

Solid-State NMR study of a multiple-cation lead mixed-halide perovskite with high efficiency

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Mixed Perovskites

- Perovskite is a hybrid organic-inorganic material used as active layer in solar cells.
- CH₃NH₃PbI₃ (MAPbI₃)** is the archetypical hybrid halide perovskite material.
- Mixtures of different cations and anions can be used to tune the optoelectronic properties. Many different materials are being developed for high-performance perovskite solar cells.

Why study **multiple-cation mixed-halide perovskites (Cs,FA,MA)Pb(I,Br)₃**?

They are novel materials with extremely high efficiencies and improved stabilities [1].

To date, there are only a few studies on triple-cation mixtures, and the origin of their excellent properties has not been fully understood yet.

The aim of the present work is to investigate the structure and dynamics of the multiple-cation lead mixed-halide perovskite **Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}** using **MAPbI₃** as a reference compound by means of solid-state nuclear magnetic resonance (SSNMR) spectroscopy.

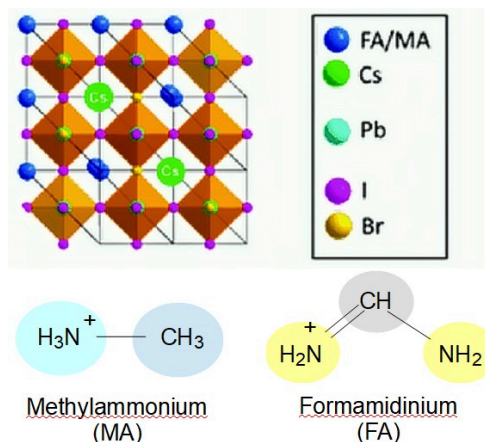


Fig. 1 – Schematic representation of a multiple-cation mixed-halide perovskite structure, and chemical structures of MA⁺ and FA⁺ cations.

Solid-State NMR

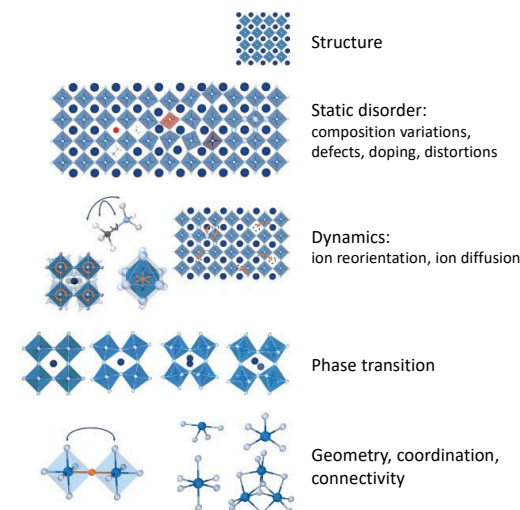


Fig. 2 – Examples of information that SSNMR can provide about perovskites. Modified from ref. [2], Copyright © 2020 American Chemical Society, licensed under a Creative Commons Attribution Non-Commercial No Derivative Works 4.0 Usage Agreement.

Materials and Methods

Samples

- Cs_{0.05}FA_{0.81}MA_{0.14}PbI_{2.55}Br_{0.45}**, here referred to as **MAPImix**.
- MAPbI₃**, here referred to as **MAPI**.

The samples were synthesized in the group of Dr. Daniela Marongiu and Prof. Michele Saba (University of Cagliari).

Solid-state NMR measurements

¹H and ¹³C NMR spectra were recorded on a Bruker Avance Neo spectrometer (magnetic field strength 11.7 T), using a 2.5 mm CP-MAS probe; Magic Angle Spinning (MAS) NMR spectra were recorded at 15 kHz of spinning frequency.

²⁰⁷Pb NMR spectra were recorded on a Varian InfinityPlus spectrometer (magnetic field strength 9.4 T), using a 3.2 mm CP-MAS probe. All experiments were performed at room temperature.

¹H MAS Spectra

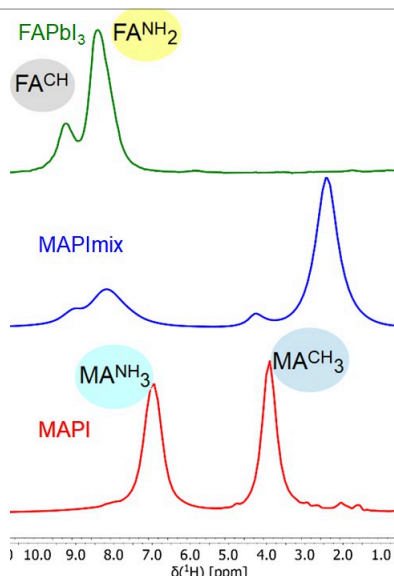
The **MAPImix** spectrum shows four signals, arising from ¹H species of the MA and FA cations. The signals between 1 and 4.5 ppm can be ascribed to CH₃ of MA, and those between 7 and 9 ppm to NH₂ of FA.

The shift in the ¹H resonances with respect to the parent compounds **MAPI** and **FAPbI₃** indicates a change in the lattice structure and thus the formation of a pure mixed-cation phase.

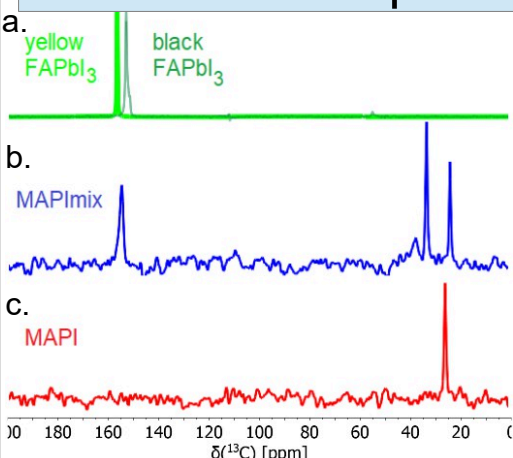
The shift is particularly evident for the signal of MA CH₃, which also seems to be splitted into two peaks with very different intensities.

