Electronic structure and luminescence mechanisms in $Cs_2Ag_xNa_{1-x}InCl_6$ alloys

Yu. Hizhnyi[1,2], D. Orlov[2], O. Makarenko[2], Ya. Lys[3,#], Ya. Zhydachevskyy[3]

[1] Donetsk Institute for Physics and Engineering of NAS of Ukraine, Kyiv, Ukraine
[2] Taras Shevchenko National University of Kyiv, Kyiv, Ukraine
[3] Institute of Physics, Polish Academy of Sciences, Warsaw, Poland

The crystals of lead-free halide perovskites family, and in particular $Cs_2Ag_xNa_{1-x}InCl_6$ (CANIC), have been actively studied in recent years as promising luminescent materials with a wide range of practical applications. In order to expand the potential applications of CANIC, it is crucial to be able to engineer the luminescent properties of these compounds. This is particularly important in the spectral region near the edge of the fundamental absorption, where their intrinsic photoluminescence (PL) of CANIC is excited. Successful engineering of the CANIC properties requires an understanding of their optical and luminescent processes at the level of atomic and electronic structure.

In this work, we perform theoretical calculations using the DFT method to determine the electronic structure of the $Cs_2Ag_xNa_{1-x}InCl_6$ (x = 0, 0.1, …1) alloys and of the defect-containing crystals $Cs_2NaInCl_6$:Ag, $Cs_2NaInCl_6$:Sb i $Cs_2Ag_{0.4}Na_{0.6}InCl_6$:Bi in order to elucidate the nature of their luminescence and explain the formation of PL excitation spectra. The calculations were performed using the supercell approach. For each *x* in $Cs_2Ag_xNa_{1-x}InCl_6$, the structures with minimal energies (i.e. the most favorable to exist in reality) were found using machine learning (ML). In this approach, a cluster expansion (CE) model was constructed using the ICET Python package to replace computationally intensive DFT calculations. The CE model was trained on 90 DFT-calculated $Cs_2Ag_xNa_{1-x}InCl_6$ structures with random distributions of Na/Ag on cationic lattice positions and validated via leave-one-out cross-validation (LOOCV). The trained and validated CE model was later used as an efficient surrogate energy model within a simulated annealing method to predict the lowest-energy Na/Ag orderings at each *x*.

All structures predicted by ML were subjected to further geometrical optimization by DFT method. The optical spectra were calculated only for the structures with the lowest total energy among all configurations modelled for each *x* value. The calculations were performed using the DFT-based band-periodic pseudopotential method implemented in the CASTEP program. To overcome the underestimation of the band gap energies E_g by the PBE functional, the optical (inter-band) absorption spectra were calculated using the GGA-PBE plus Hubbard U (GGA + U) approach.

The origin of luminescence in $Cs_2Ag_xNa_{1-x}InCl_6$ alloys, both pure and doped with Bi and Sb ions is discussed using results of the calculations and available experimental data.

corresponding author: yalys@ifpan.edu.pl