

Boosting Lithium-Ion Conductivity - Newly Discovered Lithium Pnictides reaching values above 40 mS/cm

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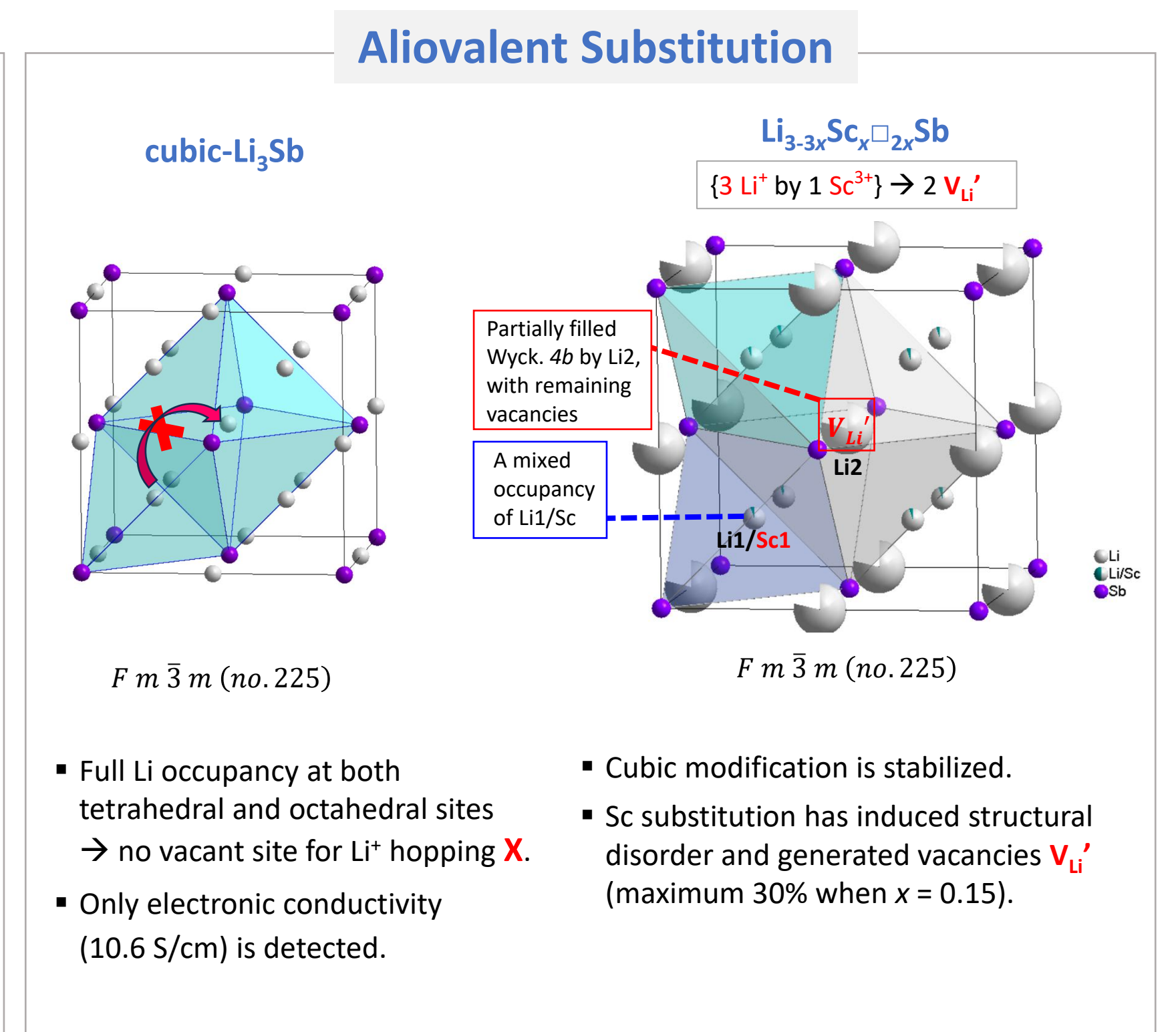
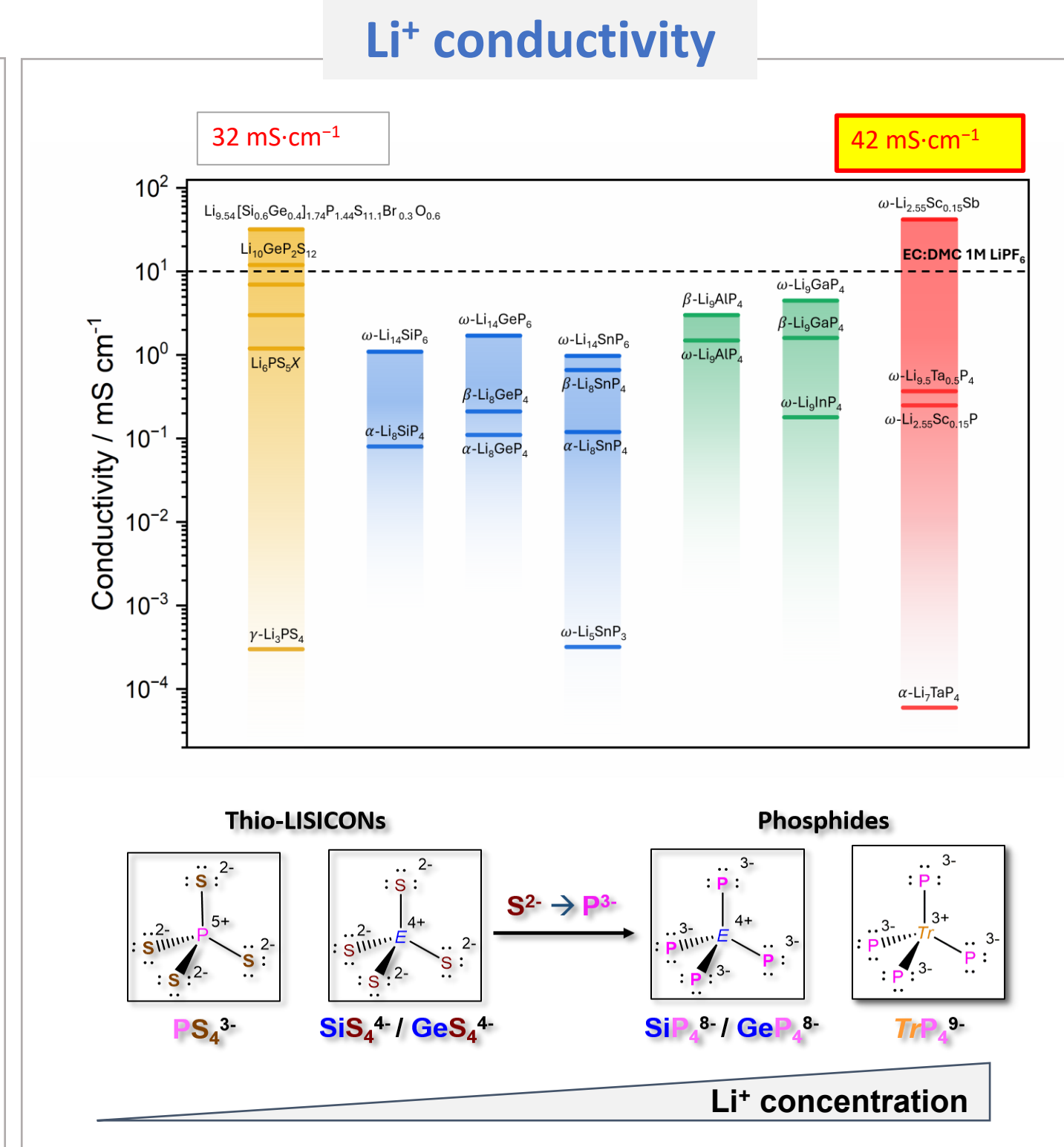
