Photoluminescent Properties in 2D $(C_6H_5CH_2NH_3)_2(Pb,Mn)Br_4$ Layered Metal Halide

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Starting from ABX_3 (A = $CH_3NH_3^+$, Cs^+; B = bivalent metal cation, X = Cl^-, Br^-, I^-) perovskite, new derivates can be obtained with the partial or full substitution of the A and B cations with different metal ions [1]. To date, since the dimension of the ion in the A site enlarges the formation of polymorphs of a lower dimensionality (2D or 0D), one strategy to tune and confer new optoelectronic properties is the insertion of an organic cation instead of an inorganic one [2].

Here, we present our recent results on the preparation of emissive 2D (Pb,Mn)-based hybrid metal halide as single crystals. Starting from the synthesis of Bz_2PbBr_4 (Bz^+ = $(C_6H_5CH_2NH_3)^+$), the Pb^{2+} was progressively replaced by Mn^{2+}; the percentage of Pb substitution strongly depends on the metal ratio in the starting materials, as demonstrated by XRF analyses. The optimized synthesis consisted of the dissolution of BzBr in acid media (HBr), followed by the addition of $PbBr_2/MnCO_3$. The mixture was stirred at 90°C for 2h, then cooled to room temperature to induce the crystallization. The crystals morphologies are composition-dependent: Bz_2PbBr_4 crystallizes as white millimeter-sized layers, whereas an increase in the Mn amount, causes the precipitation of a secondary phase with a needle shape. The emission varies from the light blue of Bz_2PbBr_4 to the typical orange one of the Mn. The PL spectrum for the samples with intermediate compositions exhibits a weak emission for the excitonic peak at 410 nm and a strong Mn emission, centered at 610 nm, ascribable to the spin-forbidden Mn^{2+} d–d transition ($^4T_1 \rightarrow {}^6A_1$). The ABS and PLE spectra demonstrate that even at low Pb concentrations, an energy-transfer process from the Pb^{2+} to Mn^{2+} emitter is observable. The emission intensity reaches the maximum for the experimental Mn composition of 8.0% (PLQY ≈ 47.9%).

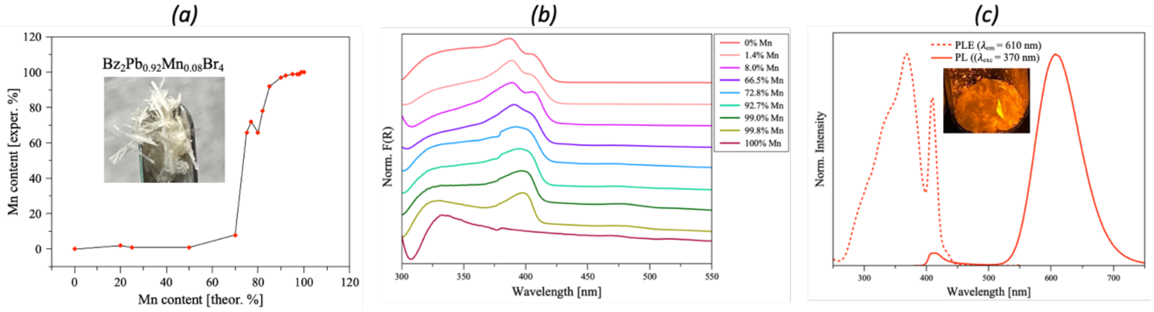

Figure 1: (a) XRF results, with the image of $Bz_2Pb_{0.92}Mn_{0.08}Br_4$ crystals, and (b) ABS spectra of $Bz_2(Pb,Mn)Br_4$ samples. (c) PLE and PL spectra, with the image under UV lamp (λ = 365 nm), of crystals' $Bz_2Pb_{0.92}Mn_{0.08}Br_4$.

[1] Meinardi, F. et al. Doped Halide Perovskite Nanocrystals for Reabsorption-Free Luminescent Solar Concentrators. ACS Energy Lett. 2017;2:2368.
[2] Akkerman, Q.A. What Defines a Halide Perovskite?. ACS Energy Lett. 2020;5:604.