International Journal of Computational and Experimental Science and ENgineering (IJCESEN)

Vol. 12-No.3 (2026) pp. 205-210
http://www.ijcesen.com

ISSN: 2149-9144

Research Article

Electronic properties of lightweight intermetallic Li-Al hydrides in the β-phase

Farouk. Ladjaïlia[1,2]*

[1]Laboratory of Photonics Group, Renewable Energy Development Research Unit in Arid Zones, El Oued University, El Oued 39000, Algeria
[2]Department of Physics, Faculty of Exact Sciences, El Oued University, El-Oued 39000, Algeria.
* **Corresponding Author Email:** farouk ladjailia2014@gmail.com- **ORCID:** 0000-0002-8621-4290

Article Info:

DOI: 10.22399/ijcesen.5401
Received : 11 January 2026
Revised : 21 May 2026
Accepted : 01 June 2026

Keywords

Ab initio calculations;
WIEN2k;
Electronic properties;
Intermetallic hydrides;
Hydrogen storage.

Abstract:

An ab initio electronic structure study of the potential light-weight hydrogen storage materials LiAlH4 in their β-phase, is presented. Electronic band structures and total and partial densities of states are calculated by using the WIEN2k simulation code. We estimate an energy bandgap of ca. 4.11 eV for the β -LiAlH4 tetragonal (I41/a space group) semiconductor. In the latter, the valence band is formed by two distinct energy bands originating from hydrogen orbitals hybridization with metal atomic orbitals. It is found that these quantities are similar but distinguishable in the β-LiAlH4 compound. The β -LiAlH4. Results are discussed with available published data.

1. Introduction

Hydrogen storage in metallic hydrides is the subject of intensive research, fundamental and applied, with the aim of discovering suitable compounds which will fit in the envisioned sustainable economy utilizing hydrogen, a clean and procurable combustible, as an energy vector [1-9]. Among complex hydrides, AMH_4 compounds form an extensive family, where A stands for an alkali metal (A=Li, Na, K from the first column of the periodic table) and M stands for a third column element (M=B, Al, Ga). Lithium-Aluminium hydrides, also known as alanates, which are serious hydrogen storage candidates owing to their fair weight and high H tenor, form several compounds depending on ambient preparation conditions [10]. These have acquired a growing importance as anode materials in solid-state lithium ion batteries due to the particular conductivity of Li^+ ions [11]. The actual phase formed depends on temperature and, more practically, on applied pressure. Vajeeston et al [12] identify three phases for our first studied $LiAlH_4$ compound: a monoclinic α-phase below 2.6 GPa, followed by a tetragonal β-phase up to 33.8 GPa when an orthorhombic γ-phase sets in. The middle has a *I41/a* symmetry. The crystallographic cell contains two formula units. The crystal structure can also be described in terms of AlH4 tetrahedra, allowing the Al atom to see an irregular octahedral surrounding. The building block of all these phases is a negatively charged tetrahedron of four H atoms surrounding an Al atom (in its center), $[AlH_4]^-$, bonded to a positively charged Li^+ ion [12]. These authors report that these phases have not been entirely unraveled and several models have been suggested to explain accessible experimental diffraction data. In this work, we investigate by *ab initio* calculations the structure of the less-studied high pressure β -phase for compounds $LiAlH_4$, in order to gain new insight into these systems. In the following, first principles computations of band structures, partial and total densities of states, are reported and discussed in the light of available published literature [12-14].

