Morphology map of β-Li_3PS_4 nanocrystal by Wulff theory

Naiara L. Marana[1,*], Silvia Casassa[1], Mauro F. Sgroi[2], Anna Ferrari[1], and Lorenzo Maschio[1]

[1]Theoretical Group of Chemistry, Chemistry Department I.F.M., Torino University, Italy

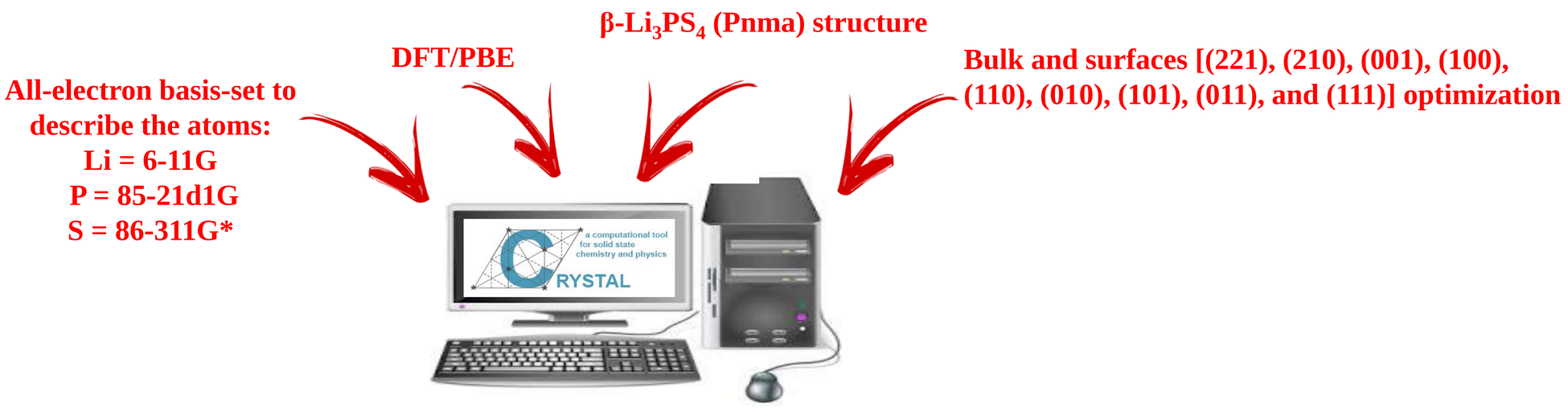
[2]Centro Ricerche Fiat S.C.p.A., Strada Torino 50, Orbassano, 10043, Italy

naiaraleticia.marana@unito.it

Introduction

β-Li_3PS_4 is very applied as a solid electrolyte in lithium batteries, it is excellent ionic conductivity and is stable with a metallic lithium anode.[1] Many are studies dedicated to obtaining ideal characteristics for this material. However, as far as we know, there are no theoretical works that discuss the changes in the morphology of the β-Li_3PS_4 and its possible crystal shapes, achieved through the modifications and stabilization of its surfaces. MODALIS^2 is a multicountry European research program that aims to investigate new materials into next-generation lithium-ion batteries to integrate electric vehicles. In this sense, supported by MODALIS^2, this study proposes a morphology map of all crystal shapes possibilities for β-Li_3PS_4, by applying the Wulff classical theory.

Theoretical model and methodology



Results

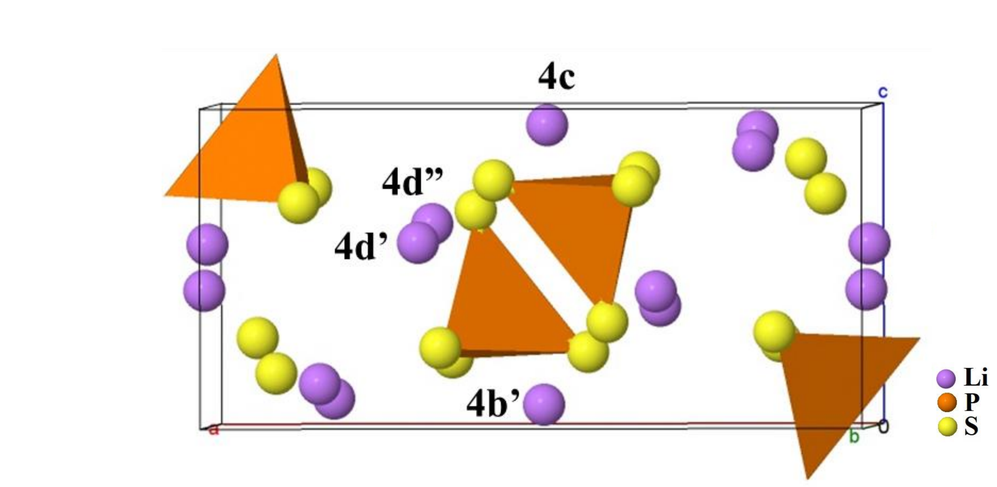


Figure 1: Optimized Pnma structure of Li_3PS_4 with Li Wyckoff positions (4b’, 4c, 4d’, and 4d”).

Table 1: Surfaces termination (up/down), surface energy (E_{surf}, in J/m^2), formation energy (E_{form}, in kJ/mol), and bandgap (E_{gap}, in eV) for the nine surfaces of β-Li_3PS_4 with 8 units each.

