Encapsulation and substitution of Fe in C12A7 (12CaO· 7Al2O3)

Kuganathan, N., Gkanas, E. & Chroneos, A.

Published PDF deposited in Coventry University’s Repository

Original citation:
Kuganathan, N, Gkanas, E & Chroneos, A 2020, 'Encapsulation and substitution of Fe in C12A7 (12CaO· 7Al2O3)' AIP Advances, vol. 10, no. 1, 015242
https://dx.doi.org/10.1063/1.5140678

DOI 10.1063/1.5140678
ESSN 2158-3226

Publisher: AIP Publishing:

Licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).

Copyright © and Moral Rights are retained by the author(s) and/or other copyright owners. A copy can be downloaded for personal non-commercial research or study, without prior permission or charge. This item cannot be reproduced or quoted extensively from without first obtaining permission in writing from the copyright holder(s). The content must not be changed in any way or sold commercially in any format or medium without the formal permission of the copyright holders.
Encapsulation and substitution of Fe in C12A7 (12CaO·7Al2O3)

Cite as: AIP Advances 10, 015242 (2020); https://doi.org/10.1063/1.5140678
Submitted: 29 November 2019. Accepted: 09 January 2020. Published Online: 27 January 2020

Navaratnarajah Kuganathan ☑, Evangelos Gkanas ☑, and Alexander Chroneos ☑

COLLECTIONS

EP This paper was selected as an Editor’s Pick

ARTICLES YOU MAY BE INTERESTED IN

Magnetic properties of MBE grown Mn₄N on MgO, SiC, GaN and Al₂O₃ substrates
AIP Advances 10, 015238 (2020); https://doi.org/10.1063/1.5130485

Determination of demagnetizing factors using first-order reversal curves and ferromagnetic resonance
AIP Advances 10, 015318 (2020); https://doi.org/10.1063/1.5129969

Magnetic field dependence of the nonlocal spin Seebeck effect in Pt/YIG/Pt systems at low temperatures
AIP Advances 10, 015031 (2020); https://doi.org/10.1063/1.5135944
Encapsulation and substitution of Fe in C12A7 (12CaO·7Al₂O₃)

I. INTRODUCTION

Rapid advancement of electronic applications necessitates the development of new oxide materials that are cheap and non-toxic and have tunable characteristics. Dodecacalcium hepta-aluminate (C12A7) is an inorganic nanoporous oxide, and it has attracted attention recently for many useful research activities due to many reasons including its non-toxicity, chemical stability, low cost, and unit cell containing 12 cages. The chemical formula of stoichiometric C12A7 is represented as [Ca₁₂₋₄₋₆Al₄₋₆O₆₄₋₆₋₄₋₆] [C₁₂A₇:Ö₂−], where two Ö₂− ions compensate the positively charged framework and occupy two out of 12 cages. Two Ö₂− ions are called extra-framework oxygen ions. The inner diameter of its cage is ~0.4 nm, and there is an opening between two adjacent cages with a diameter of ~0.1 nm. A range of atoms and ions have been encapsulated to replace extra-frame oxygen ions partially or fully. In particular, when both Ö₂− ions are replaced by four electrons, the stoichiometric form is transferred to the electronegative form [Ca₁₂₋₄₋₆Al₄₋₆O₆₄₋₆₋₄₋₆] [C₁₂A₇:e⁴⁻].

