Phase Change Perovskite Metasurfaces

Giorgio Adamo,[1] Jingyi Tian,[1] Matteo Degani,[1,2] Harish N. S. Krishnamoorthy,[1] Daniele Cortecchia,[3,4] Maciej Klein,[4] and Cesare Soci[1,4]

[1] *Centre for Disruptive Photonic Technologies & Division of Physics and Applied Physics, Nanyang Technological University, 21 Nanyang Link, Singapore 637371*

[2] *Scuola di Scienze Matematiche, Fisiche e Naturali, Università degli studi di Genova, Via Balbi, 5, 16126 Genova GE, Italy*

[3] *Center for Nano Science and Technology, Italian Institute of Technology, Via Pascoli, 70/3, 20133 Milano, Italy*

[4] *Energy Research Institute @ NTU (ERI@N), Research Techno Plaza, Nanyang Technological University, 50 Nanyang Drive, Singapore 637553*

Author e-mail address: g.adamo@ntu.edu.sg

Abstract: We report the first dielectric perovskite metasurfaces with continuously tunable optical response across the visible spectrum via a small temperature gradient around room temperature, bearing potential applications in active light-emitting devices and spatial-light-modulators.

Thanks to their cost-effectiveness and ease of processing, halide perovskites are attracting increasing interest as solution-processable materials for applications in nanophotonics and integrated optical devices such as light-emitting diodes, tunable electrically pumped lasers, and spatial light modulators. The main approach used to access the wide range of colours required for these applications has relied on chemical tuning by varying the hybrid perovskite composition.

Concurrently, the field of optically resonant nanostructures, where light is confined at the nanoscale through the excitation of highly localized optical modes, has matured to a point where, by nanostructuring, virtually any desired modification of the optical properties and functionality of artificial media can be obtained on-demand.

Recently our group demonstrated nanopatterning of metasurfaces on halide perovskite thin films, showing both color tuning of the film as well as multifold enhancement of the photoluminescence emission through a combination of mechanisms including enhancement of linear/nonlinear absorption, the Purcell effect, and improved light outcoupling efficiency [1,2]

Here we pattern nanostructured metasurfaces on halide perovskite thin films (~200 nm) which undergo a phase transition when subjected to small temperature variations around room temperature. Since this phase transition is accompanied by a significant change in the refractive index, we show that the optical response of designer metasurfaces can be engineered to be markedly distinct from that of unstructured perovskite films, and varies continuously by tuning the temperature.

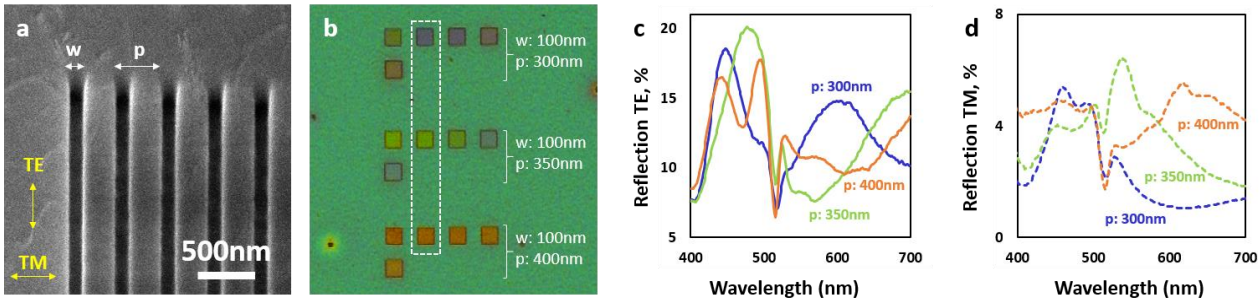

Fig. 1: (a) Nanostructuring of an BA_2PbI_4 perovskite ~200 nm thin film by focused ion beam milling with nanograting metasurface designs; (b) nanograting metasurface arrays with varying period (top to bottom lines) and milling depth (left to right squares), showing distinct structural color variation, that give access to a large color gamut clearly visible under a polarized optical microscope; (c) and (d) reflection spectra of TE (full lines) and TM (dashed lines) polarized light, for nanograting metasurface periods of 300 nm (blue), 350 nm (green) and 400 nm (orange) and the same milling depth [line colors of the spectra match those of the arrays boxed in (b)].

We selected a butylammonium lead iodide perovskite of the Ruddlesden-Popper series (BA_2PbI_4), which was found to have a strong change in absorption and photoluminescence spectra upon phase transition near room temperature between two orthorhombic phases α_{n1} and β_{n1}, respectively at 240.5 K ($\alpha_{n1} \rightarrow \beta_{n1}$) upon cooling and 270.5 ($\beta_{n1} \rightarrow \alpha_{n1}$) upon heating [3]. Perovskite thin films of thickness ~200 nm were deposited on quartz substrates by spin-coating. The optical constants of these films were estimated experimentally from ellipsometry and reflection measurements in the temperature range from 80 to 373 K and used to design nanograting metasurfaces (Fig. 1a). Small changes in the geometrical features of these nanogratings, such as period and milling depth, allow achieving a

very rich spectral response from the film that manifests itself in a very broad range of colors from violet-blue to orange-red (Fig. 1b).

