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Photoluminescence Emission Studies on a Lanthanum-Doped Lead Free Double Halide Perovskite, La:Cs_2SnCl_6

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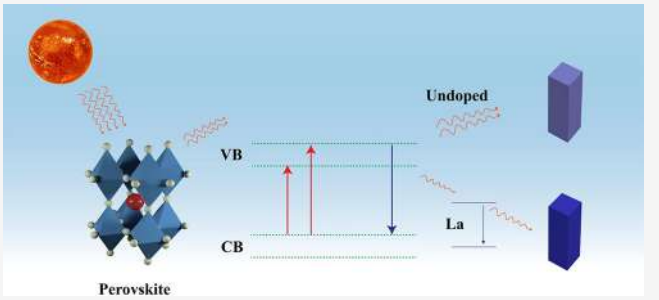
ABSTRACT: Recent advances in bandgap engineering have increased the possibility of vacancy ordered double halide perovskites (VO-DHPs), Cs_2SnX_6 where X = Cl, Br, I with designable optoelectronic features. Doping with La^{3+} ions modulates the band gap from 3.8 to 2.7 eV, allowing a steady room temperature dual emission (PL) centered at 440 and 705 nm in Cs_2SnCl_6. Pristine Cs_2SnCl_6 and La:Cs_2SnCl_6 both have a crystalline cubic structure with a space symmetry of *Fm*3*m*. The cubic phase correlates well with the Rietveld refinement. SEM analysis confirms anisotropic development with huge micrometer-sized (>10 μm) truncated octahedral structures. DFT investigations show that the insertion of La^{3+} ions into the crystal lattice leads to the band splitting. The present study elaborates the experimental understanding of the dual PL emission properties of La:Cs_2SnCl_6 leaving a scope for detailed theoretical study on the origin of the complex electronic transitions involving f-orbital electrons.



INTRODUCTION

Lead halide perovskites (LHP) are considered to be the most prominent and promising materials for optoelectronics and more specifically for photovoltaic applications.[1−5] Methylammonium lead halide perovskites ($CH_3NH_3PbX_3$) and their all-inorganic counterparts, cesium lead halide perovskites ($CsPbX_3$), where X = Cl, Br, and I, have been intensively researched for their outstanding photophysical characteristics.[6−8] However, they face serious environmental concerns of Pb toxicity and inherent instability before they would be able to find commercial success.[9,10] To overcome this, several attempts have been made to replace two Pb^{2+} ions by one monovalent metal ion (M^+: Li^+, Ag^+, Na^+, K^+, etc.) and one trivalent metal ion (M^{3+}: In^{3+}, Sb^{3+}, Bi^{3+}) that results in formation of the structure $Cs_2M^+M^{3+}X_6$.[9,11−14] The strategy for the replacement of Pb^{2+} with Sn^{2+} ions is not successful due to the intrinsic elemental tendency for oxidation to the more stable Sn^{4+}.[15,16] However, the direct replacement of Pb^{2+} with Sn^{4+} forms an interesting class of materials referred as vacancy ordered double halide perovskites (VO-DHP) and is represented by Cs_2SnX_6.[17,18] The unique crystal structure of Cs_2SnCl_6 has vacancies at the B sites of conventional ABX_3 perovskites, resulting in corner-sharing [BX_6] octahedral crystal structures that warrant extensive theoretical and experimental investigations for their structural and thermal stability.[19] Unlike the homologous series of Cs_2SnI_6, Cs_2SnCl_6 has generated little interest initially due to its large band gap exceeding 3.8 eV.[20−23] However, the recent advancement in band gap engineering that leads to exciting photophysical properties has widen the possibilities of these materials in optoelectronics.[24] For instance, blue, yellow, and red emission has been reported for nanocrystals of Cs_2SnCl_6 upon doping with Bi^{3+}, Te^{4+}, and Sb^{3+} ions, respectively.[25] Interestingly, the nanocrystals exhibit white light emission when Cs_2SnCl_6 is codoped with Bi^{3+} and Te^{4+}.[26] Sb^{3+} doping induced orange emission from Cs_2SnCl_6 has also been reported which underlines the mechanism of the emission process.[27] At cryogenic temperatures, Sb^{3+} doped in Cs_2SnCl_6 has two emission peaks, while Bi^{3+} doping exhibits just one.[28] In this study, we investigate the photophysical effects of doping in Cs_2SnCl_6 with La^{3+} and compare the results with previous studies on doping with Bi^{3+} and Sb^{3+}. Our findings demonstrate that doping with La^{3+} leads to a significant increase in the luminescence intensity, compared to the doping with Bi^{3+} and Sb^{3+}. Additionally we observed a to Moss−Burstein effect in the emission peak upon La^{3+} doping.[39] These results provide new insights into the photophysical properties of Cs_2SnCl_6 doped with various lanthanoid ions, highlighting the potential of La^{3+} as a dopant for improving the luminescence properties of Cs_2SnCl_6. Recently, in an interesting study, it has been demonstrated that pressure can significantly alter the structural characteristics of VO DHPs

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