2. Computational methods

The calculated results in this paper were obtained using the full potential linearized

augmented plane wave plus local orbitals (FP-LAPW+lo) [15-18] method within the framework of density functional theory (DFT) [17, 18] as implemented in the WIEN2k code [19, 20]. This method uses the muffin-tin geometry separating space into distinct spheres and an interstitial region. For the exchange correlation potential, we used the generalized gradient approximation as defined by Perdew et al. [21-24]. We used the scalar relativistic approach.In the calculation, the H ($1s^1$), Li ($1s^2 2s^{1)}$ and Al ($2p^6 3s^2 3p^1$) states are treated as valence electrons. The muffin-tin radii R_{MT}, which are chosen such that the MT spheres do not overlap, are taken to be 0.8 Bohr for H, 1.7 Bohr for Al and 1.5 Bohr for Li in the β-$LiAlH_4$ phase (**Fig. 1**) [12].The basis functions were expanded up to $R_{MT} \times K_{max} = 5$, where R_{MT} is the smallest of all MT sphere radii and K_{max} is the maximum value of the wave vector K. The number of K-points which ensures total energy convergence in the whole Brillouin zone, was 1000 for the orthorhombic β-$LiAlH_4$ structure. The self-consistent calculations are considered to be converged when the total energy becomes stable within 0.1 mRyd.

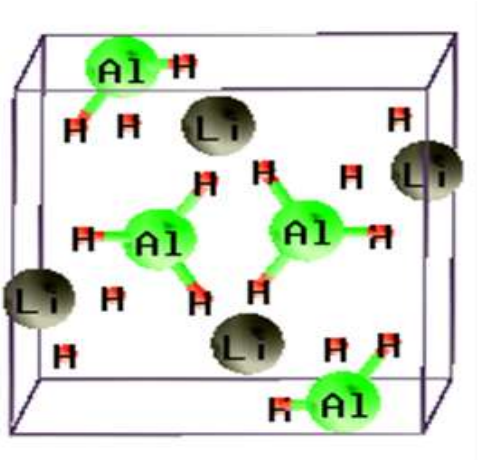


Figure 1. *β-$LiAlH_4$ phase structure (I41/a space group).*

3. Results and discussion

3.1 Structural properties

The total energy vs. volume curves E (V) were fitted to the Murnaghan equation of state (EOS) [25], for both calculated β-$LiAlH_4$. **Table 1** displays optimized structural parameters for β-$LiAlH_4$ structures along with other data from the literature. Lattice parameters and internal atomic positions identified at the equilibrium position are listed, together with available experimental data and previous theoretical works for comparison purposes [12].

Table 1. *Optimized structural parameters for β-$LiAlH_4$ (I41/a) from our calculations and other works*

Structure	**Lattice constants (in Å)**	**Atom coordinates**
β-$LiAlH_4$ *tetragonal* *(I41/a)*	a = 4.5659 [x] (4.6611) [y] c = 10.3071 [x] (10.5219) [y]	Li: 0.0000; 0.25; 0.625 [x] (0.0000; 0.25; 0.625) [y] Al: 0.0000; 0.25; 0.125 [x] (0.0000; 0.25; 0.125) [y] H: 0.2479; 0.5781; 0.5408 [x] (0.2527; 0.4237; 0.5413) [y]

[x]: This work..
[y]: Our previously calculated value at equilibrium from Ref. [12].

Table 2. *Equilibrium volume V_0 ($Bohr^3$/f.u), bulk modulus B_0 (GPa) and its corresponding pressure derivative B_0' for β-$LiAlH_4$ (I41/a) with other calculations.*

Structure	**V_0 ; B_0 (GPa) ; B_0'**	
	This work	**Other work**
β-$LiAlH_4$ *(I41/a)*	53.72 ; 25.07 ; 4.89	none ; 25.64 ; 4.35 [y]

[<y]: Calculated value from Ref. [12].

Optimized lattice parameters show a slight increase of 0.2 % when compared to the previous theoretical work of Vajeeston et al [12-15]. To our knowledge, no experimental values exist in the literature. In **Table 2**, the calculated equilibrium volume V_0 for one formula unit, the bulk modulus B_0, and the pressure derivative B_0' are displayed for β-$LiAlH_4$ *(I41/a)* structure. We can observe that our calculated B_0 and B_0' values agree well with those reported elsewhere [12].Quantum numbers are illustrated in **Table3,** [12] following: This method uses muffin-tin geometry separating space into distinct spheres and an interstitial region. For the exchange correlation potential, we used the generalized gradient approximation as defined by Perdew et al. [7-10]. In the following, we are going to use these equilibrium values to

investigate electronic of β-$LiAlH_4$ *(I41/a)* structure.

