Lithium Distribution and Site Disorder in Bromide-Substituted Lithium Argyrodites: A Structural and Transport Study

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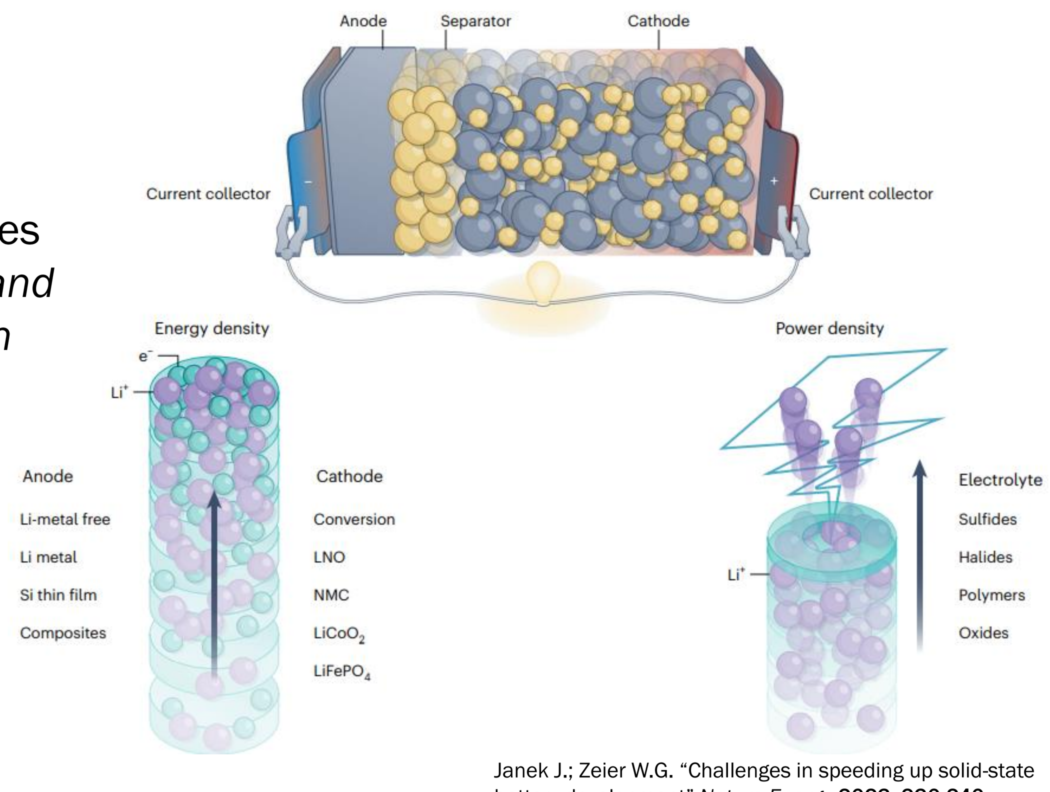
Abstract

In this study, we investigate the effect of bromide substitution on lithium argyrodite ($Li_{6-x}PS_{5-x}Br_{1+x}$, in the range $0.0 \leq x \leq 0.5$) and engineer structural disorder by changing the synthesis protocol. We reveal the correlation between the lithium substructure and ionic transport using neutron diffraction, NMR spectroscopy, and electrochemical impedance spectroscopy.

