new compounds of interest for Energy: nanocrystalline metal chalchohalides;
- ***XMI-Lab@IC***, a first-generation-synchrotron-class X-ray microsource @home: a powerful tool for investigating crystalline materials by (grazing incidence) small- and wide-angle X-ray scattering [(GI)SAXS/WAXS];
- Conclusions and perspectives

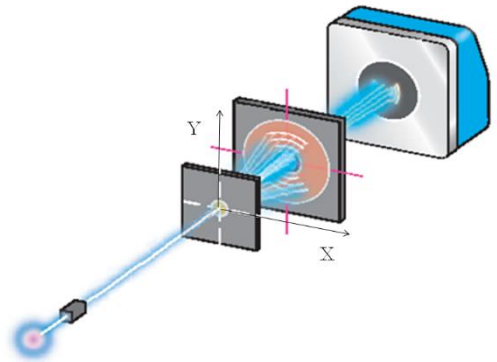


X-ray microimaging laboratory (XMI-LAB)

D. Altamura, R. Lassandro, F. A. Vittoria, L. De Caro, D. Siliqi, M. Ladisa and C. Giannini

J. Appl. Cryst. (2012). **45**, 869–873

FREE STANDING



Fiber with ???

SAXS/WAXS Detector

Software

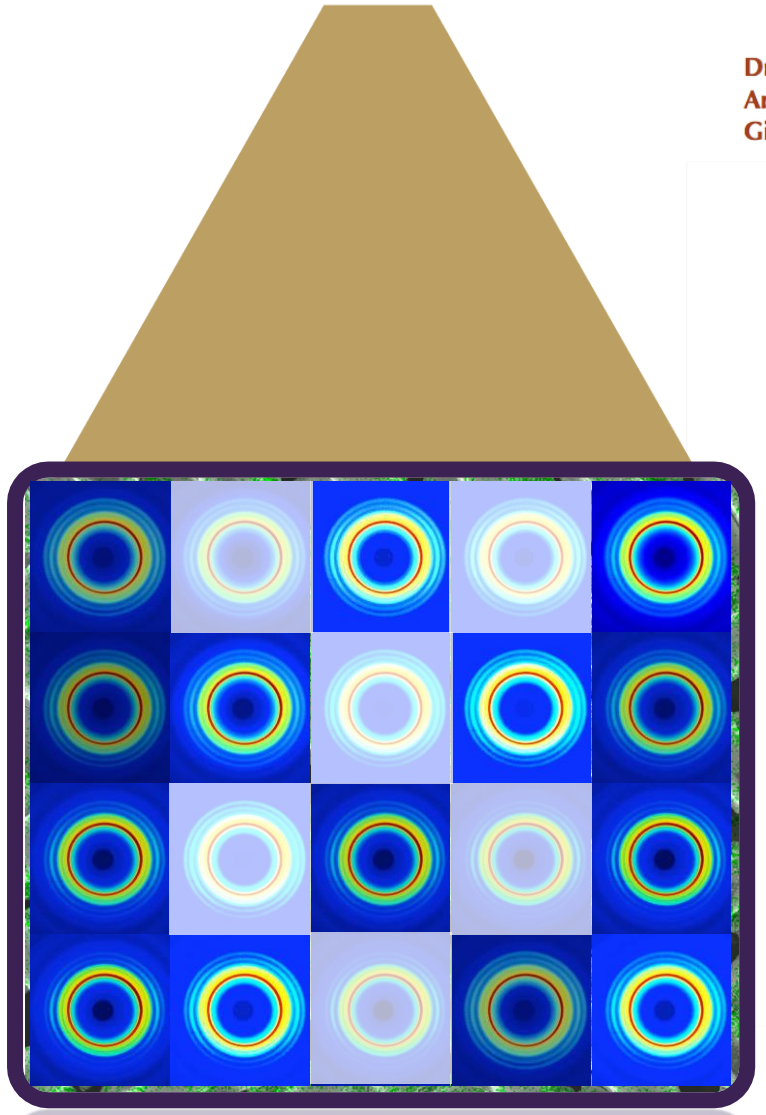
Scan Mode

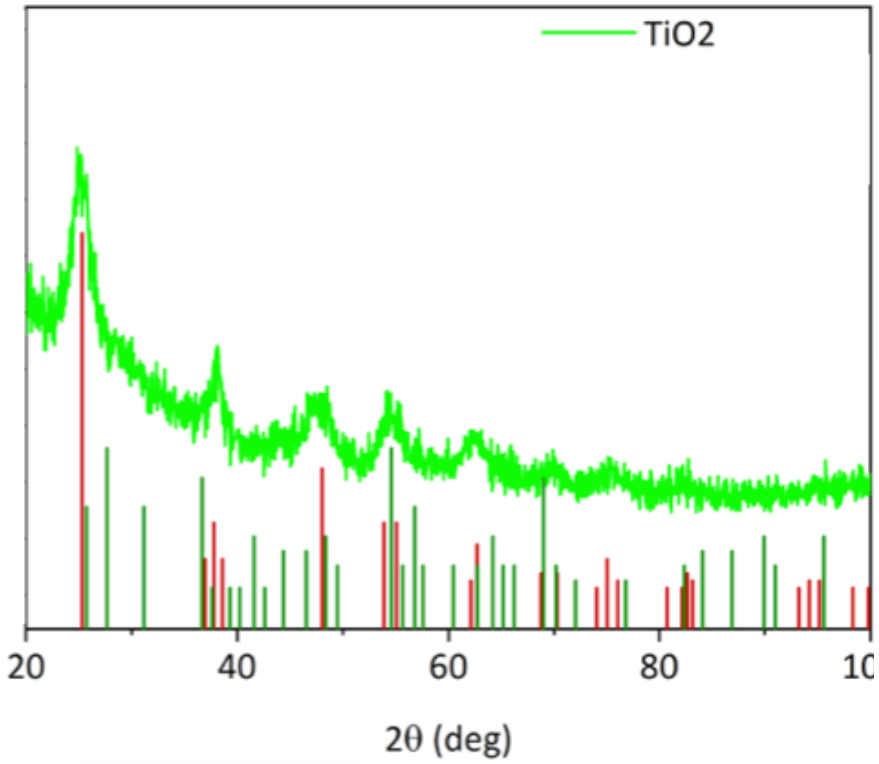
X-ray source

FREE STANDING

SUNBIM: a package for X-ray imaging of nano- and biomaterials using SAXS, WAXS, GISAXS and GIWAXS techniques

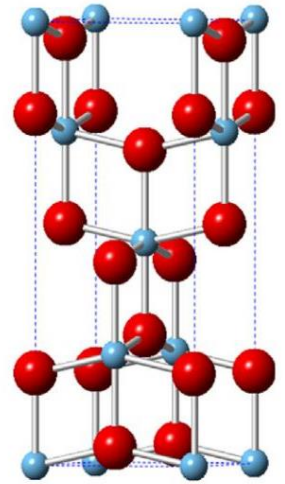
Dritan Siliqi, Liberato De Caro, Massimo Ladisa, Francesco Scattarella, Annamaria Mazzone, Davide Altamura, Teresa Sibillano and Cinzia Giannini



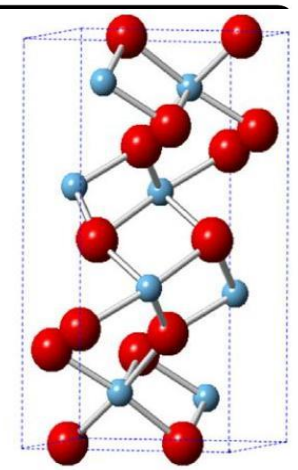


TiO_2

ANATASE



BROOKITE

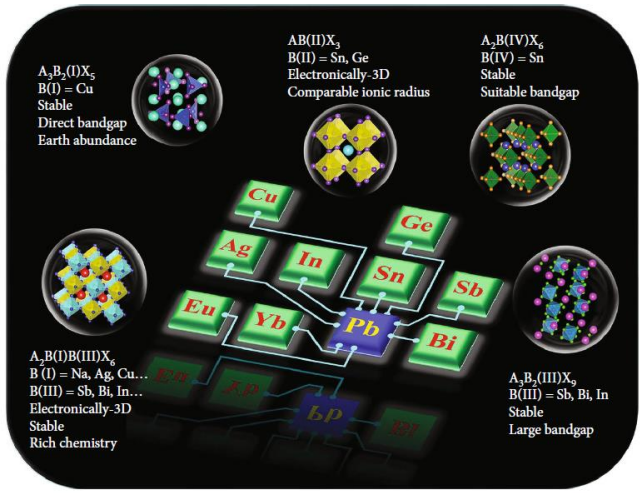


Conclusions and perspectives:

- Crystallography, combined with synchrotron radiation, sheds light on the fascinating world of perovskites and provides the correct key for reading and validating any new ‘perovskite recipe’;
