Ab initio study of electronic study of simple and transition metal-doped $Li_4Ti_5O_{12}$

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The $Li_4Ti_5O_{12}$ (LTO) defect spinel is a promising anode material for lithium-ion batteries (LIBs) because it transforms to/from $Li_7Ti_5O_{12}$ with a negligible volume change during charging/discharging. [1] However, the intrinsic insulting property of LTO is a major drawback. Doping is a direct approach to manipulate the intrinsic electronic conductivity of LTO. However, the doping-induced effects on electronic and electrochemical properties are unclear probably due to the complicated nature of interplays between dopants and LTO matrix in experiments. In this work, we systematically investigated the simple metal-doped LTO (M = Na, K, Mg, Ca, Sr, Al, and Ga) and transition metal-doped LTO (M=Zr, Nb, Ta, Cr, Mo, W, Mn, Fe, Co, Ni, and Cu) using *ab initio* calculations. The metal dopants can be classified into four types. Type I dopants do not change the electronic structure of LTO. Type II dopants provide extra electrons to the Ti 3d band and increase the electronic conductivity; they further classified into Type IIa (provides one electron as seen in Figure 1), and Type IIb (provides two electrons) dopants. Type III dopants provide extra holes but cannot contribute extra electron to the Ti 3d band, and they are not able to increase the electronic conductivity of LTO, and Type IV dopants create n-type defect levels which enhance the electronic conductivity of the $Li_4Ti_5O_{12}$ endmember.

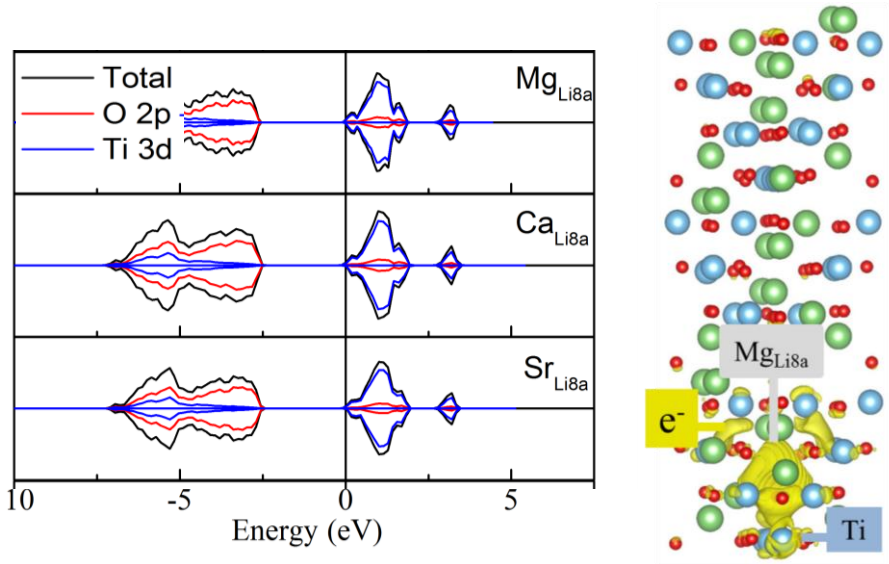

Figure 1. Type IIa simple metal-dopants and their total density of states (inset shows charge density distribution for Mg-doped LTO)

References:

[1] P.-C. Tsai, W.-D. Hsu, S.-K Lin, J. Electrochem. Soc., 161, A439-A444 (2014)