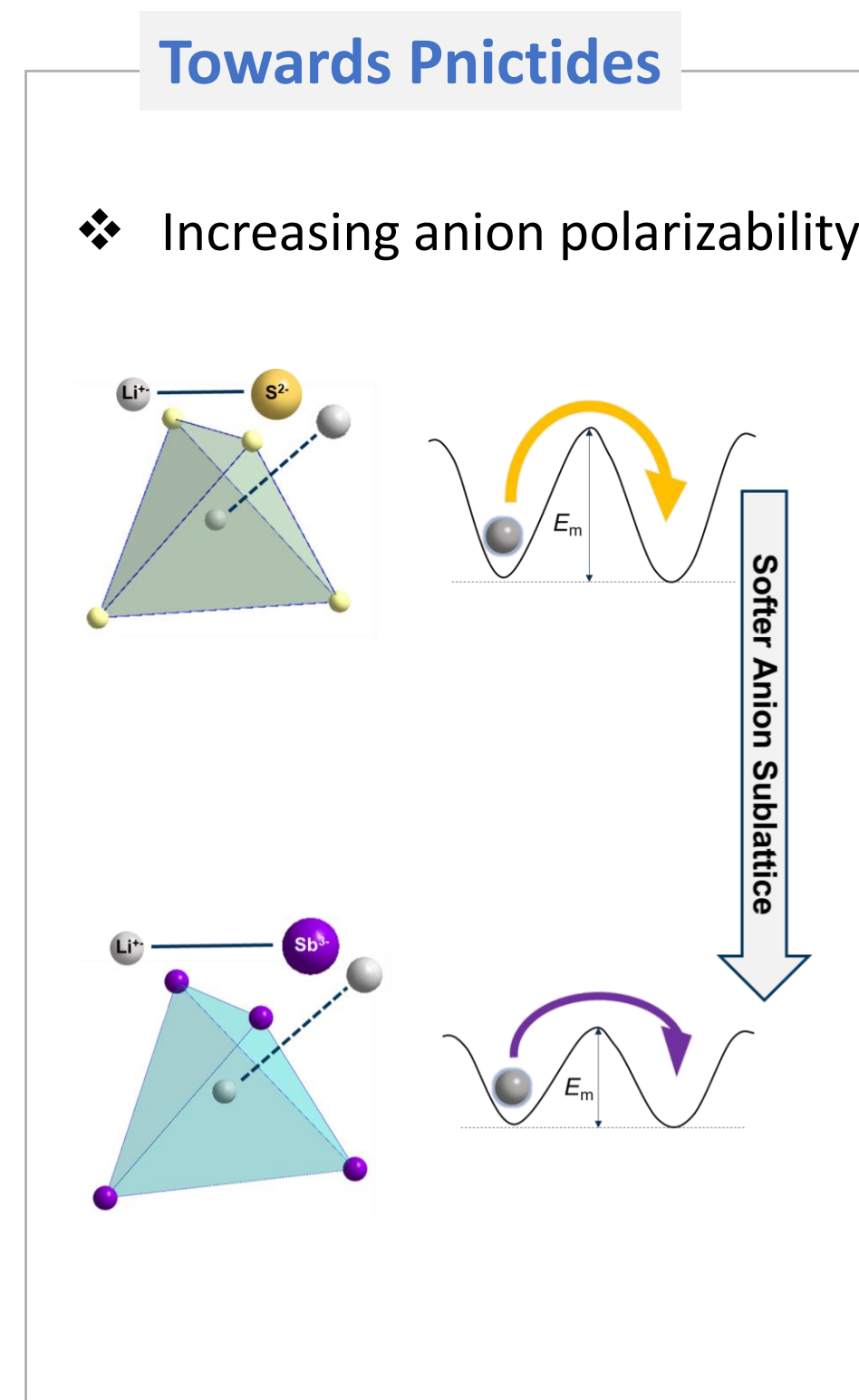
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I. Introduction

