Ab-initio calculation of electronic properties of all-inorganic Pb-based mixed-halide perovskites

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Abstract. Mixed lead-halide perovskite films have recently become a subject of intensive study in the nanophotonic community due to their unique optical properties. In this work we present theoretical investigations of the electronic band structure of full inorganic mixed-halide perovskites in a continuous range of chemical compositions. We demonstrate that in the orthorhombic geometry independently on the particular halogen concentrations the optical band gap remains direct, varying in the absolute value, with the fundamental absorption edge corresponding to the high symmetry point Γ of the band structure. This tunability of the optical band gap in inorganic mixed-halide perovskites is highly promising and has various possible nanophotonic and photovoltaic applications.

1. Introduction
Perovskites are known as attractive optical materials due to their fabrication accessibility and wide range of applications in different areas of nanophotonics. Recent works demonstrated that solar cell elements based on halide perovskites can reach up to 22% efficiency [1]. In combination with the inexpensiveness of its production in comparison to the standard silicon solar elements, this makes the perovskites a perspective candidate for replacement of silicon in photovoltaics. In this work we particularly address all-inorganic mixed halide perovskites, which exhibit high exciton binding energies in comparison to hybrid organic-inorganic halide perovskites. This property has recently allowed for observation of room-temperature polariton condensation in perovskite films [2], which extends the range of the perovskite applications to polaritonics and nanophotonics [3].

We numerically investigated the relaxed lattice geometry and the the band gap evolution in the two possible geometric phases of the bulk CsPbBr$_{3-x}$Cl$_x$ perovskite. Our results, being in accordance with recent experimental data, demonstrate that bulk perovskites at room temperature exhibit the orthorhombic phase with variation of the index $x$, exhibiting stability of its optical properties.

2. Methods
To study the properties of the mixed perovskite electronic subsystem we employed the DFT framework realized with Quantum Espresso simulation package [4]. The relaxed geometry of
Figure 1. The relaxed geometry of two phases of CsPbBr$_3$ and CsPbBr$_2$Cl$_1$ perovskite: a,c) cubic phase b,d) orthorhombic phase. One can see that Cl added to the system brings only minor changes to the orthorhombic phase, while it completely breaks the order in the cubic phase.

The initial band gap calculation was based on the assumption that the single halide perovskite exhibits the cubic phase geometry, characterised with high order symmetry of the lattice unit cell. The calculation of the relaxed geometry with experimentally obtained parameters shows that admixing a new type of halogen to the pure structure breaks its symmetry and the cubic phase incorporates some elements of orthorhombic unit cell due to the difference in the ionic...
Figure 2. The evolution of the band structure of CsPbBr$_{3-x}$Cl$_x$ (0 ≤ x ≤ 3). Note that with addition of Cl into CsPbBr$_3$ the band gap remains direct and the shape of the band edges near the Γ-point is not drastically changed, indicating well established optoelectronic properties and stable electronic transport.

Figure 3. The evolution of the band gap of CsPbBr$_{3-x}$Cl$_x$ (0 ≤ x ≤ 3). Here we show the comparison of the experimentally found positions of the PL peaks (blue line) and the energy of the band gap found as $E_{\text{LUMO}} - E_{\text{HOMO}}$ (red line) for different densities of added chlorine. Light-blue curve is a theoretical simulation of $E_{\text{LUMO}} - E_{\text{HOMO}}$ for the case when the initial and final perovskite phase is cubic. One can see that without extra forces the bulk material cannot keep the cubic phase with addition of different halogen to the compound. So the value of the band gap sharply increases.
radii of chlorine and bromine. The acquired phase stops being cubic anymore and completely loses the high order symmetry as demonstrated in the Figure 1c. This leads to the modification of the band structure and thus to the different optical properties of the compound.

With this obtained result we changed the initial conditions of our calculations with initial unit cell geometric phase changed to the orthorhombic, shown in the Figure 1b,d. Our investigations demonstrate that the addition of Cl atoms to the unit cell does not bring any crucial changes to the system.

Once the bromine atoms are completely replaced with chlorine the perovskite lattice reverts to tetragonal phase, restoring the high symmetry of the unit cell. Note that within orthorhombic geometry the gap remains direct at the Gamma point as shown in Figure 2. Figure 3 shows the position of the measured photoluminescence peaks [7] and theoretical calculation of the band-gap evolution for the CsPbBr$_{3-x}$Cl$_x$ compound with $x = [0, 3]$. The comparison with the experimentally measured PL peak positions in the films [8] confirms our statement that the perovskite phase remains orthorhombic for all mixed halide perovskites.

4. Conclusion
We have demonstrated the evolution of the lattice geometry and the band structure of all-inorganic mixed halide perovskites for cubic and orthorhombic initial phases. The grown structure [7] is characterised with orthorhombic phase and the band gap remains direct independently on the chlorine relative concentration. At the same time, the cubic phase is unstable with respect to addition of extra type of atom to the unit cell, which breaks the high order point symmetry. We note, however, that the cubic phase instability may be removed by the surface forces in the limit of thin perovskite films.

5. Acknowledgements
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6. References
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