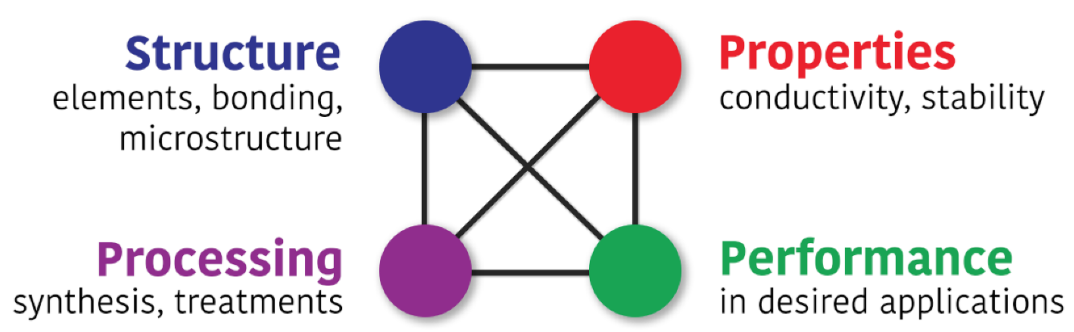
Introduction

All-solid-state batteries use solid ionic conductors that replace liquid electrolytes to achieve *higher safety, lower toxicity, and higher energy density with Li and Silicon anode*

The material requirements are:
1) fast ionic conduction, and
2) stable electrode|electrolyte interfaces
3) better chemical stability
4) high electrochemical stability