Many experimental and theoretical works have been reported on the encapsulation or doping of anions. However, very few studies on the doping of framework cations (Ca⁺² and Al⁺³) in C12A7:O are available in the literature. Co-doping of Zn and P on the Al site resulted in a reduction in the ionic conductivity compared to that determined in the undoped C12A7. In a study by Bertoni et al., a similar observation was noted for the doping of Mg⁺² on the Ca site. Si-doped C12A7:O₂⁻ has been considered as a catalyst for the decomposition of hydrocarbon by Hayashi et al. The experimental study by Palacios et al. showed that Ga substitution on the Al site introduces an expansion in the unit cell. Density functional theory (DFT) simulations were performed by Huang et al. to modify the framework of C12A7 by doping cations with +2, +3, +4, and +5 charges and examine the impact on the structural and electronic properties.
Ebbinghaus et al.\textsuperscript{21} recently reported the synthesis of 1% mol Fe substituted on the Al site in C12A7:O\textsuperscript{2−} using the floating zone method and observed the expansion of the lattice parameter by \(-0.002\) Å. Their study also confirmed the tetrahedral coordination of Fe with the +3 oxidation state. The resultant compound exhibited magnetic moment, and the oxygen diffusion had been lowered due to the strong binding nature of cage wall oxygen with Fe. Recently, Ruttanapun et al.\textsuperscript{22} calculated the optical gap and thermal conductivity of Fe-doped C12A7:O\textsuperscript{2−} and concluded that both properties were influenced by the Fe substitution. Physical properties of Fe-doped C12A7:O\textsuperscript{2−} have been studied. However, its thermodynamical stability and chemical properties have not been explored yet. Furthermore, the electrode form of C12A7 (C12A7:e\textsuperscript{−}) is also interesting to be considered for doping, and this study was not considered experimentally yet. Although a previous simulation\textsuperscript{23} considered the doping of cations including Fe in both forms of C12A7, full analysis is only available for Ca, Ir, P, and V. Furthermore, the encapsulation of Fe is also important to be considered. Theoretical simulations based on the DFT are useful to examine the chemical nature of Fe-doped and/or encapsulated C12A7, charge on the Fe atom, magnetic moment of the resultant complex, and electronic structure with charge density associated with the dopant. Dispersion forces are also important for the system containing free-electrons. Current DFT methods have the ability to calculate this additional attractive energy term arising from dispersion.

In this study, spin-polarized mode DFT together with dispersion correction is used to calculate the structures of a single Fe atom encapsulated in one of the empty cages and substituted on the Al site in both stoichiometric and electrode forms of C12A7. Simulations enabled us to calculate the incorporation and substitution energies, optimized structures, charge on the Fe atom, magnetic moment of the undoped and doped structures, and electronic structures together with charge densities.

\section*{II. COMPUTATIONAL METHODS}

All calculations were performed using a DFT code VASP (Vienna Ab initio Simulation Program).\textsuperscript{28} This code uses projected augmented wave (PAW) potentials.\textsuperscript{29} Exchange-correlation was modeled using generalized gradient approximation (GGA) with the Perdew, Burke, and Ernzerhof (PBE)\textsuperscript{30} function as implemented in the VASP code. A cubic lattice containing two molecules of C12CaO\textsubscript{7} in the VASP code. A cubic lattice containing two molecules of C12A7:O\textsuperscript{2−} was calculated using the following equation:

\[ E_{\text{sub}} = E_{(\text{Fe:C12A7:O}^\text{−})} - E_{(\text{C12A7:O}^\text{−})} - E_{(\text{Fe})}, \]

where \( E_{(\text{Fe:C12A7:O}^\text{−})} \) is the total energy of an Fe atom encapsulated in C12A7:O\textsuperscript{2−}, \( E_{(\text{C12A7:O}^\text{−})} \) is the total energy of bulk C12A7:O\textsuperscript{2−}, and \( E_{(\text{Fe})} \) is the energy of a single Fe atom.

Substitution energy for a single Fe atom to replace a single Al atom in the C12A7:O\textsuperscript{2−} was calculated using the following equation:

\[ E_{\text{enc}} = E_{(\text{Fe:C12A7:O}^\text{−})} - E_{(\text{C12A7:O}^\text{−})} - E_{(\text{Fe})}, \]

where \( E_{(\text{Fe:C12A7:O}^\text{−})} \) is the total energy of an Fe atom substituted on the Al site in C12A7:O\textsuperscript{2−}, \( E_{(\text{C12A7:O}^\text{−})} \) is the total energy of bulk C12A7:O\textsuperscript{2−}, and \( E_{(\text{Fe})} \) and \( E_{(\text{Al})} \) are the total energies of a single Fe atom and a single Al atom, respectively.

