Introduction
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Feature issue introduction: halide perovskites for optoelectronics

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Abstract: This joint *Optics Express* and *Optical Materials Express* feature issue presents a collection of nine papers on the topic of halide perovskites for optoelectronics. Perovskite materials have attracted significant attention over the past four years, initially for their outstanding performance in thin film solar cells, but more recently for applications in light-emitting devices (LEDs and lasers), photodetectors and nonlinear optics. At the same time, there is still much more to learn about the fundamental properties of these materials, and how these depend on composition, processing, and exposure to the environment. This feature issue provides a snapshot of some of the latest research in this rapidly-evolving multidisciplinary field.

OCIS codes: (250.0250) Optoelectronics; (160.6000) Semiconductor materials; (250.5230) Photoluminescence; (140.3460) Lasers.

References and links

1. D. B. Mitzi, C. A. Field, W. T. A. Harrison, and A. M. Guloy, "Conducting tin halides with a layered organic-based perovskite structure," Nature **369**(6480), 467–469 (1994).
2. D. B. Mitzi, "Synthesis, structure, and properties of organic–inorganic perovskites and related materials," Prog. Inorg. Chem. **48**, 1–121 (1999).
3. H. S. Kim, C. R. Lee, J. H. Im, K. B. Lee, T. Moehl, A. Marchioro, S. J. Moon, R. Humphry-Baker, J. H. Yum, J. E. Moser, M. Grätzel, and N. G. Park, "Lead iodide perovskite sensitized all-solid-state submicron thin film mesoscopic solar cell with efficiency exceeding 9%," Sci. Rep. **2**(1), 591 (2012).
4. W. S. Yang, B. W. Park, E. H. Jung, N. J. Jeon, Y. C. Kim, D. U. Lee, S. S. Shin, J. Seo, E. K. Kim, J. H. Noh, and S. I. Seok, "Iodide management in formamidinium-lead-halide-based perovskite layers for efficient solar cells," Science **356**(6345), 1376–1379 (2017).
5. J.-P. Correa-Baena, A. Abate, M. Saliba, W. Tress, T. J. Jespersson, M. Grätzel, and A. Hagefeldt, "The rapid evolution of highly efficient perovskite solar cells," Energy Environ. Sci. **10**(3), 710–727 (2017).
6. P. Brenner, T. Glöckler, D. Rueda-Delgado, T. Abzieher, M. Jakoby, B. S. Richards, U. W. Paetzold, I. A. Howard, and U. Lemmer, "Triple cation mixed-halide perovskites for tunable lasers," Opt. Mater. Express **7**(11), 4082–4094 (2017).
7. J. Guo, Z.-J. Shi, Y.-D. Xia, Q. Wei, Y.-H. Chen, G. Xing, and W. Huang, "Super air stable quasi-2D organic-inorganic hybrid perovskites for visible light-emitting diodes," Opt. Express **26**(2), A66–A74 (2018).
8. F. Guo, B. Zhang, J. Wang, H. Bai, R. Guo, Y. Huang, and P. Ren, "Facile solvothermal method to synthesize hybrid perovskite $CH_3NH_3PbX_3$ (X = I, Br, Cl) crystals," Opt. Mater. Express **7**(11), 4156–4162 (2017).
9. F. Gabelloni, F. Biccari, G. Andreotti, D. Balestri, S. Checcucci, A. Milanesi, N. Calisi, S. Caporali, and A. Vinattieri, "Recombination dynamics in $CsPbBr_3$ nanocrystals: role of surface states," Opt. Mater. Express **7**(12), 4367–4373 (2017).
10. J. Yi, L. Miao, J. Li, W. Hu, C. Zhao, and S. Wen, "Third-order nonlinear optical response of $CH_3NH_3PbI_3$ perovskite in the mid-infrared regime," Opt. Mater. Express **7**(11), 3894–3901 (2017).
11. H. Wang, S.-C. Liu, B. Balachandran, J. Moon, R. Haroldson, Z. Li, A. Ishteev, Q. Gu, W. Zhou, A. Zakhidov, and W. Hu, "Nanoimprinted perovskite metasurface for enhanced photoluminescence," Opt. Express **25**(24), A1162–A1171 (2017).
12. J. Gong, Y. Wang, S. Liu, P. Zeng, X. Yang, R. Liang, Q. Ou, X. Wu, and S. Zhang, "All-inorganic perovskite-based distributed feedback resonator," Opt. Express **25**(24), A1154–A1161 (2017).

