Novel Halide Solid State Electrolytes

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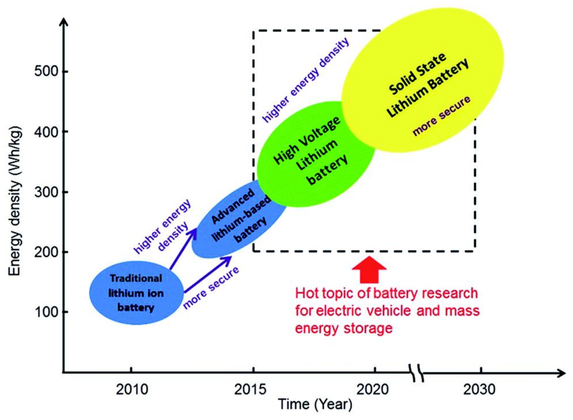
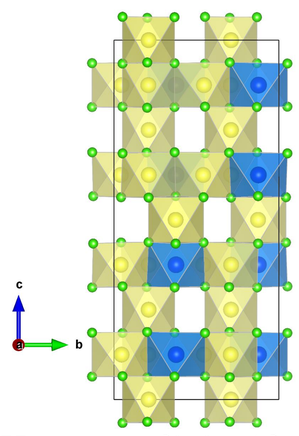
Intro

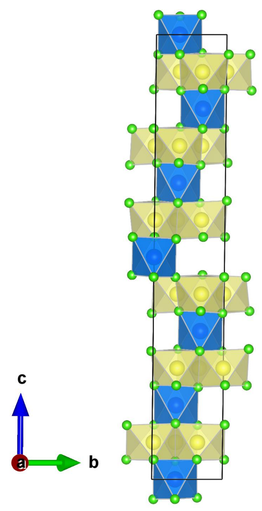
All solid-state batteries, with solid-state electrolytes, open a floodgate of prospective characteristic properties for future energy storage systems. Although, known solid-state electrolytes (sulfide, oxides, borates, and so on) do not satisfy all performance requirements, such as high ion conductivity or compatibility with anode materials, for wide implementation in various applications [1].



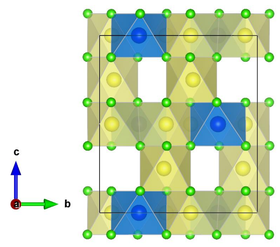
The next step of energy storage technology is all solid state batteries (ASSB), which will have the highest energy density (Wh/kg) at by 2030. The advantages of ASSB safety, high energy density, longer cycle life, and disadvantages lower ionic conductivity, poor interface stability, cost.



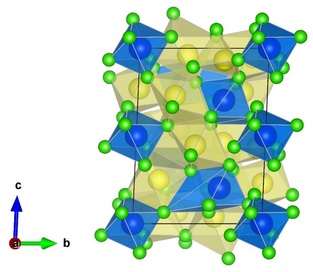
Li_3LaH_6 , monoclinic, 4 layer stacking
Space Group C2 (5)



Li_3LaH_6 , monoclinic,
Space Group C2/m (12)



Li_3LaH_6 , monoclinic, 2 layer stacking
Space Group C2 (5)



Li_3LaH_6 , monoclinic,
Space Group C2/c (15)

Halide type solid state electrolytes (SSE) are considered as materials with low ionic conductivity, but recently novel structure Li_3YBr_6 and Li_3YCl_6 were found [2], which have 1 mS cm^{-1} ionic conductivity. This finding opened the door for more deep investigation of halide SSE with similar structures. Among high ionic conductors are Li_3InCl_6 with monoclinic (C2/m space group), Li_3InBr_6 (C2/m) and Li_3LaI_6 (C2) structure [3,4].

Stability of these structures were investigated in different compositions like Li-In-Cl, Li-Y-I, Li-Sc-I, Li-La-I, but some compositions are remained not investigated.