3.2 Electronic properties

3.2.1 Band structures

a. β-$LiAlH_4$ *(I41/a)*

The calculated band structures in **Fig. 2** exhibit a finite energy gap between the valence and conduction bands for the tetragonal phase β-$LiAlH_4$. the valence band maximum and the conduction band minimum are located at the Γ point which causes a direct band gap of about 4.11 eV implying a semiconducting behavior at high temperature. The band gap of this compound was found in previous work [14] to be larger than 4eV at low pressure. However, at high pressure, the band structure changes and the band gap decreases. The valence band is represented by a single band located between -7.8 eV and E_F. The latter occurs at around 0.025 eV. Using a grid of 111 points in the 1/48 of the Brillouin zone, according to eight lines of high symmetry including the points: Γ_Δ_H_N_ Σ_ Γ _ Λ_PThe theoretical structural parameters were used to perform the calculations. Figure 2 corresponds to the band structure of the compound β-$LiAlH_4$ tetragonal (I41/a) and using the GGA approximation:

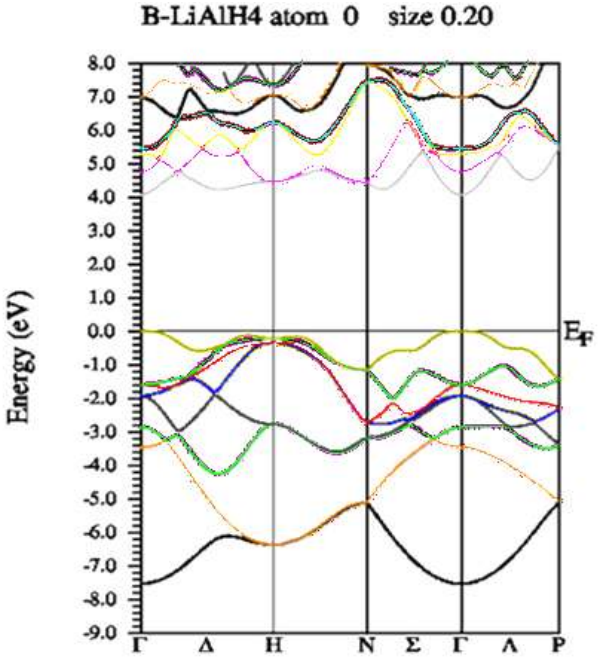


Figure 2. *Band structures of β-$LiAlH_4$*

First of all, we will bring out from the band diagram the observations that seem useful and beneficial for the discussion, then compare them with other theoretical and experimental results in order to finally be able to give a logical interpretation [17].

1) Common findings:

i) The band diagram shows that the compound β-$LiAlH_4$, possess an direct fundamental gap [Γ- Γ], the maximum of the valence band is located at the point Γ while the minimum of the conduction band is located at the point Γ.
ii) The first (i.e., lowest) valence band derives mainly from the ns^2 state, (n= 1 and 3 for H and Al, respectively). This band has a maximum dispersion between the point Γ.
iii) The upper band, which is represented by two degenerate states, originates from the np band, its dispersion is maximum between the points H and Γ.
iv) The first conduction band comes from the 3s state of the sodium atom. The values of the energies were taken at the points of high symmetry relative to the Fermi energy E_F.The width of the valence band is maximum for the compound β-$LiAlH_4$. This means that the first (lowest) valence band, which is mainly derived from the ns band of the anion, is shifted in energy much more. This corresponds perfectly with the order of the bands $1s^2$ for H and $3s^2$ for Al. Si de refers to the ionicity of the compound [12-18].