Solid-state electrolytes are the key component within the next-generation all-solid-state batteries. Whereas sulfide based solid electrolytes became more and more complex, we demonstrate here that modifications in simple binary pnictides Pn can yield record-high ionic transport properties. We follow the idea that P^{3-} and Sb^{3-} anions are better polarizable than S^{2-} and thus lower the activation energy for Li^+ migration.

Phosphide-based solid electrolytes have recently shown great potential with diverse structures and variable ionic conductivities.^[1-8] Herein, a new compound class has been uncovered by expanding to the heavier homolog Li_3Sb , showing its transformation to a superionic conductor through aliovalent substitution of lithium with scandium.



II. Synthesis and Structures

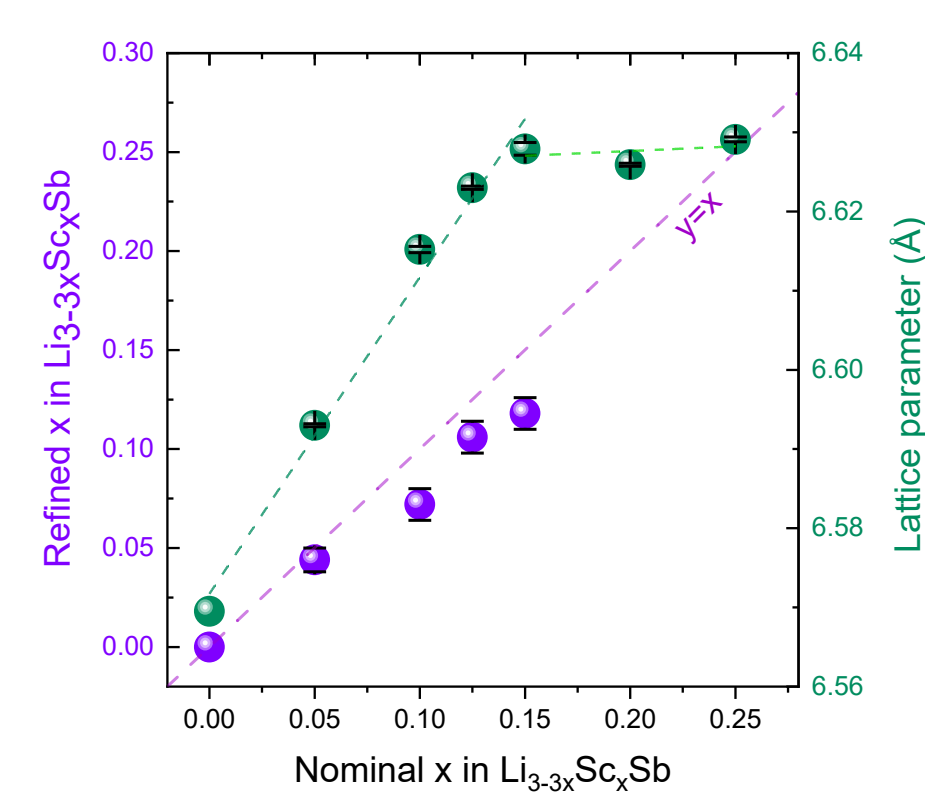
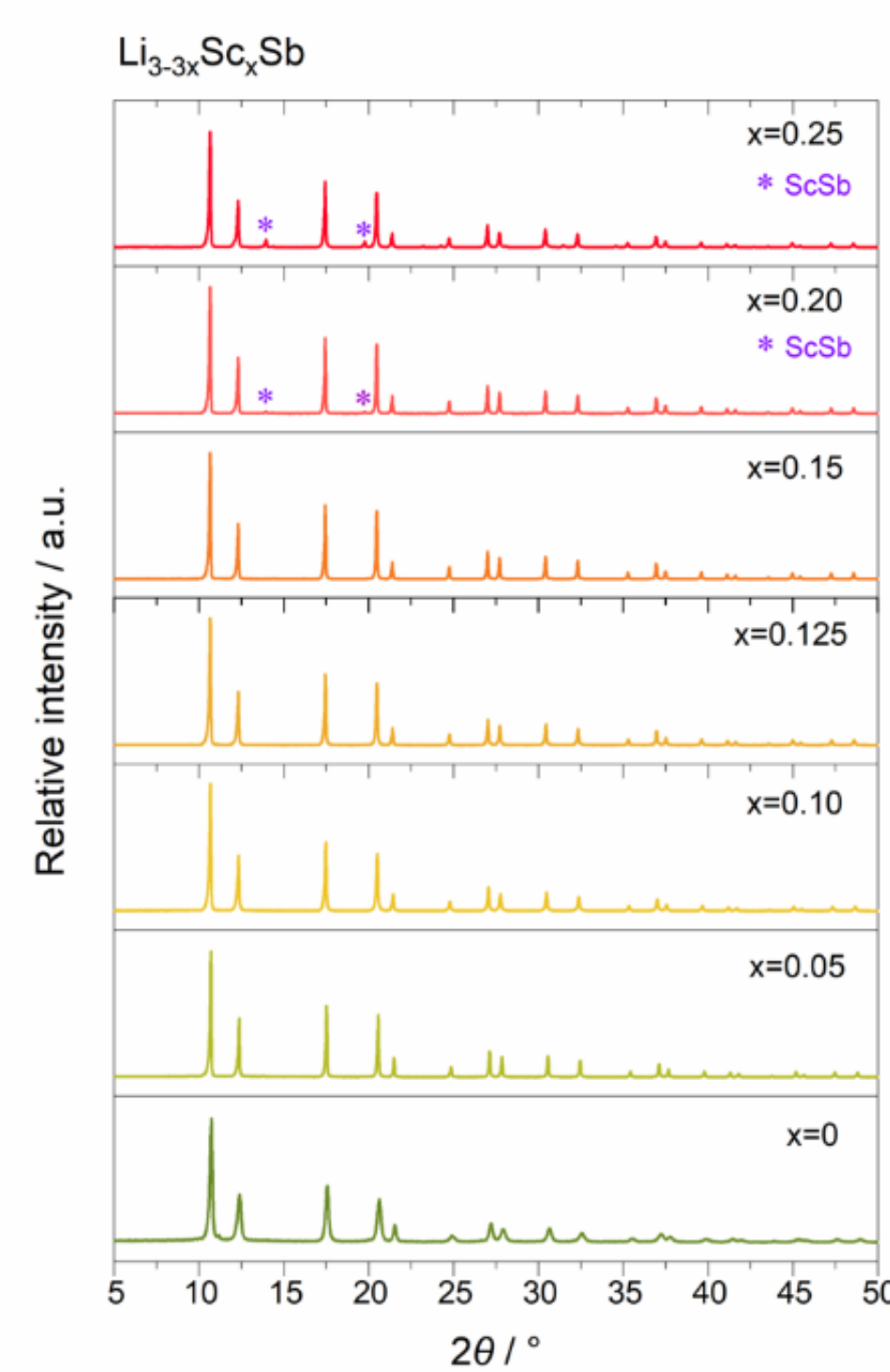
Solid-state Synthesis