The main goals of the current research are:

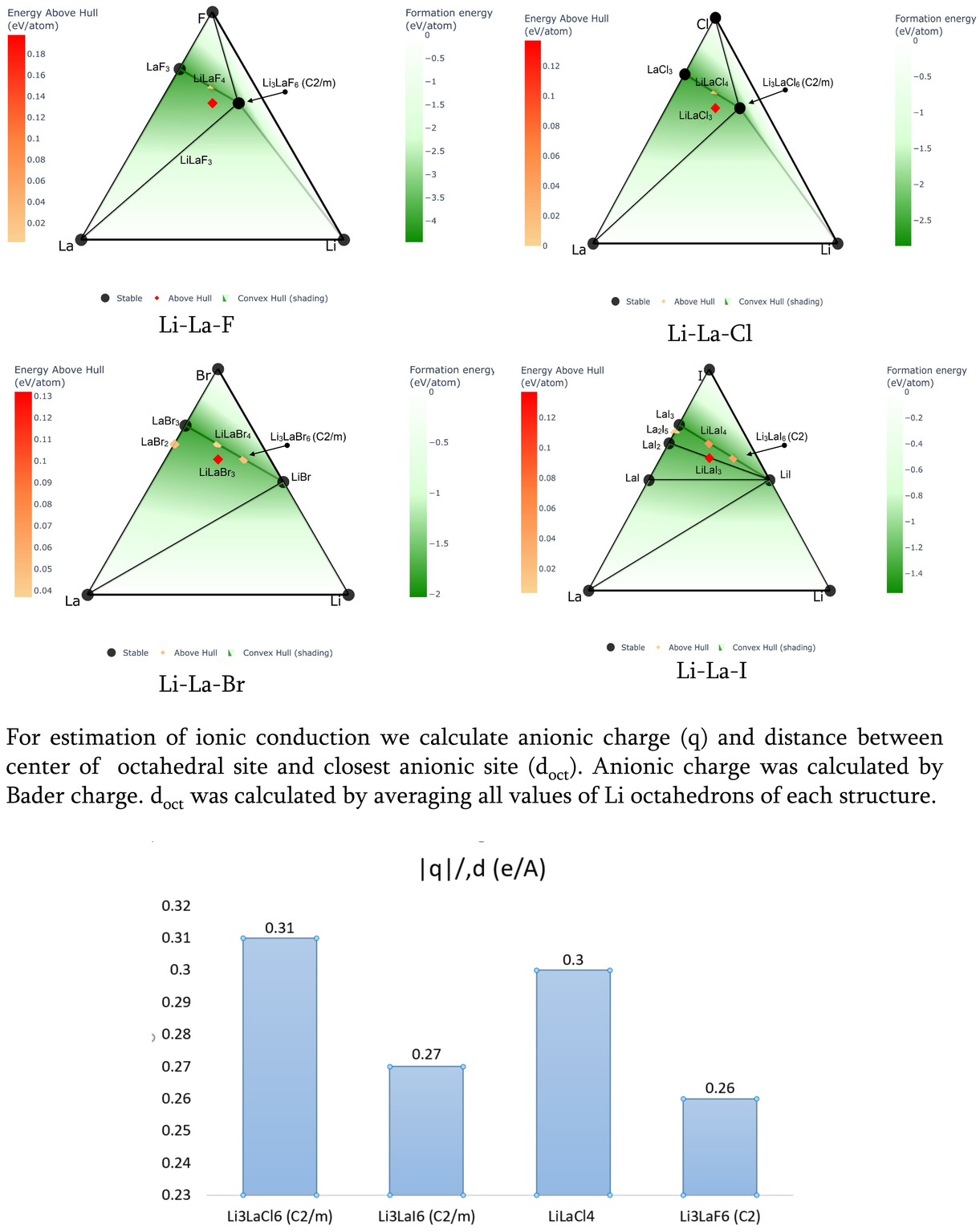
- Search novel stable materials with Li_3LaH_6 composition, where H=F, Cl, Br.
- Estimate ionic conductivity of novel stable materials.

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 atoms with La. Then relaxation calculations were carried out for novel and all known structures in the current system, which is taken for Materials Project. Stability of the novel materials was calculated by constructing convex hull diagram.

Results

Calculations revealed that only two new structures are stable in the Li-La-Cl, Li-La-F. They are Li_3LaF_6 (C2/m), Li_3LaCl_6 (C2/m).



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.

The large electronegativity difference between the anion element and non-lithium cation element leading to large |q|/d values is essential for achieving extremely fast lithium ion diffusion in a superionic conductor with Li octahedral occupations.

Conclusions

Novel stable Li_3LaCl_6 and Li_3LaF_6 materials, with monoclinic structure and C2/m Space Group were predicted. Estimation of ionic conductivity shows that Li_3LaCl_6 can have higher values than known Li_3ScI_6 and Li_3YCl_6.

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For more details please scan QR code.

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