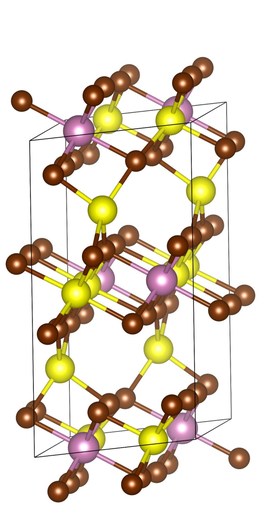
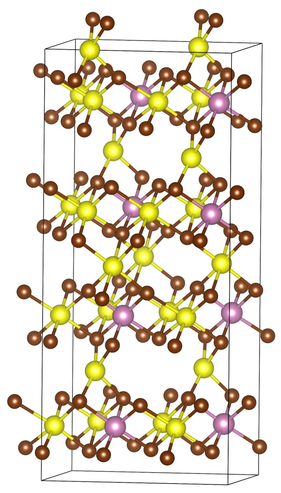
Same structure type, different compositions:

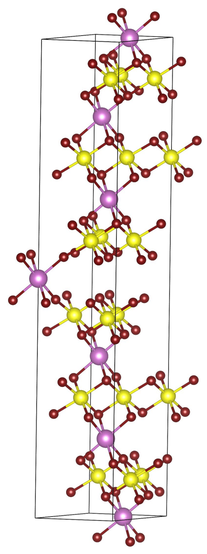
Computational search of SSE among Li-{In, Ga}-{F, Cl, I}



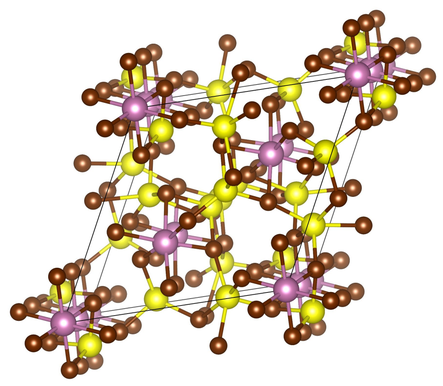
Li_3MHal_6 , monoclinic, 2 layer stacking Space Group C2 (1)



Li_3MHal_6 , monoclinic, 4 layer stacking Space Group C2 (2)

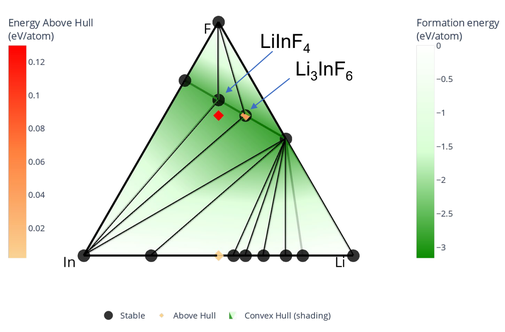


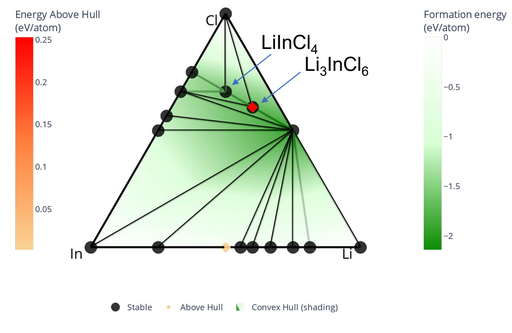
Li_3MHal_6 , monoclinic, Space Group C2/m (3)

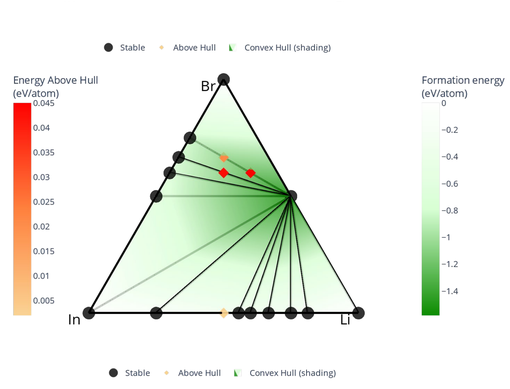


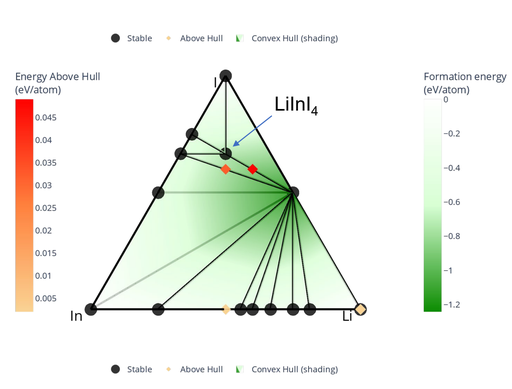
Li_3MHal_6 , monoclinic, Space Group C2/c (4)