A combination of mechanical ball milling and subsequent high-temperature annealing processes.

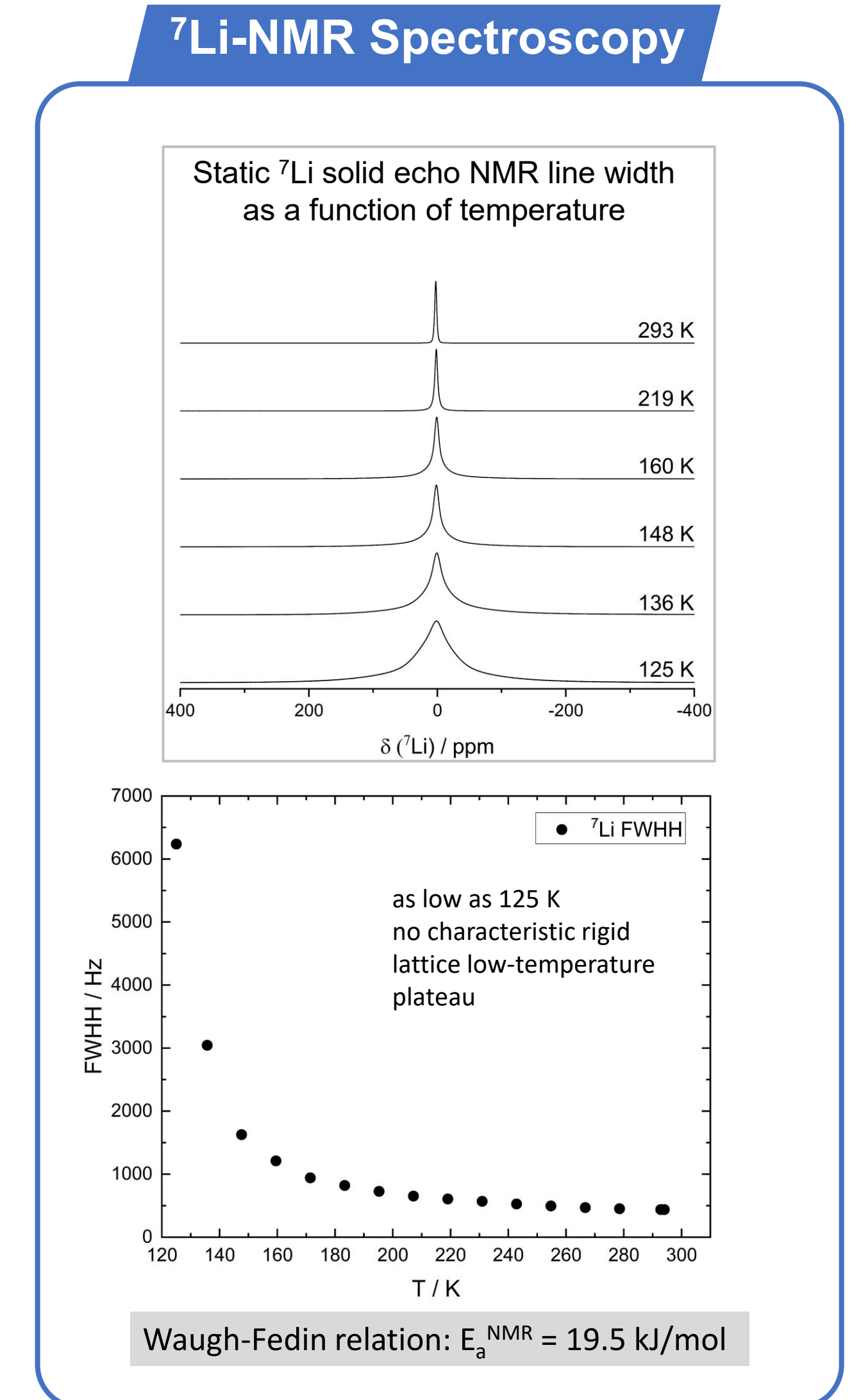
