Solid State Communications 147 (2008) 505–509

Contents lists available at ScienceDirect

Solid State Communications

journal homepage: www.elsevier.com/locate/ssc

First-principle investigations of N doping in $LiFePO_4$

Zhaojun Liu, Xuejie Huang*, Dingsheng Wang

Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China

ARTICLE INFO

Article history:
Received 22 February 2008
Accepted 11 June 2008 by E.G. Wang
Available online 18 June 2008

PACS:
74.62.Dh
71.20.-b
66.30.Dn
61.72.-y

Keywords:
A. $LiFePO_4$
A. N doping
D. Electronic band structure
D. Ion transport

ABSTRACT

N doped $LiFePO_4$ has been investigated by using first-principle calculations with the projector augmented wave (PAW) method. The effect of N doping on its crystal structure, charge distribution and transport properties have been studied within the Generalized Gradient Approximation (GGA) + U framework. To maintain charge balance, the valence of the Fe nearest to N appears as Fe^{3+}, and it will benefit for the hopping of electrons. The Elastic band method was used to calculate the activation energy for Li diffusion. N doping leads to slightly lower activation energy.

© 2008 Elsevier Ltd. All rights reserved.

1. Introduction

In 1997, Pahdi et al. [1,2] proposed $LiFePO_4$ as an alternative to the currently used transition metal oxide cathode materials for Lithium ion batteries. The material has attracted much scientific and technological interest since then. Major drawbacks of $LiFePO_4$ are its relatively low electronic conductivity [3], $LiFePO_4/FePO_4$ phase separation [4], and its slow intrinsic ion transport which occurs mainly at interfaces of the two existing phases [5]. The electron conductivity is $\sim 10^{-9}$ S cm^{-2} with activation energy of about 0.6 eV [6], and the activation energy for Li diffusion is also about 0.6 eV [7]. Various approaches have been used to improve its electronic and ionic conductivity, e. g. surface coating [8], cation doping [9]. Chiang et al. reported that its electrochemical performances can be significantly improved by Li site doping [10], and shi et al. reported much enhanced electron conductivity of $LiFePO_4$ after Cr doping. [11] Controversy still exists concerning whether the supervalent ions have substituted the Li ions, or the improved conductivity is caused by a conductive nano-network [12,13].

Bates et al. found that N doped Li_3PO_4 leads to higher ionic conductivity [14]. We expect that N doping will influence the transport properties of $LiFePO_4$. Different from Li_3PO_4, the valence of Fe is variable in $LiFePO_4$, the doping of N may induce an Fe^{3+} ion. And the coexistence of Fe^{2+}/Fe^{3+} couple leads to better electron conductivity. The activation energy for Li diffusion is also expected to be affected by N doping. To give a quantitive analysis, first-principle calculation is carried out to investigate the effect of Nitrogen doping in $LiFePO_4$.

2. Method

Usually the calculated lattice parameters, ground state energy, and electronic structure from LDA/GGA (Local Density Approximation/Generalized Gradient Approximation) agree well with the experimental results. However, it will lead to considerable errors when dealing with transition metal compounds, because LDA/GGA tends to delocalize the strongly correlated 3d electrons. To avoid such embarrassment, the DFT + U approach can be implemented [15,16]. The rotationally invariant approach by Dudarev et al. [17] is used in this work. The results of GGA + U are dependant on the U value, based on the self-consistent calculated effective U_{eff} value of 3.7 eV for $LiFePO_4$ and 4.9 for $FePO_4$ [18], we use an average U value $U_{eff} = 4.3$ eV in both the pure and N doped case. The band gap and Li intercalation voltage plateau calculated with such a U value agrees well with experiments [1,18,19]. The Elastic band method is used to calculate the activation energy for Li hopping [20]. This approach duplicates a series of images between the start point and end point of ion hopping. With the positions of the start point and end point fixed, images are allowed to relax perpendicular to the diffusion path, and an elastic force is applied to

---

* Corresponding address: Institute of Physics, Chinese Academy of Sciences, Beijing 100080, China. Tel.: +86 10 82648073; fax: +86 10 82649046.
E-mail address: xjhuang@aphy.iphy.ac.cn (X. Huang).

