

borohydride garnet ionic conductor

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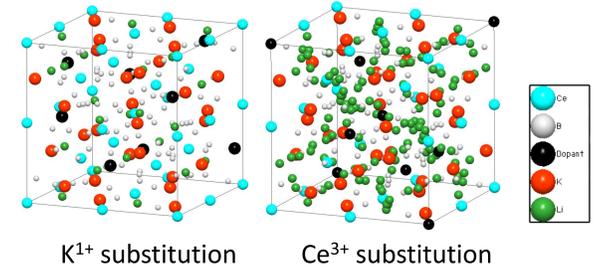
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MOTIVATION

Cation substitution (via mono and divalent cations) in garnet-type $\text{Li}_3\text{Ce}_2\text{K}_3(\text{BH}_4)_{12}$ is investigated as a tool to achieve higher Li-mobility. In analogy to oxide garnet fast ionics, two possible scenarios schematized on the right are explored to test doping in borohydrides and tailor ionic conductivity

1. Divalent cation - for lower valency cation (K^+) increases the vacancy population on Li^+ site.
2. Monovalent cation - for higher valency cation (Ce^{3+}) increases Li-content the structure.

Samples are synthesized by mechanochemistry and characterized by synchrotron X-ray powder diffraction (S-XPD) and electrochemical impedance spectroscopy to investigate the ionic conductivity. The doping mechanism is systematically studied with different mono and divalent cation.



K^+ substitution

Ce^{3+} substitution

Topological study of conduction mechanism on garnet

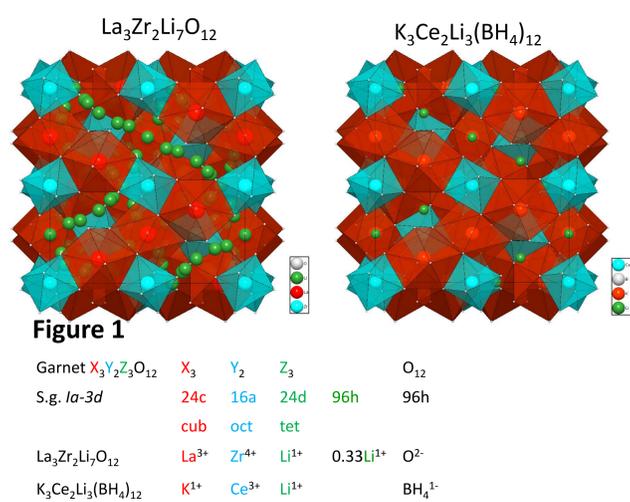


Figure 1 shows a comparison between the reference $\text{La}_3\text{Zr}_2\text{Li}_7\text{O}_{12}$ garnet and the studied $\text{K}_3\text{Ce}_2\text{Li}_3(\text{BH}_4)_{12}$ garnet. The green balls depict lithium, and show the conduction channel on the left.

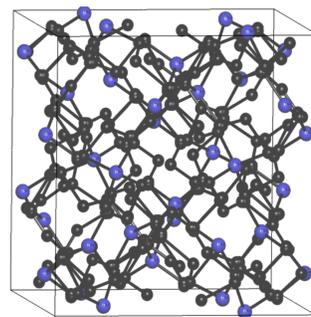


Figure 2

Figure 2 Topological analysis (TOPOS) shows the same framework for mobile Li in both structures.

- Lithium
- Voids
- Conduction channel

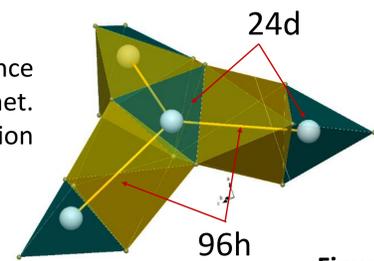


Figure 3

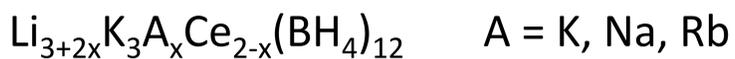
Figure 3 shows the node for Li on Wyckoff site 24d. Doping mechanism consists of:

- Substitution of Ce^{3+} with low valency cation
- Incorporation of Li^{1+} on the general position 96h

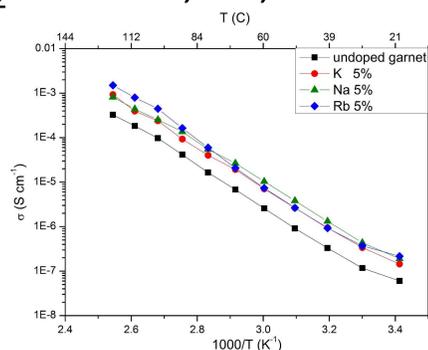
This creates the conditions for conduction pathways as in the oxide garnet.