We fabricated nanograting metasurfaces arrays of 25 μm × 25 μm area by focused ion beam (FIB) milling, with a fixed groove width (w) of ~100 nm, periods (p) ranging from 300 to 400 nm, and gradually increasing milling depth. The metasurfaces were measured under normal incidence across the entire visible spectrum, with light polarised both parallel (TE) and orthogonal (TM) to the grating length. We could clearly observe resonances introduced by the subwavelength structuring of the films due to the interaction of the interference in the thin film with the grating modes, for both TE and TM polarization (Fig 1c and 1d).

Full wave electromagnetic FDTD simulations confirm that optical response of the metasurfaces can be controlled by small variations of the temperature; for example, a TM polarized wave, incident on a BA_2PbI_4 nanograting carved on a 200 nm thin film with w=100 nm and p=300 nm induces an optical mode, confined within the perovskite ridges, corresponding to a resonant peak in reflection, which is significantly red-shifted when the temperature of the perovskite film is reduced from 293 to 250K (Fig 2a).

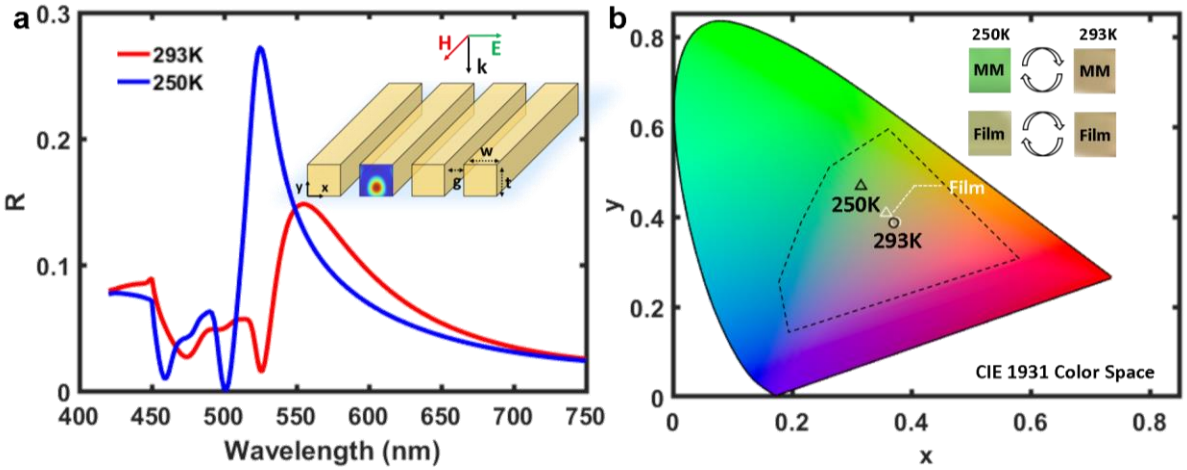

Fig. 2: (a) Reflection spectra of BA_2PbI_4 perovskite nanograting metasurface with w = 100nm and period p=300nm (gap g=200nm) at temperatures 293K (red) and 250K (blue) showing a clear temperature dependent spectral switching [inset: grating structure showing TM incident polarization and the optical mode confined inside the perovskite ridge (b) Perovoskite nanograting metasurfaces structural colors under TM illumination (black dashed line), when varying the parameters w= [150-350]nm, g=[50-200]nm, milling depth [0-200]nm and temperatures T=293K and T=250K; The change in color with temperature of both the flat film and the metasurface of Fig 1a is reported both on the CIE diagram (white and black triangles respectively) and in the inset.

The metasurface paradigm allows to dramatically expand the accessible color gamut: the simplest nanograting design already gives a multifold increase in color availability (Fig 2b black dashed line) with respect to the gamut obtainable with the flat film with the simple variation in temperature (Fig 2b white triangles). Furthermore, metasurface designs can be tailored with specific applications in mind to obtained the desired response from the perovskite films (e.g. narrow-line emission for lasing, holography, etc.)

In conclusion, we have identified a new class of hybrid perovskite materials for reconfigurable/actively tunable dielectric metamaterials and reported, for the first time, an experimental demonstration of its highly tunable optical response by both structural and phase variations around room temperature. We show that nanostructuring of perovskite films with metasurface designs, in combination with the temperature-induces structural phase transitions of the intrinsic perovskite material, provide a simple and versatile mechanism to engineer and actively control their optical response. With this novel approach, we are able to tune the colour of the perovskite metasurface across a very large gamut, which adds to the relatively limited library of phase change materials such as chalcogenides (e.g. GeSbTe AgInSbTe, Sb2S3 etc) and oxides (VO_2, MgO, etc.) used for active metamaterials in the visible and infrared part of the spectrum.

References

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