- Crystallography is the key for opening the door to new explorations and helping crystal engineering in the project and synthesis of new perovskites with optimized optoelectronic properties.
- Crystallography can provide effective tools for studying at the nanoscale yet unexplored nanomaterials (*i.e.*, methal chalcohalides) of great interest for Energy.

Perspectives

To contribute to test and validate new ‘recipes’ written by pressing the ‘green keys’ of the Mendeleev ‘keyboard’:



Some examples of lead-free perovskite candidates with their crystal structure(**)

(**) Zhang, F., Ma, Z., Shi, Z., Chen, X., Wu, D., Li, X., Shan, C., *Energy Material Advances*, Volume 2021, Article ID 5198145. DOI: 10.34133/2021/5198145

Acknowledgments

Thank you for your kind attention!

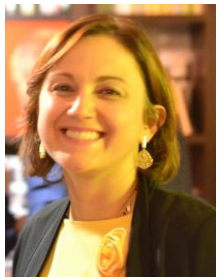
Liberato Manna and his team

Francesco Baldassarre

Liberato De Caro

Cinzia Giannini

Davide Altamura



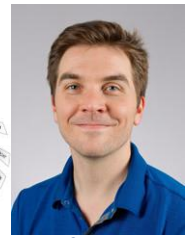
Teresa Sibillano

Luisa De Marco and co-workers

Carlo Giansante and co-workers

Beamline scientists:

Carlotta Giacobbe



Vincent Olieric

Nicola P.M. Casati

Rocco Caliandro

Alberta Terzi

Roberto Lassandro

Dritan Siliqi