Aliovalent cation substitution

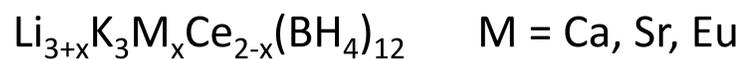
Monovalent dopants



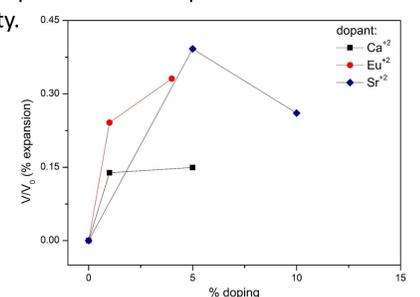
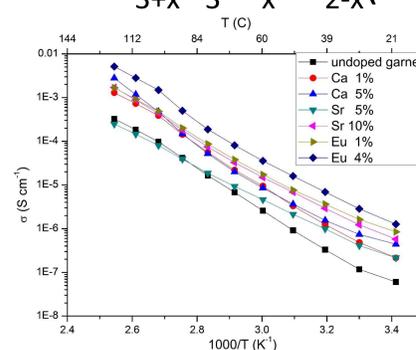
- Conductivity slightly increases for doping concentrations lower than 5%mol
- Shift in conductivity is almost constant in the whole temperature range



Divalent dopants

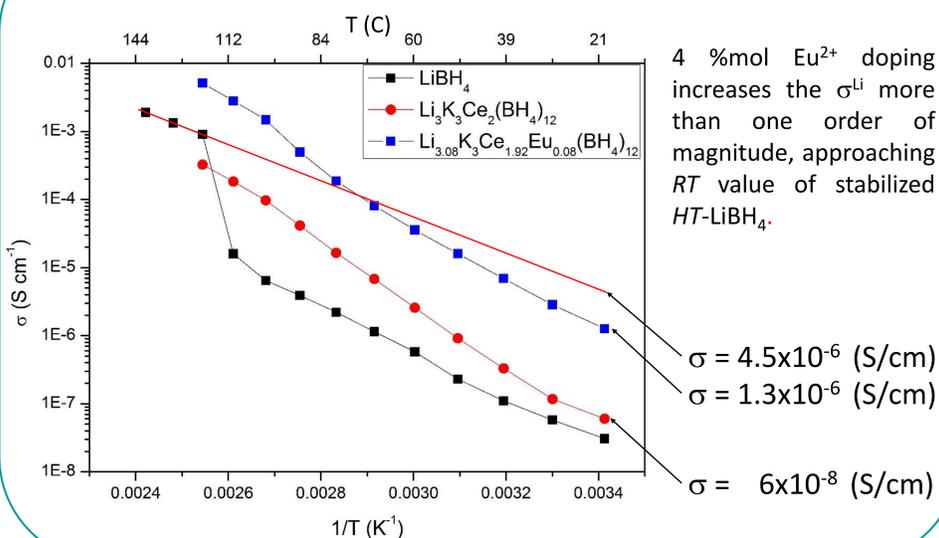


Eu^{2+} and Ca^{2+} doping show correlation between unit cell expansion and improvement of ionic conductivity.



Unit cell expansion is observed also for Ca^{2+} -doped samples, which is counterintuitive due to the smaller ionic radius as compared to Ce^{3+} ($r/r_0=0.99$). A possible origin may be found in higher Li content in the lattice. The effect of anionic substitution $\text{Cl} \leftrightarrow \text{BH}_4^-$ (chlorides-based synthesis protocol) should cause a lattice contraction. This can explain the counterintuitive trend for Sr-doping.

Conductivity comparison



CONCLUSION

- First results show that tailoring ionic conductivity in simple structure by aliovalent substitution is a promising way to design borohydride conductors, in analogy to other well studied chemical systems such as chemical metal oxides.
- Substitution on the Ce^{3+} site, as determined by S-XPD, increases the fast Li-conductivity. The higher value of σ^{Li} is mainly owed to the higher Li-content in the structure that facilitates site-jumps of mobile cations due to the partial occupation of Wyckoff site 96h.
- No doping-induced change of conduction mechanism, the activation energy is approximately identical for different dopant concentration.
- Doping with concentration higher than 15 %mol does not lead to further conductivity-increase, both for monovalent as well as divalent cations; the host lattice seems to be incapable of accommodating more than 15 %mol Li.