

# Can LiFePO<sub>4</sub> be aliovalently doped?

Jishnu Bhattacharya, Chris Wolverton

Northwestern University

LiFePO<sub>4</sub> is an attractive cathode material for Li-ion batteries. However, low conductivity is a major drawback. Many researchers have explored several treatments to improve the conductivity, one of which is doping the material with other metals. Since the report of conductivity enhancement by 8 orders by alloying LiFePO<sub>4</sub> with aliovalent dopants<sup>1</sup>, there has been significant controversy over the possibility of large scale doping. Some argue that significant amounts (more than 10 at%) of aliovalent dopants (Zr/Nb/V/Mo) can be inserted into bulk LiFePO<sub>4</sub> and the doping causes the conductivity improvement<sup>1-3</sup>. Others argue that bulk-LiFePO<sub>4</sub> accepts only less than 3 at% of dopant and the observed improvement of conductivity is due to the presence of carbon or due to surface/grain-boundary effects<sup>4-6</sup>. While several theoretical studies<sup>6</sup> investigated the thermodynamic possibility of doping, lack of information on the complete phase diagram and hence assumptions about the possible ground states and defect configurations have left the debate unsettled. We shed light on this controversy by calculating the solubility limit of supervalent dopant (Zr) in LiFePO<sub>4</sub> under experimental synthesis conditions from first-principles calculations. We construct complete quinary phase diagram as a function of the chemical potential of oxygen (a function of synthesis condition) by calculating all possible phases from the ICSD (Inorganic Crystal Structure Database) with DFT and applying GCLP<sup>7</sup> (Grand Canonical Monte Carlo) simulations to identify relevant ground states. Several possible defects which incorporate dopant atoms in bulk LiFePO<sub>4</sub> are calculated with DFT as a function of supercell size. We find that there is at least one low energy defect which can be significant enough at high synthesis temperature to incorporate a large amount of Zr in LiFePO<sub>4</sub>. Our study shows that thermodynamic solubility limit for supervalent metals can be quite high in olivine LiFePO<sub>4</sub> and thereby settles the decade-old debate on the possibility of doping.

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