Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office via the User Portal:
https://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** XRD and phase transition study of organohalide Bi doped-perovskites thin films and microwires	**Experiment number**: 25-01-1044
Beamline:	**Date of experiment**: from: 17 Oct 2017 to: 20 Oct 2017	**Date of report**:
Shifts:	**Local contact(s)**: Eduardo Salas colera	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Javier Bartolomé Vilches*. Universidad Complutense de Madrid

Alicia de Andrés*. Instituto de Ciencia de Materiales de Madrid, Consejo Superior de Investigaciones Científicas, C/ Sor Juana Inés de la Cruz 3, 28049 Madrid, Spain.

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Report:

The experiments contributed to the publication of two scientific papers:

1- Javier Bartolomé, Esteban Climent-Pascual, Carlos Redondo-Obispo, Carlos Zaldo, Ángel L. Álvarez, Alicia de Andrés and Carmen Coya. "**Huge Photo-Stability Enhancement in Bismuth Doped Methylammonium Lead Iodide Hybrid Perovskites by Light Induced Transformation**". Chem.Mater. (2019), 31,10,3662-3671. DOI: 10.1021/acs.chemmater.9b00270.

Abstract. The doping strategy of hybrid perovskites is being extensively explored not only for higher efficiency but also to overcome issues in photovoltaic materials such as self-degradation pathways in an ambient atmosphere or under visible irradiation. Here, BiI_3 is introduced in the synthesis of $MAPbI_3$ films (MA: $CH_3{-}NH_3^+$) to stabilize the material. Around 25% of nominal Bi^{3+} is accommodated in the perovskite structure, producing a shrinking of the unit cell and a small increase of the band gap. The presence of empty Bi gap states quenches the 770 nm red interband emission and results in a near-infrared emission at 1100 nm. However, high enough visible irradiation density induces a progressive segregation of Bi^{3+} out of the perovskite lattice and promotes the re-emergence of the red emission. This emission is blueshifted,
and its intensity increases strongly with time until it reaches a saturation value which remains stable in the transformed films for extremely high power densities, around 1000 times higher than for undoped samples. We propose that the underlying processes include the formation of BiI_3 and BiOI, probably at the surface of the crystals, hampering the usual decomposition pathways into PbI_2 and PbOx for undoped $MAPbI_3$. These results provide a new path for obtaining highly stable materials which would allow an additional boost of hybrid perovskite-based optoelectronics.

2- C. Redondo-Obispo, I. Suárez, S.J. Quesada, T.S. Ripolles, J. P. Martínez-Pastor, A. L. Álvarez, A. de Andrés and Carmen Coya. "**Enhanced Nonlinear Optical Coefficients of MAPbI3 Thin Films by Bismuth Doping**". (2020), Journal of Physical Chemistry Letters (2020). DOI: 10.1021/acs.jpclett.0c00319.

Abstract. The poor photo stability under ambient conditions of hybrid halide perovskites has hindered their recently explored promising nonlinear optical properties. Here, we show how Bi^{3+} can partially substitute Pb^{2+} homogenously in the commonly studied $MAPbI_3$ improving both environmental stability and photo-stability under high laser irradiation. Bi content around 2 at. % produces thin films where the nonlinear refractive (n_2) and absorptive coefficients (β), that modify the refractive index (Δn) of the material with light fluency (I), increase up to factors 4 and 3.5 respectively compared to undoped $MAPbI_3$. Higher doping inhibits the nonlinear parameters, however, the samples show higher fluency damage thresholds. Thus, these results show a roadmap on how $MAPbI_3$ can be engineered for practical cost-effective nonlinear applications, by means of Bi doping including optical limiting devices and multiple-harmonic generation into optoelectronics devices.