Doping density and carrier-phonon coupling in tin based perovskites

Giulia Folpini,[1,2] Lorenzo Gatto,[3] Isabella Poli,[4] Antonella Treglia,[2] Daniele Meggiolaro,[5] Federico Grandi,[3] Michele Devetta,[1] Caterina Vozzi,[1] Filippo De Angelis,[5,7] Annamaria Petrozza,[2] Eugenio Cinquanta [1]

[1]*Istituto di Fotonica e Nanotecnologie, CNR, Italy*
[2]*Center for NanoScience and Technology, IIT, Italy*
[3]*Dipartimento di Fisica, Politecnico di Milano, Italy*
[4]*Centre for Sustainable Future Technologies, IIT, Italy*
[5]*CLHYO, CNR - SCITEC, Italy*
[6]*Department of Chemistry, Biology and Biotechnology, University of Perugia, Italy*

Abstract: We use time resolved THz spectroscopy to measure the doping density in tin-based perovskites, where tin oxidation results in a significant background hole population and analyze its effect on carrier phonon coupling and polaron formation.

Tin-based halide perovskites (THPs) have emerged as promising candidates for both photovoltaics and near - IR light emitting applications thanks to their high carrier mobilities low band gap, ideal for pairing with Silicon in tandem solar cells [1]. A key characteristic of THPs is the remarkable stability of acceptor defects such as Sn vacancies and I interstitials, resulting in a large population of self – doping holes that can negatively impact device performance if not adequately managed. As such, it is of critical importance to devise strategies to both quantify and control the dopant hole densities in THPs by compensating the oxidation state of Sn during material fabrication using additives such as SnF_2 [2].

In this context, terahertz (THz) spectroscopy represents a powerful tool to characterize the carrier populations and dynamics in THPs [3]. THz radiation is sensitive to mobile charge carriers [4], as well as their coupling with lattice phonons [5]: this can shed light on charge transport properties in THPs, as low frequency phonons in the THz range have been shown to limit their thermal and electrical conductivity. However, as the doping density affects both transparency to THz radiation and carrier phonon coupling, THz absorption spectroscopies can be used as a sensitive, contactless probe to characterize the self – doping density even in samples where it has been brought down to levels comparable to background carrier densities suitable for device applications (e.g. 10^{15} - 10^{16} cm^{-3}), and that could be challenging to characterize by traditional Hall effect measurements. Furthermore, time resolved THz spectroscopy after optical excitation of the material allows to follow the dynamics of photogenerated carriers with fs temporal resolution enabling the retrieval of radiative and nonradiative carrier recombination rates and identifying the additives effect on defect-assisted carrier recombination.

In this work, we study $FACsSnI_3$ thin films with both high and low doping concentrations with time resolved THz spectroscopy, and develop a robust technique to study doping hole density by fitting the THz conductivity with a Drude – Smith model. By supporting our results with DFT calculations, we also investigate the effect of doping concentration and defect states on optical phonon frequencies and their coupling to charge carriers.

Acknowledgements**:** *The authors would like to acknowledge funding from the ERC grant SOPHY (G.*A. 771528), *the MSCA – ITN Smart –X (GA 860553), the integrated infrastructure initiative I-PHOQS and the PRIN project HAPPY.*

Contacts:
Giulia Folpini (giulia.folpini@cnr.it)

References

[1] S. Martani et al., “Defect engineering to achieve photostable wide bandgap metal halide perovskites”, *ACS Energy Let.*, **8(6)**, 2801-2808 (2023)
[2] F. Yuan et al., “Bright and stable near-infrared lead-free perovskite light-emitting diodes”, *Nat. Phot.,* **18 (2)**, 170-176 (2024)
[3] L.Gatto et al., “Charge-Phonon Coupling in Tin Halide Perovskites”, *ACS Energy letters* **10 (3),** 1382-1388 (2025)
[4] A. M. Ulatowski et al., “Terahertz Conductivity Analysis for Highly Doped Thin-Film Semiconductors“,*J. Infrared Milli. Terahertz Waves*, **41**, 1431-1449, (2020)
[5] E. Cinquanta et al., “Ultrafast THz probe of photoinduced polarons in lead-halide perovskites” *PRL*, **122.16**, 166601, (2019)