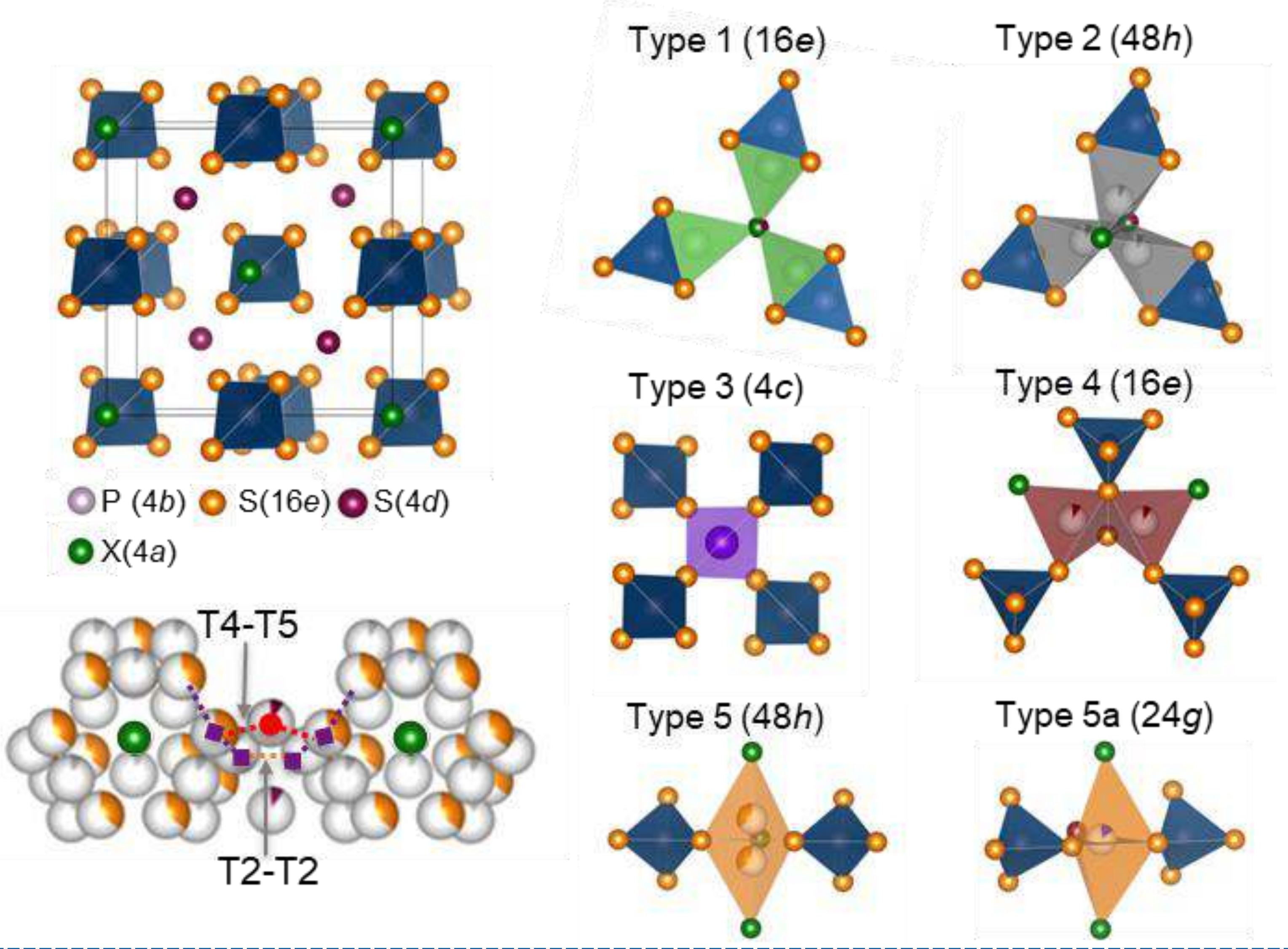


Janek J.; Zeier W.G. "Challenges in speeding up solid-state battery development" *Nature Energy* **2023**, 230-240