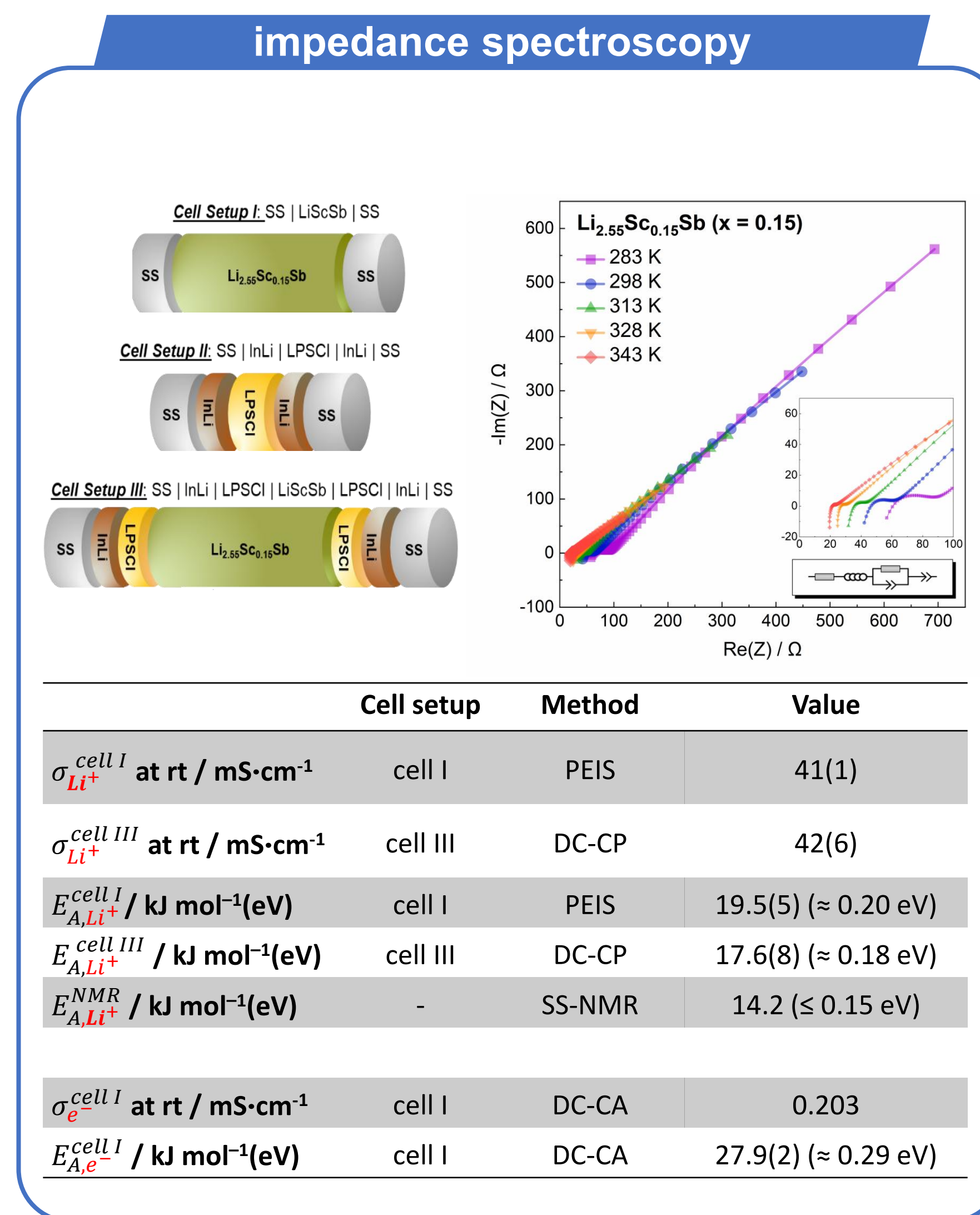
Structure of $Li_{3-3x}Sc_x□_{2x}Sb$ ($0 < x \leq 0.15$)

