Comprehensive First Principles Study of Intrinsic Point Defects in Li_3PS_4

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The realisation of solid-state batteries (SSBs) is contingent on the development of highly conductive solid electrolytes. Li_3PS_4, as the archetypal member of the promising thiophosphate family of Li-ion conductors emerges as a pivotal candidate, boasting distinctive properties essential to this application. With its outstanding lithium-ion conductivity, stability when paired with lithium metal and superior formability, Li_3PS_4, and its derivatives, stand as frontrunners in the pursuit of safer and more efficient energy storage. Despite these promising attributes, the efficacy of Li_3PS_4, and indeed other promising multinary electrolytic systems, is intricately linked to a nuanced understanding of defects within their structural framework - of which little is understood. The structural freedom, disorder, and somewhat amorphous nature of such materials, while rendering them uniquely promising, also present vast challenges in adequate defect exploration. On this basis, we provide a comprehensive defect study employing a global structure searching strategy [1] on two of main polymorphs of Li_3PS_4, namely γ and β. It is hoped that this study serves as an exemplar, setting a precedent for a rigorous investigation into the battery defect configurational landscape.

[1] I. Mosquera-Lois, et.al., "ShakeNBreak: Navigating the defect configurational landscape", J., 7. 4817. (2022)