Table 3; *The calculated energy gap Eg (eV) of β-$LiAlH_4$ tetragonal structure at the equilibrim volume, with other calculations*

E_g(eV)	
Structure **other calculations**	**this work**
β-$LiAlH_4$ 4.25[y]	4.11

[y]: Calculated value from Ref. [12].

It is interesting to compare our calculated band gaps with other results. In Table 3 we have compared our work and other results. The GGA calculations on β-$LiAlH_4$, by Vajeeston et al.[12].

3.2.2 Total and partial densities of states

a. β-$LiAlH_4$ (I41/a)

The distribution of charge density associated with the valence band is an important aspect of electronic structure since it indicates the nature of crystal bonds. It is in this context that we studied the distribution of the charge density of the compound β-$LiAlH_4$ tetragon (I41/a). We performed the representation of the contour using a self-consistent calculation based on the GGA [12]..The observations that can be made are:

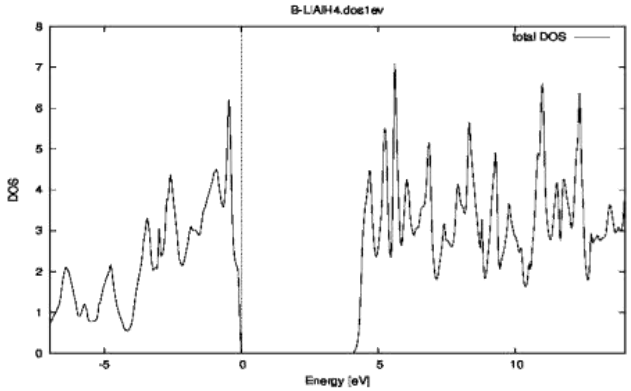
i)The distribution of the charge density is essentially around anion $[AlH4]^-$.

ii) Between the atoms (Li and [AlH4]), there is a fraction of this charge. It seems that it is pronounced in the compound β-$LiAlH_4$.

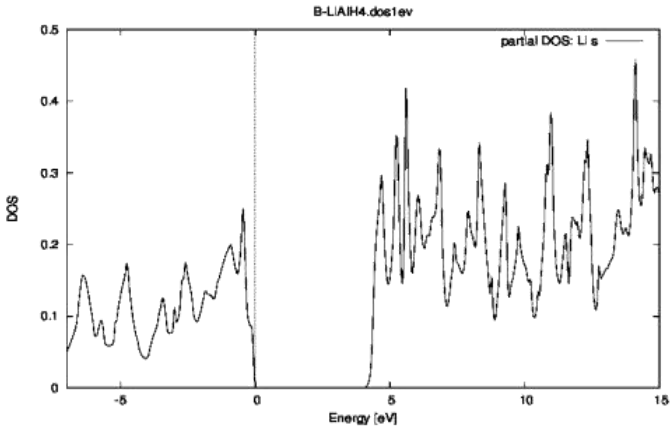
iii) The distribution of the charge density around the anion is more spread out around the [AlH4]. One of the peculiarities of these compounds lies in the Li^+ atom which is very small in front of the $[AlH4]^-$ anion, so it is obvious that most of the charge is around the anions. It is also accepted that this compound is a partially ionic insulator[25] and therefore the charge density between the atoms will not be important in any way, which is perfectly consistent with our results.