- Cubic close packing of Sb atoms.
- Tetrahedral voids are fully occupied by Li1 and Sc with statistical disorder.
- Octahedral voids are partially occupied by Li2, with 10%-30% remaining vacant due to gradual Sc substitution.

Space group $Fm\bar{3}m$
Lattice parameter $a / \text{\AA}$ 6.5930(2) - 6.6279(8)



III. Li-ion Mobility in $Li_{2.55}Sc_{0.15}Sb$

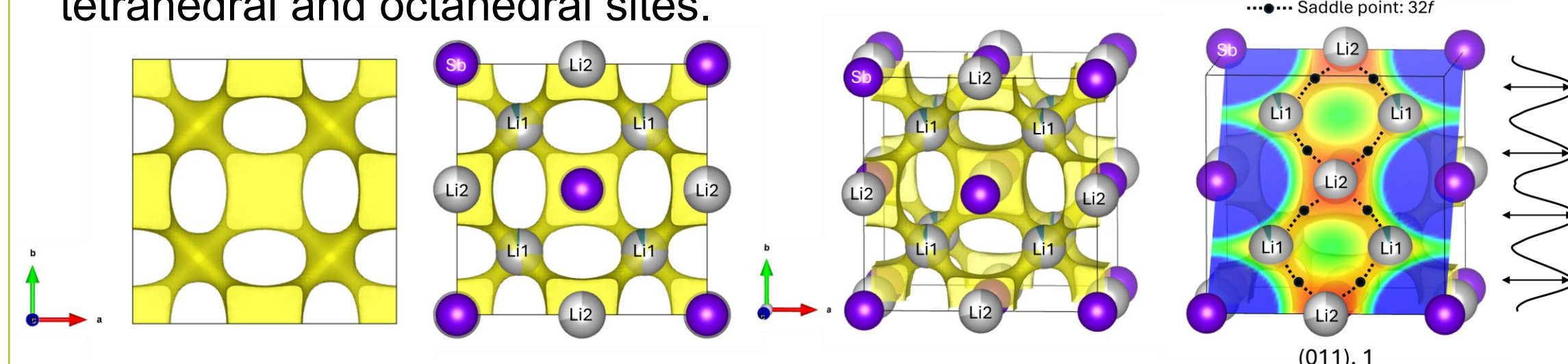


V. Conclusion

- The series of new compounds $Li_{3-3x}Sc_x□_{2x}Sb$, maintains the β - Li_3Sb structure up to a nominal composition of $x(\text{Sc}) = 0.15$, with Sc^{3+} ions occupying the tetrahedral voids of the face-centered cubic Sb anion arrangement.
- Aliovalent substitution of Li with Sc has induced structural disorder and created vacancies at the octahedral site that generate energy-favorable ion migration landscape and facilitate efficient Li^+ transport.
- $Li_{2.55}Sc_{0.15}Sb$ exhibits the fastest Li-ion conductivity (42 mS/cm at 298 K) with a very low activation energy of 17.6(8) kJ·mol⁻¹, outperforming the state-of-the-art HEM sulfides while maintaining a concise chemical composition.
- This work proposes a general design strategy for vacancy engineering in which replacement of Li with Sc in simple binary compounds has a direct impact on the ion mobility.

IV. Lithium Diffusion Pathways

- A continuous 3D diffusion network
- Li-ion motion occurs preferably via hopping between the face sharing tetrahedral and octahedral sites.



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