\section*{III. RESULTS AND DISCUSSION}

\subsection*{A. Structure and electronic properties of C12A7}

C12A7 exhibits a cubic structure with a space group of \( \text{I}4\text{3d} \).\textsuperscript{1} Its experimentally observed lattice parameters are \( a = b = c = 11.99 \) Å and \( a = \beta = \gamma = 90^\circ \).\textsuperscript{2} Both C12A7:O\textsuperscript{2−} and C12A7:e\textsuperscript{−} bulk structures were optimized under constant pressure to calculate their equilibrium lattice constants. Figure 1 shows the optimized structures and cages occupied with extra-framework oxygen and electrons. The calculated lattice parameters for C12A7:O\textsuperscript{2−} (\( a = 12.05 \) Å, \( b = c = 12.01 \) Å, \( \alpha = 90.02^\circ \), \( \beta = 89.95^\circ \), and \( \gamma = 89.93^\circ \)) are in good agreement with the experiment.\textsuperscript{1} There is a slight distortion observed in the lattice constants and angles due to the electrostatic attraction formed between the cage pole Ca\textsuperscript{2+} ions and extra-framework O\textsuperscript{2−} ions, as shown in Fig. 1(b). The cage pole distance (4.21 Å) is \( \sim 1.50 \) Å shorter than that calculated in an empty cage. In the case of C12A7:e\textsuperscript{−} bulk, there is a slight elongation in the lattice constants (\( a = b = c = 12.06 \) Å and \( \alpha = \beta = \gamma = 90^\circ \)), but the relaxed structure maintains its cubic form.

Calculated electronic properties of both C12A7:O\textsuperscript{2−} and C12A7:e\textsuperscript{−} have been discussed in previous studies.\textsuperscript{13,14,16,24} C12A7:O\textsuperscript{2−} is an insulator, and C12A7:e\textsuperscript{−} is metallic [refer to DOS plots in Fig. 1. Relaxed structures of (a) C12A7:O\textsuperscript{2−} bulk, (b) a cage showing the occupation of extra-framework O\textsuperscript{2−} ion in C12A7:O\textsuperscript{2−}, (c) C12A7:e\textsuperscript{−} bulk, and (d) a cage occupied with 1/3e\textsuperscript{−} in C12A7:e\textsuperscript{−}.]
FIG. 2. DOS plots of (a) C12A7:O$_{2}^-$ bulk and (b) C12A7:e$^-$ bulk and constant charge density plots associated with (c) the extra-framework O$_{2}^-$ ion in C12A7:O$_{2}^-$ and (d) electrons in C12A7:e$^-$. Figs. 2(a) and 2(b). The metallic nature of C12A7:e$^-$ is due to the delocalized extra-framework electrons in the lattice [refer to Fig. 2(d)]. Peaks associated with the extra-framework O$_{2}^-$ ions (between 2.50 eV and 3.00 eV) in C12A7:O$_{2}^-$ are slightly further away from the valence bands, and these peaks correspond to the non-bonded $p$ electrons of O$_{2}^-$ ions oriented perpendicular to the bonding direction [refer to Figs. 2(c) and 1(b)].

B. Encapsulation of a single Fe atom in C12A7:O$_{2}^-$

Here, we consider a single Fe atom occupying an empty cage in C12A7:O$_{2}^-$. Figure 3(a) shows the optimized cage containing the Fe atom. The position of the Fe atom is off from the center of the cage. This is due to the strong attraction between Fe and cage wall O$_{2}^-$ ions. This is further confirmed by the short Fe–O bond distances (2.07 and 2.43 Å). The Bader charge on Fe is +0.14 $|e|$, meaning that a small amount of electrons have been transferred from Fe to the nearest neighboring atoms in the cage. Encapsulation energy is exoergic ($-2.00$ eV), implying that the Fe atom is more stable inside the cage of C12A7:O$_{2}^-$ than in its isolated form. Encapsulation does not alter the Bader charges of the extra-framework oxygen ions, as reported in Table I. The resultant encapsulated structure is magnetic, and its magnetic moment is calculated to be 4.00 $\mu_B$. The valence electronic configuration of Fe is $d^6s^2$. In the $d$ shell, two electrons are paired, and the other four electrons are unpaired. In the resultant complex, the Fe atom retains its electronic configuration according to the
Bader charge. The magnetic moment of C12A7:O^{2-} is zero, and the resultant complex has a magnetic moment of 4.00 \( \mu \). This implies that the electronic configuration of Fe is unaltered. Encapsulation introduces a very small expansion (~0.12\%) in the volume.