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13. F. Mathies, P. Brenner, G. Hernandez-Sosa, I. A. Howard, U. W. Paetzold, and U. Lemmer, "Inkjet-printed perovskite distributed feedback lasers," Opt. Express **26**(2), A144–A152 (2018).
14. A. Safdar, Y. Wang, and T. F. Krauss, "Random lasing in uniform perovskite thin films," Opt. Express **26**(2), A75–A84 (2018).

1. Introduction

Perovskite semiconductors have been studied for more than two decades [1,2], but it has only been in the last five years that they have become a worldwide research phenomenon. This has been driven largely by the astonishing progress of perovskite solar cells, which have increased in efficiency from <10% to >22% in less than 5 years [3-5]. The same properties that make perovskites so attractive for photovoltaics – high radiative efficiency, long carrier diffusion lengths, strong optical absorption, tolerance to defects, bandgap tunability, and simplicity of processing – also make them interesting candidates for other optoelectronic applications. Thus, the global effort to improve perovskite solar cell performance has spawned many new research activities to exploit these fascinating materials in LEDs, lasers, photodetectors, and other active devices.

Perovskites are a large group of materials with the crystal structure ABX_3 that can display electrical properties ranging from insulating to superconducting depending on the components A, B and X. The class of perovskites that have attracted the most attention for photovoltaic and optoelectronic applications are hybrid organic-inorganic halide materials, in which A is an organic cation (eg: methylammonium (MA) $CH_3NH_3^+$, formamidinium (FA) $CH(NH_2)_2^+$) B is a divalent metallic cation (eg: Pb^{2+}, Sn^{2+}), and X is a halide anion (eg: Cl^-, Br^-, I^-). Inorganic A-site substitutes such as Rb and Cs have also been widely studied in efforts to improve thermal and chemical stability [5].

Early perovskite solar cell research focused on the relatively simple $MAPbI_3$, but attention has more recently turned to carefully-optimised mixtures of cations (organic and inorganic) and halides. Such *compositional-engineering* offers exciting opportunities to tailor the chemical, structural, physical and optical properties of perovskites for specific applications. Examples in this feature issue include the work of Brenner *et al.* on triple-cation, mixed-halide perovskites for tunable lasers [6], and that of Guo *et al.* on quasi-2D perovskites for light-emitting diodes [7].

The scope of this feature issue was limited to halide perovskites as this already very large class of materials has received most of the attention for optoelectronic applications. Submissions were invited on perovskite material properties, processing, simulation, characterisation and novel devices. Nine papers were accepted for publication: four in Optical Materials Express and five in Optics Express. These included one paper on material synthesis [8], two papers related to photophysical properties and recombination dynamics [9,10]; two papers on the topic of light emission and LEDs [7,11]; and four papers on lasers [6,12–14]. While these papers cover only a very small selection of current perovskite research, they provide a flavor of the diverse range of topics and the exciting potential for perovskite optoelectronics.

2. Summary of feature issue papers

The wide material and processing parameter space occupied by halide perovskites presents numerous opportunities for fundamental characterization studies. This issue includes three examples of such studies.

In Ref [8]. Guo *et al.*, describe a solvothermal synthesis technique for growing $CH_3NH_3PbX_3$ (X = I, Br, Cl) crystals using various acids (HI, HBr and HCl) as halogen sources, and study the growth behavior as a function of reaction conditions and halide composition. The atomic structure, microstructure and morphology of the crystals are investigated using TEM, XRD and SEM, while photoluminescence spectroscopy is used to probe the material quality.

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Material quality and recombination dynamics are the focus of Ref [9], where Gabelloni *et al.,* study nanocrystalline films of the inorganic perovskite $CsPbBr_3$ using time-resolved photoluminescence. An increase in photoluminescence lifetime is observed with increasing temperature, which is attributed to carrier capture and release from traps on the surface of the nanocrystals. The authors suggest that the results provide a means to probe nanocrystal surfaces, which may lead to improved surface treatments to control recombination.