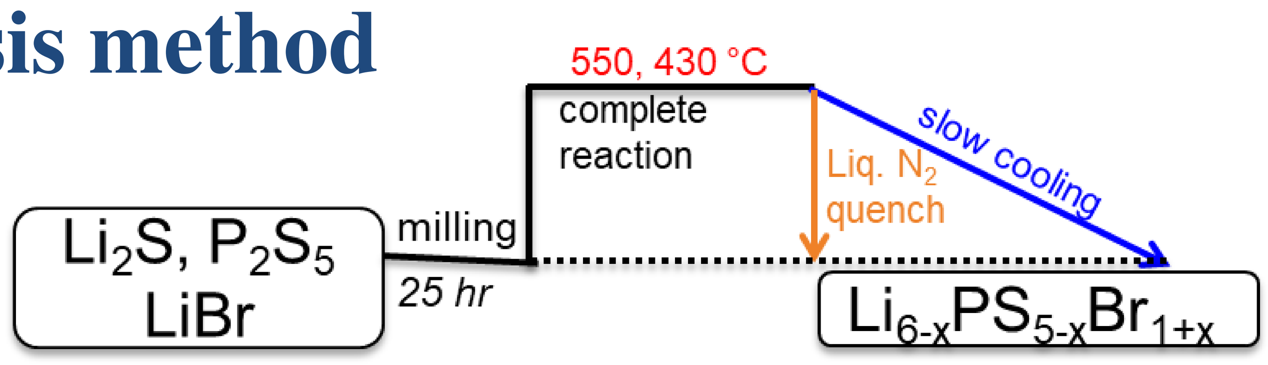


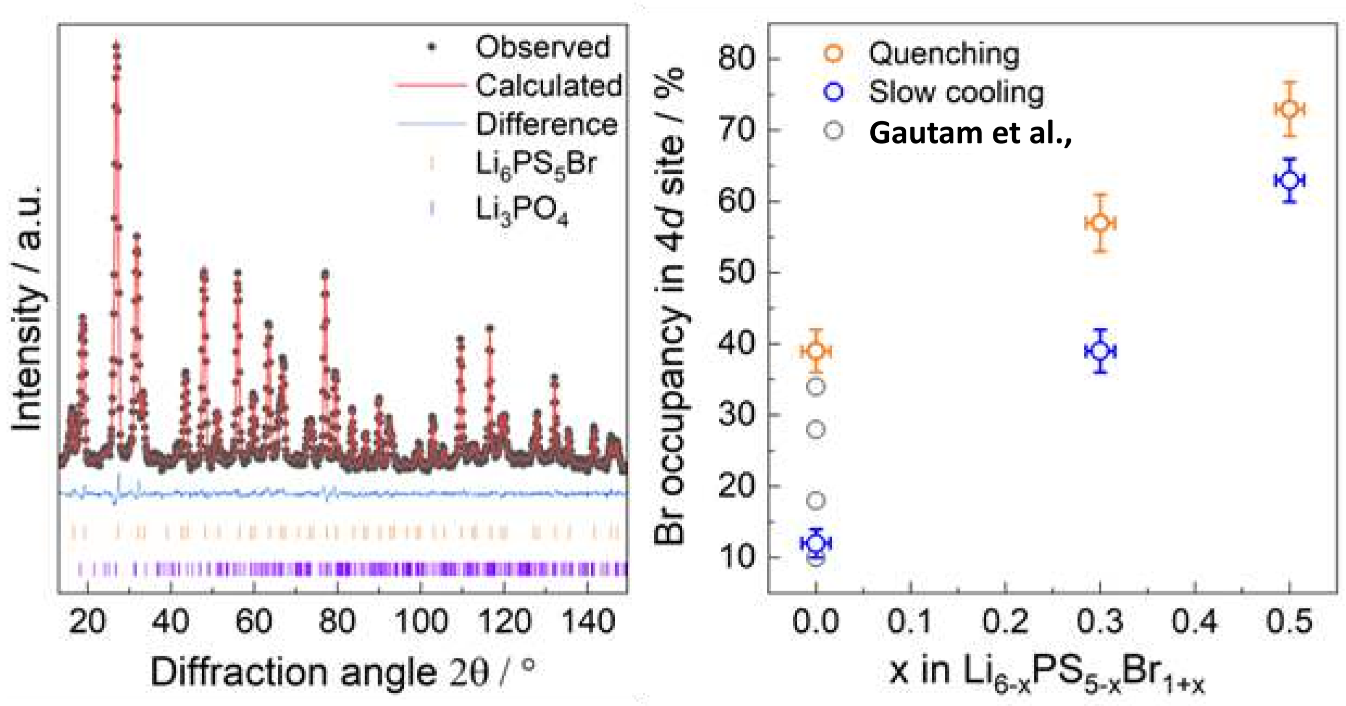
We aim to understand fundamental structural and compositional effects on the resulting conductivity and to control these via synthesis and processing.

Introduction of lithium argyrodite framework



Structural changes induced by Br content and synthesis method





- Site disordering ((in this case Br occupancy on the *4d* site) occurs quickly and is a function of temperature and kinetically traps by varying cooling methods.