Iodide-type compound Li_3LaI_6 with stable octahedral Li occupation is found to be a better ionic conductor than any sulfide-type known. Xu et al. found strong relation between Li migration enthalpies in face-centered-cubic anion frameworks and charge to bond length ratio and also lithium coordination number. In current work we study other materials with different compositions but the same iodide-type structure to explore the influence of the composition on the relevant properties such as stability and ionic conductivity of the materials.



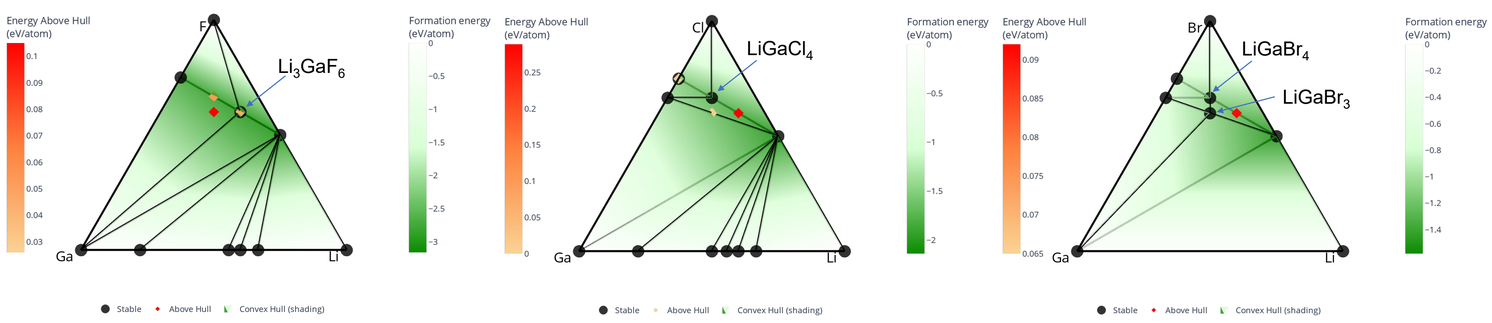






Li_3InCl_6 with monoclinic (C2/m space group), Li_3InBr_6 (C2/m) and Li_3LaI_6 (C2) structures are shown to be a material with high ionic conductivity[3,4]. These structure types are considered to build promising environment for high ionic conductivity, however, very few compositions were investigated (Li-Y-I, Li-In-Cl,I, Li-Sc-I, Li-La-I[4] etc).

In this work we systematically explore 2 new composition sets with the same structure framework to investigate the effect of composition on stability and ionic conductivity.



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Methods

- All calculations were performed using the Vienna Ab-initio simulation package (VASP) software, based on the projector-augmented wave method, within the framework of DFT. The generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof exchange functional was used.
- The structures were constructed by taking already known one and substituting metal or halogen atoms. Then relaxation calculations were carried out for novel and all known structures in the current system, which were taken from Materials Project. Ion-electron interaction was described by the augmented plane waves method (PAW) with energy cutoff chosen from variation between 400-800eV and gamma centered k-point mesh varying Rk value (k-points per axis) between 2-8 untill converged. Stability of the novel materials were analyzed by constructing convex hull diagram.

The $|q_{anion}| / d_{octahedron}$ value is crucial for achieving fast lithium ion diffusion in a superionic conductor with Li octahedral occupations, as Xu et al proposed. The larger this value the better ionic conductivity is awaited.

Material	Mean Li-Anion distance (A)	Mean anion charge (e)	$\|q\| / d_{oct}$
Li3InF6_4	1,91	0,80	0,42
Li3GaF6_1	1,97	0,80	0,41
Li3GaF6_mp-15558	1,90	0,80	0,42
Li3InBr6_2	2,68	0,68	0,25
Li3InF6_1	1,99	0,80	0,40
Li3InBr6_1	2,64	0,68	0,26

For estimation of ionic conduction we calculate anionic charge (q) and distance between center of octahedral site and closest anionic site (d_{oct}). Anionic charge was calculated by Bader charge. d_{oct} was calculated by averaging all values of Li octahedrons of each structure.

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