	Termination	E_{surf}	E_{form}	E_{gap}
(001)	LiS_2/LiS_2	2.15	31.94	1.82
(100)	LiS_2/LiS_2	0.91	2.19	4.66
(010)	LiS_2/Li	1.83	5.16	2.70
(101)	PS_3/SPLi	8.20	54.10	0.46
(011)	PS_3/Li	1.43	5.24	4.24
(110)	SLi_2/Li	2.27	32.22	1.99
(111)	LiS_3/Li	1.60	10.91	2.21
(210)	SPLi/Li	0.99	5.88	4.20
(211)	LiS_2/SPLi	1.57	11.84	2.14

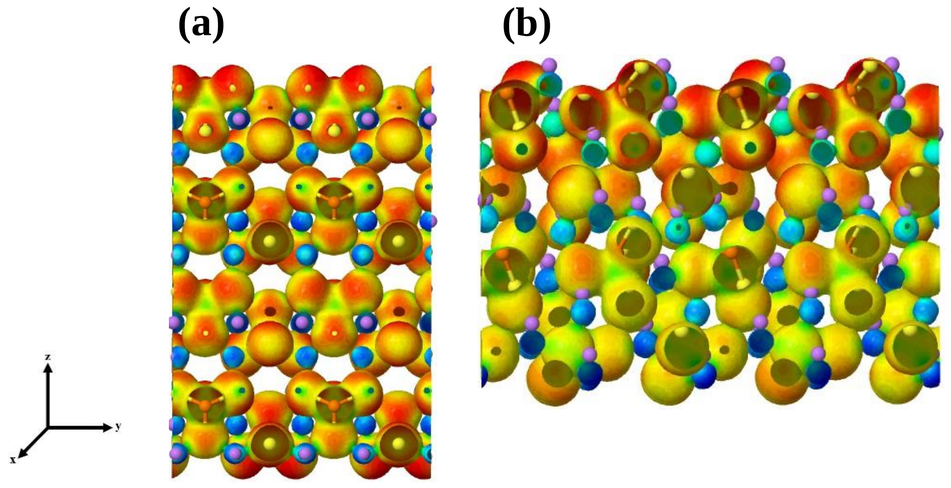


Figure 2:Three-dimensional maps of the electronic charge density superimposed to the electrostatic potential of β-Li_3PS_4 surfaces along z-direction: (a) (100) and (c) (011). The scale maps range from negative (-) in blue to positive (+) in red.

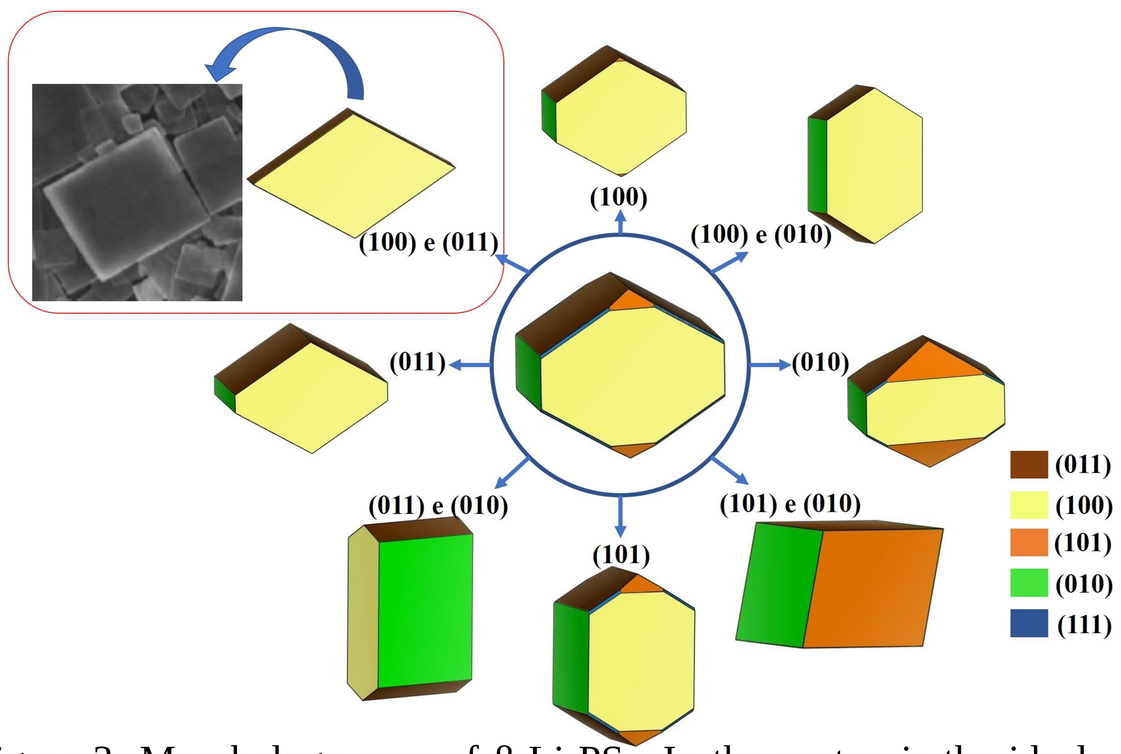


Figure 3: Morphology map of β-Li_3PS_4. In the center, is the ideal crystal. Each arrow indicates the direction of stabilization of one or two surfaces by decreasing the E_{surf}. On the left, is the SEM of β-Li_3PS_4 obtained by Hood and co-authors[2].

Acknowledgmets

The financial support by the MODALIS2 project, grant agreement No. 875193 of the European Union’s Horizon 2020 research and innovation program, is gratefully acknowledged

References

[1]J. C. Bachman, S. Muy, et. al, Chem. Rev.2015, 116, 140;
[2]Hood, Z. D., Wang, H., et. al, Adv. Energy Mater. 2018, 8, 1800014.