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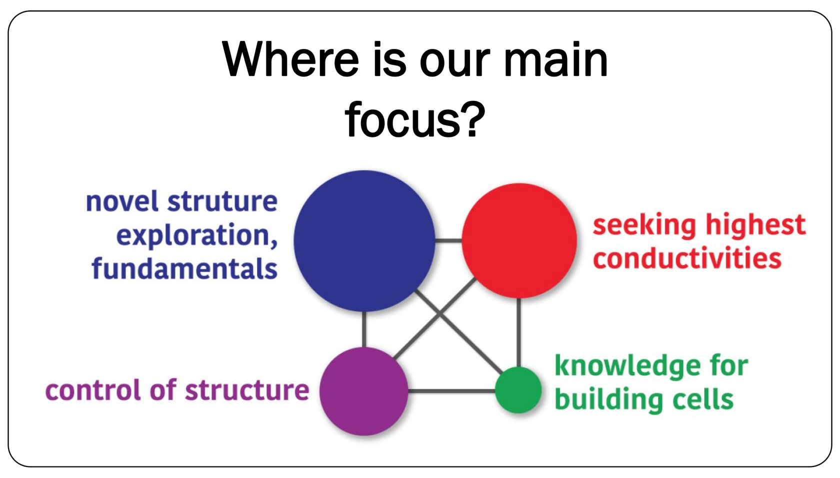
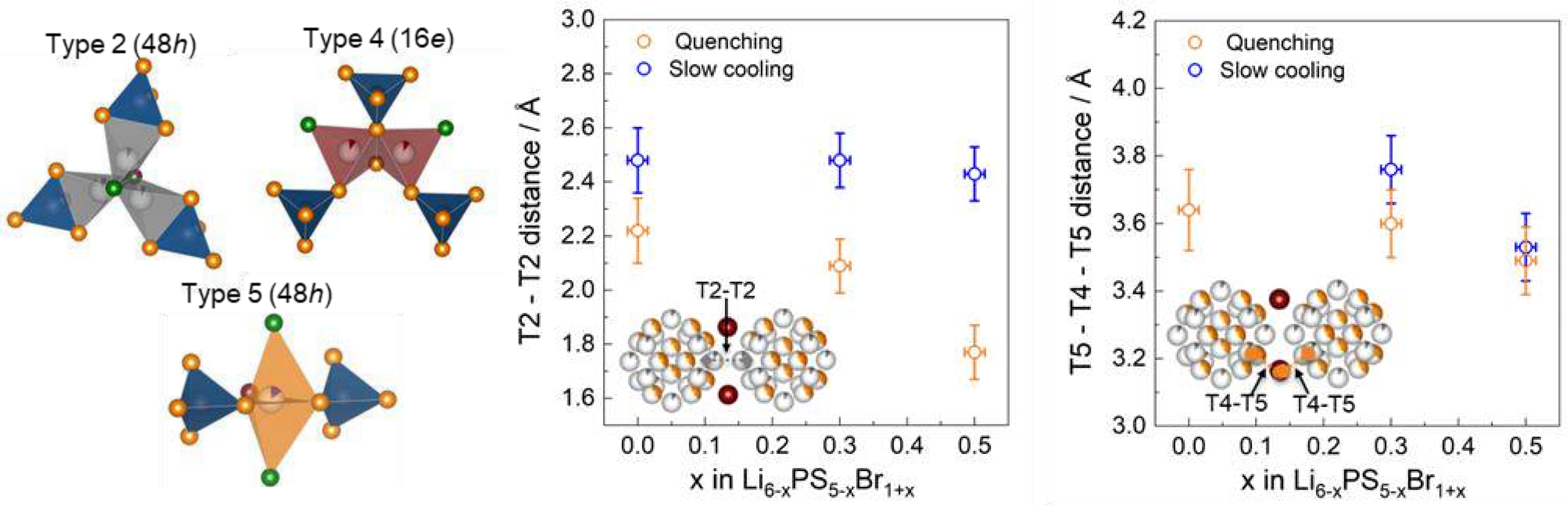