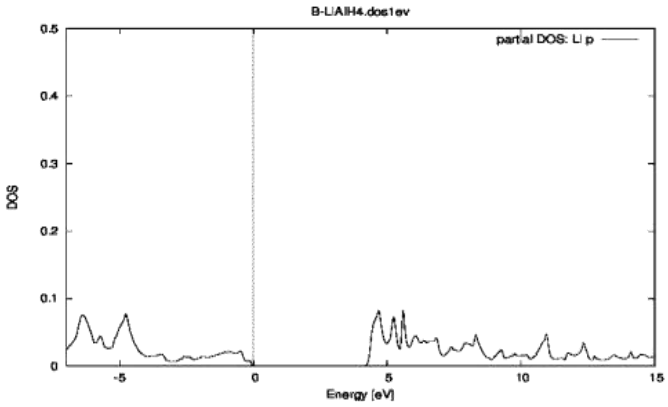
iv) Especially since the Li atom does not have p-type electrons that are generally responsible for establishing covalent bonds. This is probably due to the difference between the electronegativities of these anions. And the reason why the cohesion energy and compressibility modulus doubled.The total densities and partial densities of states are illustrated as **Fig.3-4-5-6 a** (total for compound), **b** (partial for s and p orbitals in Li), **c** (partial for s, p, and d orbitals in Al), and **d** (partial for s orbital in H). Based on **Fig.3-4-5-6**. The lowest valence band in each structure has a maximum dispersion in the vicinity of the point . It is located at an energy equal to (-6.5 eV,-3.6 eV) for β-$LiAlH_4$. This band corresponds to the

(a)

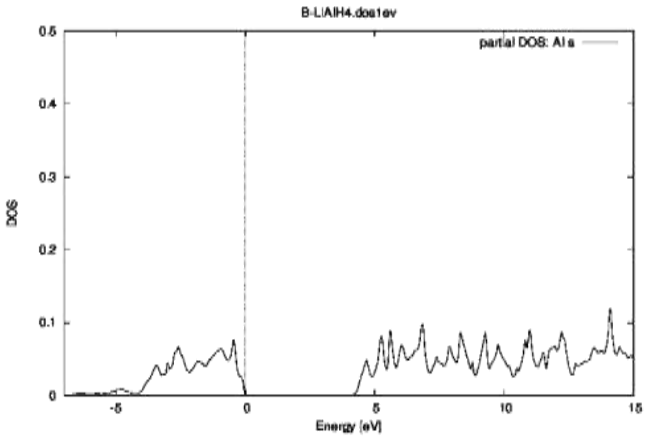


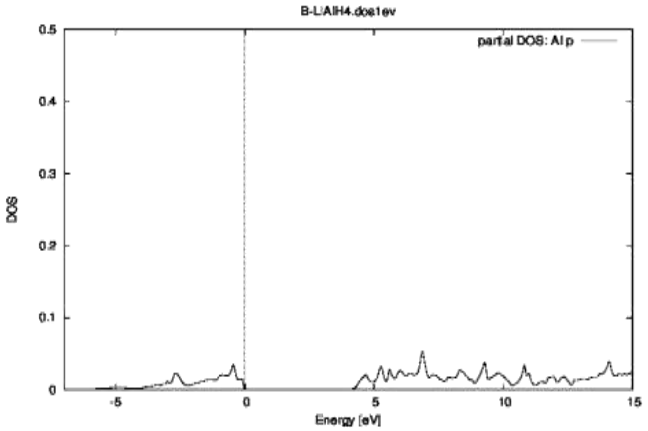
(b)