The third paper on the theme of fundamental properties is a study by Yi *et al.* of the third-order nonlinear response of $CH_3NH_3PbI_3$ [10]. Using a standard single-beam Z-scan technique, the authors measured the nonlinear response of solution-processed thin films at wavelengths of 1560nm and 1930nm. Samples were found to exhibit low-threshold broadband saturable absorption and a large Kerr nonlinearity. The authors conclude that perovskite materials with these properties may have applications for integrated mid-IR photonic devices.

Applications for, and techniques to enhance, light emission from perovskites were addressed in the remaining six papers in this feature issue.

In Ref [11], Wang *et al.* report the fabrication of perovskite metasurfaces by thermal nanoimprinting, and demonstrate an eight-fold enhancement of photoluminescence intensity from patterned films compared to planar films. The perovskite films that were subjected to imprinting exhibited improved morphology and crystallinity compared to as-deposited films. Proposed applications for the nanoimprinted metasurfaces include perovskite LEDs, photodetectors, solar cells and lasers.

Guo *et al.* [8] present a study of perovskite LEDs based on layered organic-inorganic hybrid perovskites. The formation of quasi-2D layered materials was induced by the addition of a fluorine-containing organic molecule 3,4,5-Trifluoroaniline (TFA) hydrobromide to a $CH_3NH_3PbBr_3$ precursor solution. High quality, air-stable films were fabricated and optimised by varying the precursor concentration to tune the layer structure. LEDs fabricated with these films exhibited luminance as high as 1200 cd/m^2. The authors suggest that the use of hydrophobic, fluorine-containing organics can improve performance and stability of perovskite LEDs.

In the first of the laser-related papers, Brenner *et al.* study emission properties of triple-cation, mixed-halide perovskites containing the cations Cs, MA and FA, and varying ratios of Cl, Br and I [6] under nanosecond-excitation at room temperature. Amplified spontaneous emission (ASE) threshold and gain stability were investigated as a function of stoichiometry for films with emission wavelength from the visible to the near-IR, adjusted by varying the halide composition. ASE was observed for wavelengths 545nm to 555 nm and 680nm to 810 nm, with the wavelength/composition gap attributed to incomplete crystallization. The addition of Cs, and a moderate Pb deficiency in the precursor were found to be essential for achieving low ASE thresholds and good stability under high pump powers.

Distributed feedback lasers consisting of perovskite films deposited onto textured substrates were the topic of two papers by Gong *et al.* [12] and Mathies *et al.* [13]. In Ref [12], the inorganic perovskite $CsPbBrI_2$ was chosen for its better thermal and chemical stability compared to organic-inorganic hybrid materials. Gain and loss coefficients of planar films were measured to be 161.1 cm^{-1} and 30.9 cm^{-1} respectively. For films deposited on the patterned substrates, single-mode lasing at 654nm was observed using picosecond pulsed excitation, with a threshold of 33μJ/cm^2. The second DFB paper [13] demonstrated the use of inkjet printing to deposit $MAPbI_3$ perovskite films onto to both rigid and flexible substrates patterned with nanoimprinted DFB gratings. High-quality, uniform perovskite films were obtained by optimizing the solvent composition and the printing parameters, with the printing process allowing deposition of arbitrary shapes. 784nm laser emission was demonstrated using nanosecond pump pulses, with thresholds of 235 kW/cm^2 and 270 kW/cm^2 for rigid and flexible substrates respectively. Proposed applications include integrated, custom-shaped laser sources for lab-on-a-chip devices.

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The fourth laser paper demonstrates that nanostructured substrates or carefully-engineered resonant cavities are not required to achieve lasing in perovskite films. Safdar *et al.* [14] study random lasing in rough $MAPbI_3$ films, where the required optical feedback is provided by multiple scattering from within the films themselves. Film processing conditions, which affect crystallization and morphology, were found to play a key role in determining whether or not lasing action occurred. The best films displayed room-temperature lasing with thresholds as low as 10 μJ/cm^2, which compares favorably to many engineered-feedback structures reported by other groups. Unusually for random lasers, some of the films exhibited single- or dual-mode lasing. The authors describe the random lasers as “the ultimate in simplicity”.

To conclude, the editors would like to thank all of the authors who submitted manuscripts to this feature issue; the peer reviewers who assessed submissions; and the *Optics Express* and *Optical Materials Express* journal staff for supporting the submission, review and publication process. It is hoped that this feature issue will provide inspiration for new research activities and novel applications in the rapidly evolving field of perovskite optoelectronics.