K32: pe-LED prototypes base on stable Er^{3+}/Ho^{3+}/Sb^{3+} doped halide double perovskites $Cs_2NaInCl_6$

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New kind of alternative lead-free perovskites with low toxicity and good stability are required for optoelectronic applications. For this purpose $2Pb^{2+}$ ions in $CsPbX_3$ can be substituted by Na^+ and In^{3+} cations to obtain $Cs_2M^+M^{3+}X_6$ ($X = Cl^-$, Br^-) halide double perovskites (HDPs) with good stability [1]. However, this type of compounds have low PL quantum yield and impurity doping with Sb^{3+} can help to overcome this disadvantage. Er^{3+}, Ho^{3+} doping helps to develop the efficient multimodal emission of HDPs using down- and upconversion to cover the full visible–near-infrared (NIR) gamut.

The luminescence properties of stable halide double perovskites $Cs_2NaInCl_6$, doped with Sb^{3+}, Er^{3+}, Ho^{3+} in the region 250-1600 nm obtained by precipitation technique were investigated for the first time and reveal significant potential for advanced application. We employed X-ray diffraction, and Raman spectroscopy to check the crystal structures, and vibrational characteristics of the samples. The crystal structures of (1) $Cs_2NaIn_{0.9}Cl_6\cdot\mathbf{0.1ErCl_3}$, Sp.Gr. Fm-3m, a = 10.5371(2) nm; (2) $Cs_2NaIn_{0.7}Cl_6\cdot\mathbf{0.3ErCl_3}$ Sp.Gr. Fm-3m, a = 10.5414(2) nm; (3) $Cs_2NaIn_{0.8}Cl_6\cdot\mathbf{0.1ErCl_3\cdot0.1SbCl_3}$, Sp.Gr. I4/mmm, a= 7.4647(3), c=10.5253(6) nm; (4) $Cs_2NaIn_{0.6}Cl_6\cdot\mathbf{0.3ErCl_3\cdot0.1SbCl_3}$, Sp.Gr. I4/mmm, a= 7.4595(3), c= 10.5321(7) nm; (5) $Cs_2NaIn_{0.9}Cl_6\cdot\mathbf{0.1HoCl_3}$, Sp.Gr. Fm-3m; a = 10.5369(2) nm; (6) $Cs_2NaIn_{0.7}Cl_6\cdot\mathbf{0.3HoCl_3}$, Sp.Gr. Fm-3m, a = 10.5379(2) nm; (7) $Cs_2NaIn_{0.8}Cl_6\cdot\mathbf{0.1HoCl_3\cdot0.1SbCl_3}$, Sp.Gr. I4/mmm, a= 7.4362(4), c= 10.5310(2) nm; (8) $Cs_2NaIn_{0.6}Cl_6\cdot\mathbf{0.3HoCl_3\cdot0.1SbCl_3}$, Sp.Gr. I4/mmm, a= 7.4572(4), c= 10.5330(9) nm were calculated. From emission spectra measurement it was established that the excited Sb^{3+} ions emit blue light at 450 nm due to electronic absorption at sub-band gap levels, facilitating energy transfer to Er^{3+} and Ho^{3+} ions. Notably, the Er^{3+} emit radiation at 1540 nm, a wavelength particularly advantageous for optical communication applications. Additionally, emissions at 525 nm (green), 552 nm (green), 665 (red) nm and 805 nm were observed, corresponding to $^2H_{11/2} \rightarrow {}^4I_{15/2}$,$^4S_{3/2} \rightarrow {}^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^4I_{15/2}$, $^4I_{9/2} \rightarrow {}^4I_{15/2}$ transitions in the f-shell of the Er^{3+} ions. While the emissions at 490 nm, 545 nm, 650 (red) nm correspond to *f-f* transitions $^5F_3 \rightarrow {}^5I_8$, $^4F_4 \rightarrow {}^5I_8$, $^5F_5 \rightarrow {}^5I_8$ in the Ho^{3+} ions.

It is possible to describe the emission mechanism as following: the A-, B-, and C-band absorptions by Sb^{3+} dopants lead to intense blue emissions at 450 nm. The excited Sb^{3+} states transfer their energy to the RE^{3+} with following emission at different wavelengths, which correspond to green and red emission due to f-f electronic transitions in the RE ions.

Leveraging the synthesized materials, we successfully have developed a LED prototype that utilizes a UV chip (320 nm) combined with the $Cs_2NaIn_{0.3}Er_{0.3}Ho_{0.3}Sb_{0.1}Cl_6$ powder as a stable and effective luminophore for possible application in pe-LED production.

Acknowledgement:

This research is part of the project No. 2022/47/P/ST5/01816 within the POLONEZ BIS programme co-funded by the National Science Centre and the European Union's Horizon 2020 research and innovation programme under the Marie Skłodowska-Curie grant agreement No. 945339.

Literatura:

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