¹H chemical shifts are considerably less sensitive to the nature of halide ions: the ¹H signal corresponding to CH₃ is at about 3.5 ppm and that of NH₃ is at about 6.5 ppm for all the MAPX₃ compounds [3].

Fig. 2 – ¹H spectra of **MAPImix** and **MAPI** at 11.7 T and 12 kHz MAS compared with ¹H spectrum of **FAPbI₃** at 21 T and 20 kHz MAS [4].



¹³C MAS Spectra



Focusing on the **MAPI** and **MAPImix** spectra, the change in MA resonance upon addition of FA suggests that MA and FA phases are intimately mixed on the microscopic scale, and no pure MAPI phase is present in the **MAPImix** sample.

The absence of the signal of the photo-inactive **yellow phase** of **FAPbI₃** confirms the fact that Cs is able to stabilize the photo-active **black phase**, thus resulting in better-performant perovskite solar cells [6].

Fig. 3 – (a) ¹³C CP MAS spectra of the **yellow phase** and of the **black phase** of **FAPbI₃** [5], here reported for comparison. (b) ¹³C CP MAS spectrum of **MAPImix**. (c) ¹³C direct excitation MAS spectrum of **MAPI**.

²⁰⁷Pb Static Spectra

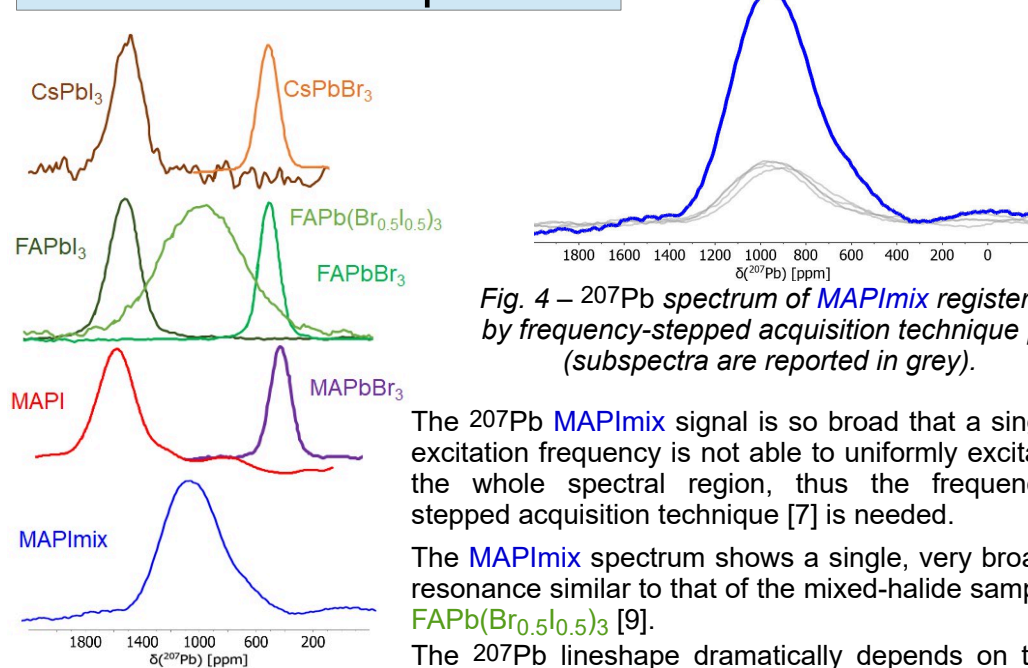


Fig. 5 – ²⁰⁷Pb static spectra of **MAPI** and **MAPImix**, compared with spectra of **MAPbBr₃** and FA-based and Cs-based perovskites from the literature [8][9][10].

Fig. 4 – ²⁰⁷Pb spectrum of **MAPImix** registered by frequency-stepped acquisition technique [7] (subspectra are reported in grey).

The ²⁰⁷Pb **MAPImix** signal is so broad that a single excitation frequency is not able to uniformly excite the whole spectral region, thus the frequency-stepped acquisition technique [7] is needed.

The **MAPImix** spectrum shows a single, very broad, resonance similar to that of the mixed-halide sample **FAPb(Br_{0.5}I_{0.5})₃** [9].

The ²⁰⁷Pb lineshape dramatically depends on the chemical environment, therefore the chemical shift distribution reflects the random distribution of halide atoms, especially in the coordination octahedra surrounding each lead nucleus.

The absence of **MAPbBr₃** and **FAPbBr₃** signals in the **MAPImix** spectrum suggests that Br ion incorporation into the lattice has occurred.

Concluding Remarks

This study reports the characterization of a triple-cation mixed-halide perovskite sample (**MAPImix**) by multinuclear solid-state NMR. In particular, we showed that:

- ¹H, ¹³C and ²⁰⁷Pb spectra are very sensitive to chemical composition changes as proven by the comparison with the MA-based and FA-based parent compounds;
- the splitting of the MA signals in ¹H and ¹³C spectra indicates that MA cations are subject to different chemical environments. This will be further investigated with additional experiments;
- all the experiments indicate that a single, pure mixed-ion phase is present and that no ion segregation occurs in the sample.

Acknowledgements

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