Charge densities associated with the encapsulated Fe and the extra-framework O\(^{2-}\) ions are shown in Figs. 3(b) and 3(c), respectively. Figure 3(d) shows the total DOS plot of the encapsulated structure. Additional states appear between the top of the valence band and the Fermi energy. These states belong to the \( d \) states of the Fe atom, as shown in the atomic DOS of Fe [refer to Fig. 3(e)]. Atomic DOS of extra-framework O\(^{2-}\) ions are shown in Fig. 3(f). The charge density plot of extra-framework O\(^{2-}\) ions shows that charge is almost localized around the O\(^{2-}\) ions, confirming again that encapsulation does not alter the extra-framework O\(^{2-}\) ions.

### C. Encapsulation of a single Fe atom in C12A7:e\(^{-}\)

Next, we considered the encapsulation of a single Fe atom in one of 12 empty cages in C12A7:e\(^{-}\). Table II reports the encapsulation energy, Bader charge on the Fe atom, magnetic moments, and volumes calculated in the optimized structures of both C12A7:e\(^{-}\) and Fe@C12A7:e\(^{-}\). The encapsulation energy is ~1.32 eV, suggesting that the Fe atom is more stable than its isolated form. This is less negative by 0.68 eV than that calculated for single Fe atom encapsulation in C12A7:O\(^{2-}\). This can be due to the repulsion between the \( d \) electrons of Fe and the extra-framework electrons in C12A7:e\(^{-}\). Bader charge analysis shows that there is a charge transfer (0.86 \( |e| \)) from the extra-framework electrons in C12A7:e\(^{-}\) to Fe. The encapsulated Fe atom occupies the center of the cage (refer to Fig. 4). This is due to the electrostatic attraction between the negatively charged Fe and two cage pole Ca\(^{2+}\) ions. Zero magnetic moment is calculated for C12A7:e\(^{-}\). Conversely, Fe@C12A7:e\(^{-}\) exhibits a magnetic moment of 0.46 \( \mu \). As mentioned earlier, a single Fe atom has four unpaired electrons in its \( d \) orbital. Hence, it is expected that the net magnetic moment of Fe@ C12A7:e\(^{-}\) would be four. A significant reduction in the magnetic moment can be due to the pairing of four electrons of C12A7:e\(^{-}\) with four unpaired electrons of Fe. Figure 4(b) shows the charge density associated with the electrons. The reduction in the charge density is due to the 0.86 electrons transferred to Fe. The total DOS plot shows the extra peaks associated with the \( d \) states of Fe [refer to Figs. 4(c) and 4(d)]. The change in volume due to encapsulation is not significant.

### D. Substitution of a single Fe atom for Al in C12A7:O^{2-}

Here, we substitute a single Fe atom on the Al site in C12A7:O\(^{2-}\). The substitution energy is 3.02 eV, suggesting that Al–O bonds are stronger than the Fe–O bonds. This is further supported by the Bader charges of Al and Fe, bond distances, and bond angles (refer to Fig. 5 and Table III). The Bader charges of Al in C12A7:O\(^{2-}\) and Fe in Fe@C12A7:O\(^{2-}\) are +3.00 \( |e| \) and +1.71 \( |e| \), respectively. This indicates that substitution requires energy to replace Al in the lattice. Bond distances and bond angles calculated in an AlO\(_3\) structure.
tetrahedral unit in C12A7:O\textsuperscript{2−} are 1.73–1.79 Å and 97.3°–120.3°, respectively. In a FeO\textsubscript{4} tetrahedral unit, bond distances are slightly longer than that calculated in the AlO\textsubscript{4} unit (refer to Fig. 5). Bond angles (O–Fe–O) calculated in FeO\textsubscript{4} also deviate slightly from the bond angles calculated (O–Al–O) in the AlO\textsubscript{4} unit. The Bader charges of the extra-framework O\textsuperscript{2−} ions show that substitution results in a negligible change (refer to Table III). The resultant substituted structure is magnetic (magnetic moment = 5.00 μ). Substitution introduced a very small expansion in the volume by ~0.3%.