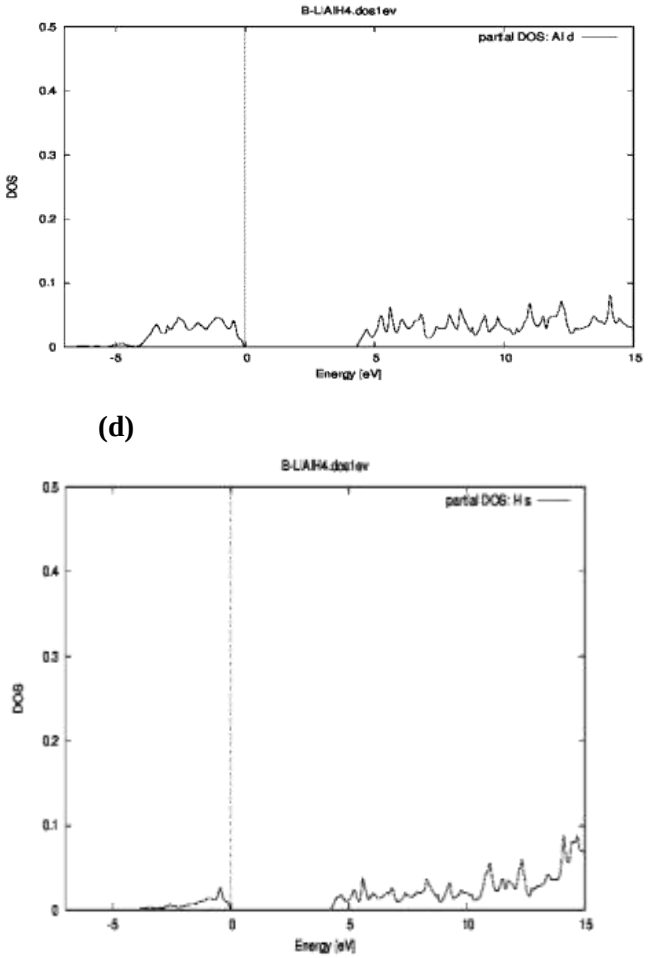




(c)







Figures 3-4-5-6. *Total (a) and partial densities of states for Li (b), Al (c) and H (d) atoms in β-LiAlH₄.*

first peak that appears in the total density of states. It is essentially. formed by the 1s and 3s states of the H and Al atoms respectively [12-24]..The rest of the valence bands corresponding to the structure extended between (-2.7eV and 0.15497 eV) for β-$LiAlH_4$ is usually due to the 3p states of the Al atom and the 1s state of the H atom, with a small contribution of the 3s state of the Li atom.Continuing in increasing energy, we see that the compound is insulating by direct gap [Γ- Γ] equal to (4.11 eV) for β-$LiAlH_4$.Above the fermi level (E_F = - 0.0286456616 eV) the structure corresponding to the conduction band corresponding to the extended structure between (4.11373 eV, 14.98529 eV) is a mixture of the s and p states of the atoms constituting the compounds studied. The results on the covalent interaction is strong operating between the H ion and the AL ion forming in the $[AlH4]^-$ tetrahedron ion. Also the charge transfer occurs mainly between the Li ion (cation) and the $[AlH4]^-$ ion (tetrahedron) by the ionic interaction [24].

4. Conclusion

The present calculations use the full-potential linearized augmented plane wave plus local orbitals (FP-LAPW+lo) method with the generalized gradient approximation (GGA). The structural properties were calculated at the equilibrium volume values and utilized to compute electronic properties. The band structure for the tetragon phase β-$LiAlH_4$ displays a direct band gap [Γ- Γ] of about 4.11 eV. The total and partial density was also calculated by explanation on : total for β-$LiAlH_4$, **and** partial for s and p orbitals in Li, **and** partial for s, p, and d orbitals in Al, and partial for s orbital in H.Our calculations show that the results for β-$LiAlH_4$ agree well with previous theoretical and experimental data.

Table 3: *Showing the distribution of electrons on shells using quantum numbers:*

Layer	Principal Quantum Number: N	Undercoat	Secondary quantum number: L	Magnetic quantum number: M	Spin With Z	Number Quantum States	Number stations by states	Electron number Per shell
K	1	S	0	(0)	+1/2, -1/2	1	2	2
L	2	S P	0 1	(0) (-1,0,1)	+1/2 -1/2	1 3	2 6	8
M	3	S P d	0 1 2	(0) (-1,0,+1) (-2,,-1,0, +1,+2)	+1/2 -1/2	1 3 5	2 6 10	18

Author Statements:

- **Ethical approval:** The conducted research is not related to either human or animal use.
- **Conflict of interest:** The authors declare that they have no known competing financial interests or personal relationships that could

have appeared to influence the work reported in this paper

- **Acknowledgement:** The authors declare that they have nobody or no-company to acknowledge.
- **Author contributions:** The authors declare that they have equal right on this paper.
- **Funding information:** The authors declare that there is no funding to be acknowledged.