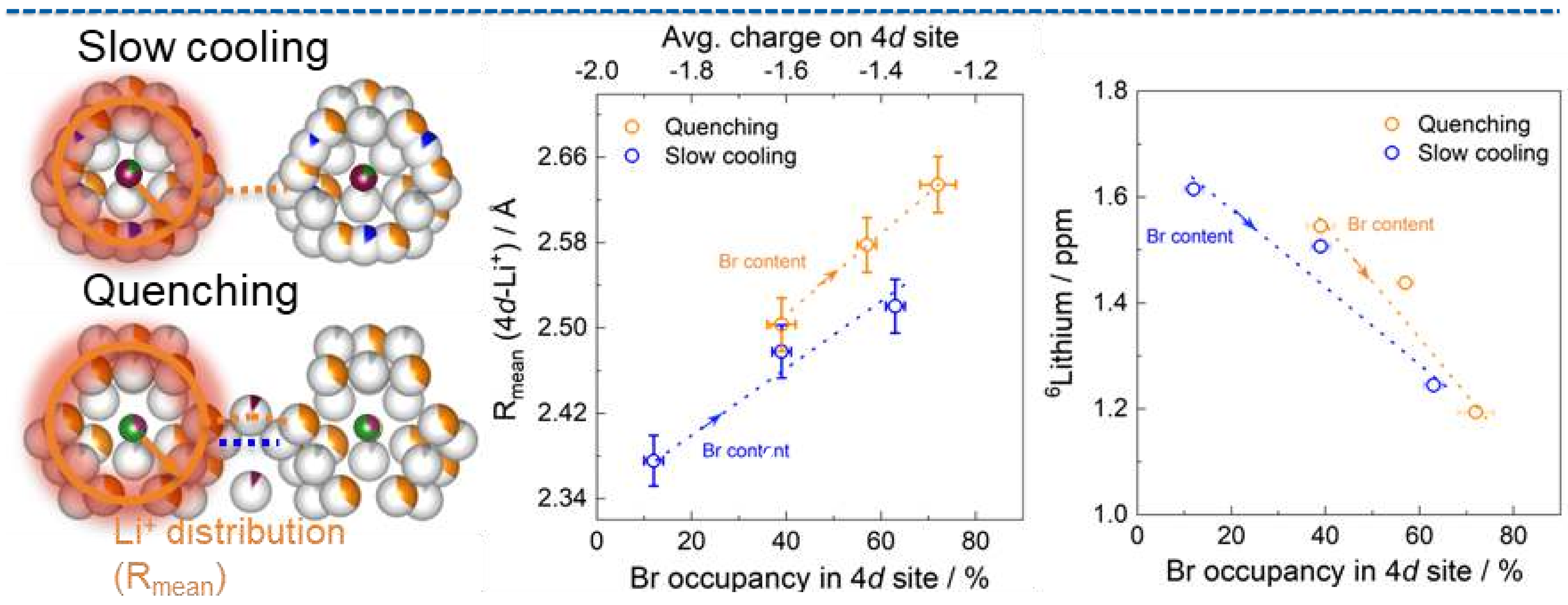
Structure-processing relations on improving conductivity