0038-1098/$ – see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2008.06.013

Table 1
Oxygen vacancy formation energy in undoped and doped $LiFePO_4$

	$Li_4Fe_4P_4O_{16}$	$Li_4Fe_4P_4O_{14}N_2$ (conf1)	$Li_4Fe_4P_4O_{14}N_2$ (conf2)
E_{Vo} (eV)	−182.29	−181.44	−182.39
μo (eV)	−4.89	−4.89	−4.89
E_{LiFePO_4} (eV)	−191.87	−191.09	−190.81
$E_{form}(V_o)$ (eV)	4.69	4.76	3.53

The oxygen vacancy formation energy is calculated with the formula $E_{form}(V_o) = E_{Vo} + \mu_o - E_{LiFePO_4}$. Conf1 is the configuration with N atoms and O vacancy located near one Fe site; conf2 is the configuration with N atoms and O vacancy located near one P site.

the images to ensure all the images relaxed to the minimum energy path(MEP).

Calculations were performed in a plane wave basis set using the projector augmented wave (PAW) [21] method in the GGA + U framework implemented in the VASP program. An energy cutoff of 600 eV and a $3 \times 5 \times 6$ k-point mesh were chosen to ensure the total ground state energy to be converged was within 2 meV per atom. Internal coordinates and cell parameters were fully relaxed. The relaxed cell parameters of $LiFePO_{3.75}N_{0.25}$ are $a = 10.39$ $b = 6.00$ and $c = 4.76$ while that of $LiFePO_4$ is $a = 10.42$ $b = 6.06$ $c = 4.74$. Fermi level was smeared by the Gaussian method with a smearing width of 0.03 eV. This ensures the entropy term of the electron is far below 1 meV. For elastic band calculations, due to the relative flatness of the band structure below the Fermi level, two unit cells were chosen for the calculation and only the Γ point was considered. Lattice parameters were fixed at the experimental values of $a = 10.329$ $b = 6.006$ and $c = 4.698$. Internal coordinates were fully relaxed at the starting point and end point of the migration. All coordinates were linearly interpolated to form 3 images in the migration pathway.

3. Results and discussion

$LiFePO_4$ has orthorhombic structure and belongs to the Pnma space group [22]. There are four formula units in each unit cell. Oxygen atoms occupy two 4c sites and one 8d site, labeled as O1, O2 and O3 sites. Iron and lithium occupy the centers of the slightly distorted oxygen octahedra while phosphors occupy the centers of oxygen tetrahedra. The corner sharing octahedra are separated by tetrahedrons. The shared corner of the Fe–O6 octahedra is the O3 site. When O is replaced by N, to maintain charge neutrality, either Fe^{3+}or O vacancy must appear. The formation energy of O vacancy can be described as

$$E_{form}(V_o) = E_{Vo} + \mu_o - E_{LiFePO_4}.$$

Here μ_O is the chemical potential of oxygen. E_{Vo} and E_{LiFePO_4} are the total free energies of $LiFePO_4$ with and without oxygen vacancies, respectively. [23] Taking half of the O_2 molecular ground state energy as the chemical potential of oxygen, the vacancy formation energies of doped and pure $LiFePO_4$ are listed in Table 1. The oxygen vacancy formation energy of $LiFePO_{3.5}N_{0.5}$ is 4.76 eV and 3.53 eV for two different O_{vac}/N configurations, while that of $LiFePO_4$ is 4.69 eV. The formation energy of the oxygen vacancies is rather high both in the doped and pure $LiFePO_4$ though it varies with the O_{vac}/N ordering. This is comparable with the case in KH_2PO_4 (KDP), the oxygen vacancy formation energy is 5.25 eV and the percentage oxygen vacancy in a KDP crystal is about 1 ppm [23]. The oxygen vacancy concentration can be estimated by $n/n_0 = \exp(-E_f/2K_bT)$, if $E_f = 3.53$ eV and $T = 1073$ K, $n/n_0 = 5 \times 10^{-9}$. Very low concentration of oxygen vacancy is expected in pure and N doped $LiFePO_4$.

