UV-NIR Eco-sustainable light sources based on halide perovskites for biomedical applications

The innovations in the field of nanoscience, materials, photonics, and electronics have stimulated the interest in miniaturizing and integrating light sources. Halide perovskites (PVK), hybrid organic-inorganic (H-PVK) and fully inorganic (I-PVK) are an emerging class of semiconductors of extreme relevance for optoelectronics[1] [2],energy harvesting [3], sensors [4], [5] and more recently medical diagnostics/therapy. Moreover, PVKs have characteristics that are ideal for light emission devices [6]. Their compositional and design features are tunable to meet important requirements:

1) highly-efficient radiative recombination, being direct band-gap materials. Therefore, they are excellent for light emitters (LEDs and Lasers)
2) tunability of light emission that varies with the material composition for covering the spectral range from ultraviolet (UV) to near-infrared (NIR) [7]–[9]
3) high carrier mobility
4) defect tolerance
5) low-cost and easiness of synthesis and deposition [10], unlike other semiconductors as Si, GaAs, GaN, etc. This is a crucial aspect, since the expensive processes typically required for the fabrication of solid-state light emitters counter to the demand of the market for lower-cost devices
6) design of the material structure, bulk, nanostructures, polycrystalline thin films, depending on the specific protocol of growth/synthesis. The final behavior of a device is related to the characteristics of the material structure.

The performances and stability of H-PVK are limited by several issues such as thermal and chemical instabilities, especially in the presence of moisture and after UV light exposure, also a sensibility to O_2, thus altering in the end the overall performance [11], [12]. The key to solving the H-PVK degradation is removing the organic part, responsible for all instabilities. The replacement of the organic part with an inorganic ions as in I-PVK offers [7] significant improved stability, while maintaining the same performances. **This PhD project proposal aims to develop eco sustainable light sources, with a focus on LEDS, VCSELs and lasers using fully I-PVK in the range UV-NIR for biomedical applications.**

I-PVK are semiconductor materials defined by the formula ABX_3, with A inorganic cation (Cs^+, Rb^+, …), B metal cation (Pb^{2+}, Sn^{2+}, …), and X halogen anion (Cl^-, Br^-, I^-). This project will focus on all-inorganic cesium lead halide perovskites $CsPbX_3$, X = Cl, Br, I, and mixed Cl/Br and Br/I systems. $CsPbX_3$ can be design so that the bandgap can cover the range 400-780 nm [7], [9]. **The project proposes to**:

- Synthesize and characterize $CsPbX_3$ thin films (10-500 nm) on different substrates (semiconductors, metals and oxides). A requirement will be the high homogeneity of the film with a roughness of few nm for few tens of nm thick film on cm^2 areas. The thin films will be deposited using radio frequency (RF) Magnetron Sputtering (RF-MS), as the group in the Department of Physics and Astronomy (University of Florence) already demonstrated [8], [13], [14]. This technique also allows doping and multi-layer deposition with nanometric controlled characteristics

- Perform high resolution (in space and time) optical spectroscopy studies to extract quantitative information concerning the carrier recombination dynamics [6]
- Characterize the defects through thermally-activated current measurements (TSC) as a function of temperature to determine activation energies, cross sections and density of non-radiative defects in the bandgap of the material [6]
- Tailor the material electronic properties and morphology for manufacturing state-of-the-art eco sustainable light sources in the range of UV-VIS for biomedical application.
- Integrate the thin films between Bragg/metallic mirrors so to realize efficient lasing at room temperature (RT)
- Provide electrical injection by the realization of a structure composed by ETL (electron transport layer)/active medium/ HTL (hole transport layer).

Research objectives:

The project will focus on $CsPbX_3$ and aims at obtaining thin films on different substrates with high uniformity in composition, thickness and optical properties. The group in the Department of Physics and Astronomy (University of Florence) recently demonstrated [15] that RF-MS is a powerful technique for the realization of highly uniform (on several cm^2) nanometric thin films with excellent quality in terms of structural and optical properties. Even more, this technique offers the possibility of growing consecutive layers of different materials with a limited contamination from unwanted elements and, conversely, an easiness of doping, all requirements for an electrical injected optical device (LED/laser). In addition, the growth can be performed at RT avoiding, or at least limiting, the material stress due to the large mismatch between the thermal expansion coefficient (CTE) of the perovskites (specifically CTE = $3.8x10^{-5}$ /K for $CsPbBr_3$ at RT [16]) and those of the substrate (typically glasses with CTE < $6x10^{-6}$/K) that is largely responsible for the layers cracking and degradation [17]–[19]. After obtaining the thin films, the next step will be defects characterization through TSC measurements by photoluminescence (PL) spectroscopy in a wide temperature range. This will lead to tailoring the material electronic properties and morphology for integrating the thin films between Bragg/metallic mirrors to realize efficient lasing at room temperature. Another objective will be providing electric injection by the realization of a structure composed by ETL (electron transport layer)/active medium/ HTL (hole transport layer) with the purpose of developing a prototype for the industrial application.

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