The argyrodites, with the composition Li_6PS_5X (X = Cl, Br, I), are promising electrolytes with high ionic conductivity. They can be substituted isovalently or aliovalently, with all sites P, S, and X able to be substituted, with drastic and not yet completely understood effects on properties. Site disorder (without compositional change) has been explored in this project, along with methods for control.



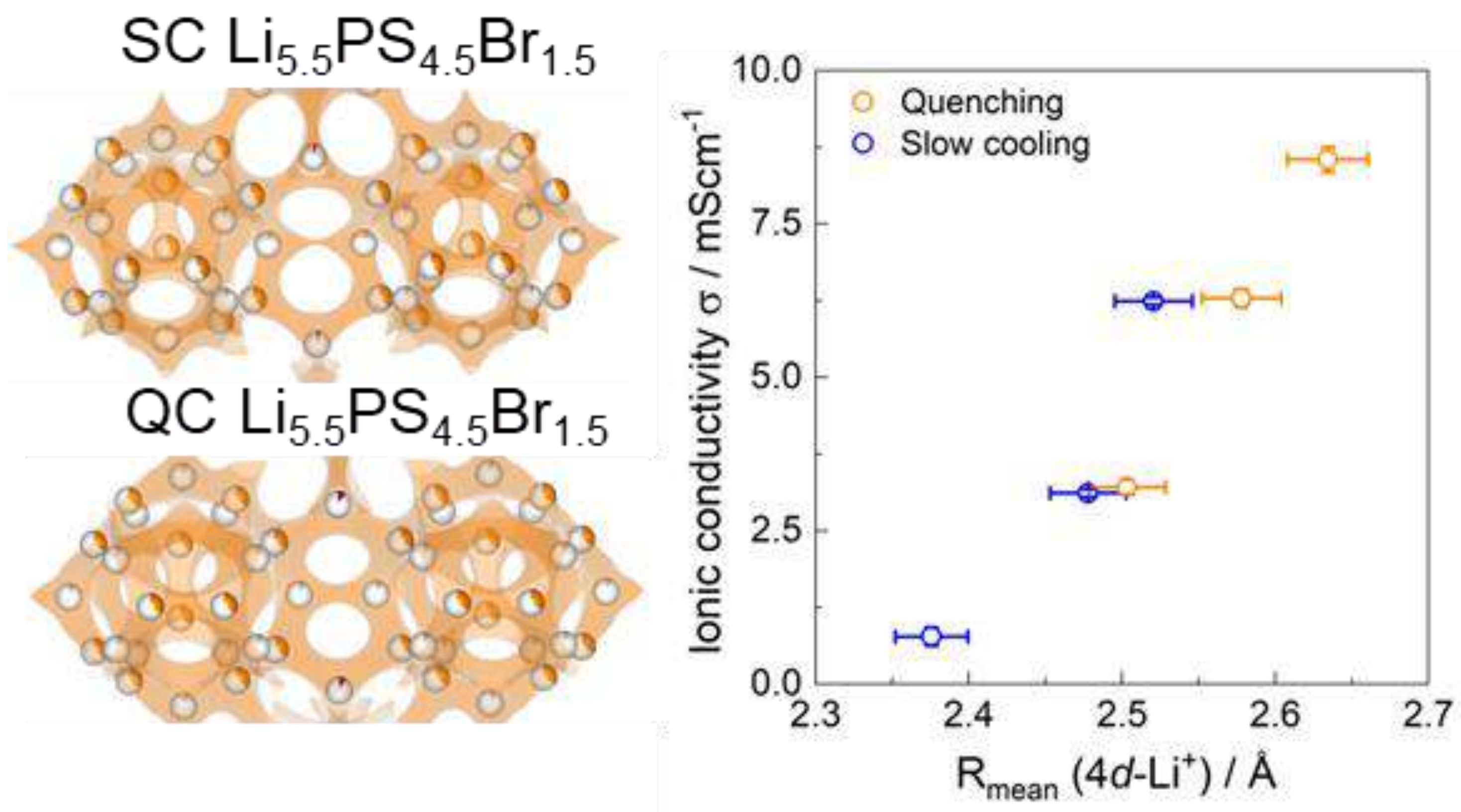


- Displays T2−T2 and T5−T4−T5 distances as functions of bromide content.
- T2−T2 inter-cage distance reduced only for quenched cooling.
- T5−T4−T5 inter-cage distance decreases for both methods with bromide increase.

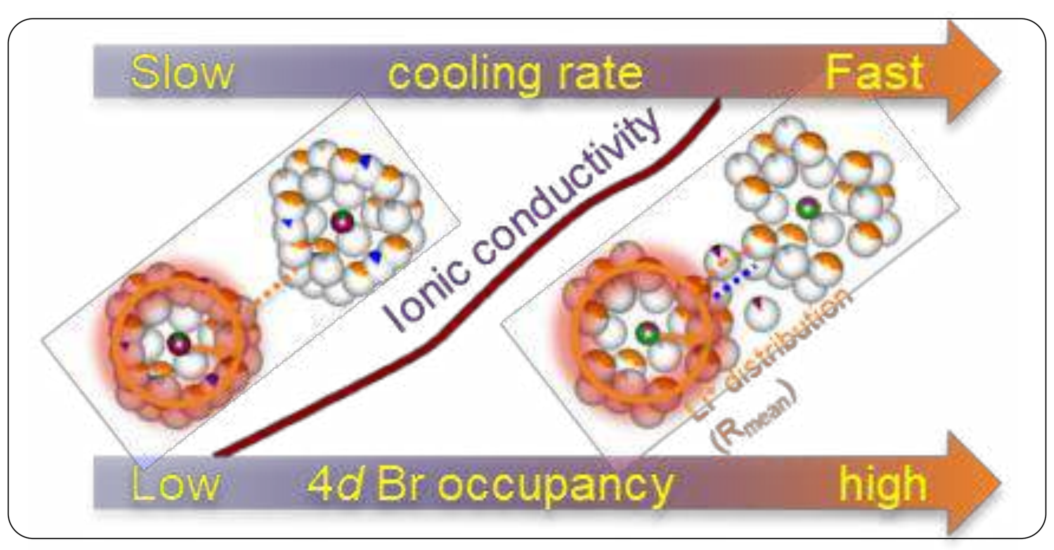


- More Br− on the *4d* site leads to a lower negative charge as sulfide is replaced by Br.
- Li-atoms move away, increasing R_{mean}.
- Increased radius results in reduced T2−T2 and T5−T4−T5 distances.

Conclusion



- The altered Br distribution on 4d sites enhances connectivity between cages.
- This leads to the observed increase in overall conductivity.



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