The total energy of $LiFePO_4$ after N doping at the O3 site is 83 meV and 91 meV lower than that at the O1 and O2 site. N doping causes local distortions in the lattice. The P–N bond length becomes slightly longer than the P–O bond while the Fe–N bond is shorter than the Fe–O bond. The distortion of the Fe–O octahedron is significant as shown in Fig. 1. The distance between O3 site and its two adjacent Fe sites are 2.261 Å and 2.086 Å, and the N on O3 site tends to be attracted to the neighboring Fe atom.

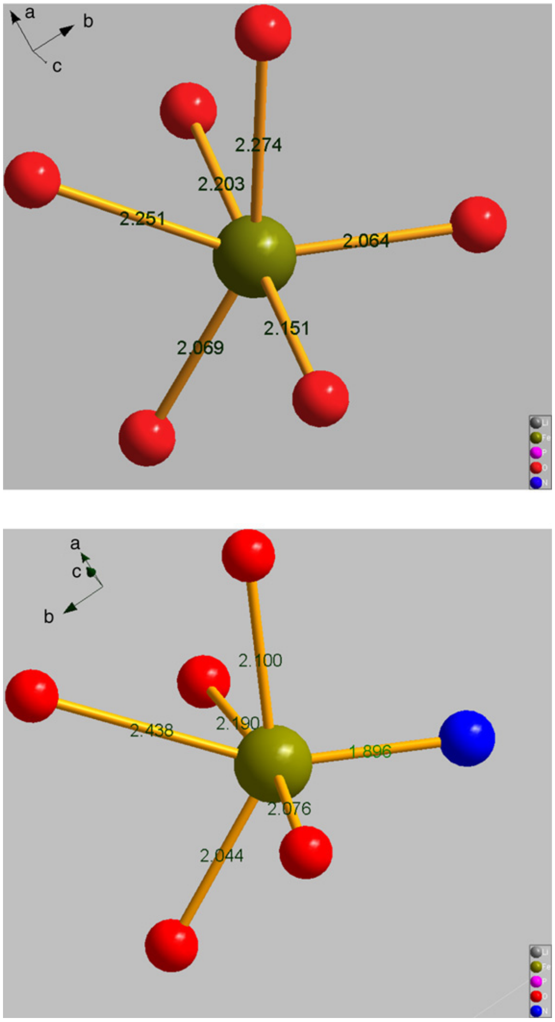

Fig. 1. The distortion of the Fe–O octahedral caused by N doping, up: Fe–O octahedral. down: distortion of the octahedral when O is replaced by N, the Fe–N bond is shorter than the Fe–O bond, N doping also affects the Fe–O bond length.

The calculation result of the electron occupation matrix shows the valence of Fe in $LiFePO_4$ is +1.9. Fe ion bonded with N shows lower ionicity(+2.2) than that in $FePO_4$(+2.3). Further analysis with differential spin integration agrees well with this result. Due to the strong inductive effect of the $(PO_4)^{3-}$ anion, the difference between the Fe^{3+} and Fe^{2+} in $LiFePO_{3.75}N_{0.25}$ is more significant than that in Fe_3O_4 (0.2e as calculated by Jeng etc. [24]).

Fig. 2 shows the density of states (DOS) of pure and N doped $LiFePO_4$. New states appear in the band gap of pure $LiFePO_4$ after N doping, and the band gap drops from 3.7 eV to 1.3 eV. The hybridization of Fe3d and N2p leads to a narrower band gap. From the atom projected DOS we can see that the new states in the band gap of $LiFePO_4$ are induced by the interaction of the Fe–N bond and it is localized around the Fe and N ions.

The charge density distribution on the Fe–N–P plane and the Fe–N line is shown in Fig. 3(a) and (b). The energy resolved charge density distribution on the valence band top and conduction band bottom are shown in Fig. 3(c) and (d). From the electron density distribution on the Fe–N bond, we can see that Fe and N are not completely ionized. Charge near the valence band top localizes around the Fe atoms and the N atom. The valence of the Fe nearest

Download English Version:

https://daneshyari.com/en/article/1595314

Download Persian Version:

https://daneshyari.com/article/1595314

Daneshyari.com