- **Data availability statement:** The data that support the findings of this study are available on request from the corresponding author. The data are not publicly available due to privacy or ethical restrictions.
- **Use of AI Tools:** The author(s) declare that no generative AI or AI-assisted technologies were used in the writing process of this manuscript.

References

[1] L. Zaluski, A. Zaluska and J.O. Ström-Olsen, J. Alloys Compd., 290 (1999) 71.

[2] V.P. Balema, V.K. Pecharsky and K.W. Dennis, J. Alloys Compd., 313 (2000) 69.

[3] J. Chen, N. Kuriyana, Q. Xu, H.T. Takeshita and T. Sakai, J. Phys. Chem. B, 105 (2001) 11214.

[4] D. Singh, Planes Waves, Pseudo-Potentials and the LAPW Method, Kluwer Academic Publishers Boston, (1994) Dordrecht, London.

[5] K. Schwarz and P. Blaha, Comput. Mater. Sci., 28 (2003) 259.

[6] W. Kohn and L. Sham, Phys. Rev. A, 140 (1965) 1133.

[7] P. Hohenberg and W. Kohn, Phys. Rev. B, 136 (1964) 864.

[8] P. Blaha, K. Schwarz, G.K.H. Madsen, D. Kvasnicka and J. Luitz, WIEN2k: An Augmented Planewave+Local Orbitals Program for Calculating Crystal Properties, (2001) Techn. Universit. Wien, Austria,

[9] J.P. Perdew, K. Burke and M. Ernzerhof, Phys. Rev. Lett., 77 (1996) 3865.

[10] G. Kresse and J. Furthmüller, Comput. Mater. Sci., 6 (1996) 15.

[11] P. Vajeeston, P. Ravindran, R. Vidya, H. Fjellvåg and A. Kjekshus, Phys. Rev. B, 68 (2003) 212101.

[12] P. Vajeeston, P. Ravindran, A. Kjekshus and H. Fjellvåg, Phys. Rev. B, 69 (2004) 020104.

[13] F.D Murnaghan, Proc. Natl. Acad. Sci. U. S. A., 30 (1944) 244.

[14] S. Djeroud and F. Adjailia, Adv. Quantum Chem., 68 (2014) 293.

[15] M.J.V. Setten, V.A. Popa, G.A.D. Wijs and G. Brocks, Phys. Rev. B, 75 (2007) 035204.

[16] K. Miwa, N. Ohba and S. Towata, Phys. Rev. B, 69 (2004) 245120.

[17] O. Madelung, Introduction to Solid State Theory, Springer, (1978) Berlin, Heidelberg.

[18] F. Wooten, Optical Properties of Solids, (1972) Academic, New York.

[19] C. Ambrosch-Draxl and J.O. Sofo, Comput. Phys. Commun., 175 (2006) 1.

[20] S. Yang, H. Xu, D. Bo, S. Mao and Z. Ding, Chin. J. Chem. Phys., 29 (2016) 663.

[21] L. Silvestri, S. Forgia, L. Farina, D. Meggiolaro, S. Panero, A. La Barbera, S. Brutti and P. Reale, ChemElectroChem., 2 (2015) 877.

[22] P. Huen and D. B. Ravnsbæk, Electrochem. Commun., 87 (2018) 81.

[23] L. Silvestri, L. Farina,D. Meggiolaro, S. Panero, F. Padella, S. Brutti and P. Reale, J. Phys. Chem. C, 119 (2015) 28766.

[24] S. Yang, H. Wang, H. Man, Z. Long, J. Yang, S. Sun, J. Ruan, Y. Song and F. Fang, Int. J. Electrochem. Sci., 15 (2020) 9487.