E. Substitution of a single Fe atom for Al in C12A7:O\textsuperscript{2−}

Finally, C12A7:e\textsuperscript{−} was considered for Fe substitution. The substitution energy is calculated to be 1.42 eV, inferring the stronger chemical bonding of Al\textsuperscript{3+} with adjacent framework O\textsuperscript{2−} ions than Fe\textsuperscript{3+} with O\textsuperscript{2−} ions. This is consistent with the longer Fe–O bond distances and bond angles in the FeO\textsubscript{4} unit [refer to Fig. 6(b)] than

| System       | Substitution energy (eV) | Bader charge on Fe (|e|) | Bader charge on extra-framework oxygen (|e|) | Magnetic moment (μ) | Volume (Å\textsuperscript{3}) |
|--------------|--------------------------|--------------------------|---------------------------------------------|---------------------|--------------------------|
| Fe.C12A7:O\textsuperscript{2−} | 3.02                     | +1.71                    | −1.39, −1.40                               | 5.00                | 1743.84                  |
| C12A7:O\textsuperscript{2−}    | . . .                     | . . .                    | −1.40, −1.41                               | 0.00                | 1738.66                  |
with those found in the AlO$_4$ unit. The Al–O bond distances and bond angles in C12A7: Fe$^{e-}$ are 1.74–1.79 Å and 99.9°–117.9°, respectively. The Bader charges on the substituted Fe and Al in C12A7 are +1.60 |e| and +3.00 |e|, respectively, again confirming the strong bonding between the Al$^{3+}$ ion and nearest neighboring O$^{2-}$ ions. The resultant compound becomes magnetic, and its magnetic moment is 3.67 μ (refer to Table IV). Substitution reveals an insignificant change (≈0.24%) in the volume.

Figure 6 shows the optimized structures of Fe substituted on the Al site in C12A7: Fe$^{e-}$ and the FeO$_4$ unit showing bond distances and bond angles, constant charge density plot associated with the Fe atom and electrons, (d) the total DOS plot, and (e) the atomic DOS plot of Fe.

### Table IV. Calculated substitution energy, Bader charge, magnetic moment, and volume for a single Fe atom substituted in C12A7: Fe$^{e-}$; the available data calculated for C12A7: Fe$^{e}$ are also reported.

| System       | Substitution energy (eV) | Bader charge on Fe (|e|) | Magnetic moment (μ) | Volume (Å$^3$) |
|--------------|--------------------------|--------------------------|---------------------|----------------|
| Fe.C12A7: Fe$^{e-}$ | 1.42                     | +1.60                    | 3.67                | 1756.68        |
| C12A7: Fe$^{e}$       | . . . .                   | . . . .                   | . . . .              | . . . .         |

Current simulation results can be further expanded by making use of thermodynamic models of defects, as discussed recently by Sarlis and Skordas. Current models, defect formation parameters are interconnected via thermodynamical relations.

### IV. CONCLUSIONS

Electronic structure calculations based on DFT were applied to examine the thermodynamical stability, charge transfer, electronic structures, and magnetic behavior of a single Fe atom encapsulated and substituted by stoichiometric and electride forms of C12A7. In both forms of C12A7, encapsulation is exothermic, and the Fe atom is more stable than its isolated form. Encapsulated structures are magnetic in contrast to their host structures, meaning that they can be of interest in the development of spintronic devices. In the electride form, the encapsulated Fe atom becomes negatively charged to provide novel chemical functionality. Substitution energies are endothermic for both forms of C12A7 due to the strong chemical bonding between Al$^{3+}$ and framework O$^{2-}$ ions. Substitution of Fe for Al in the electride form is thermodynamically more favorable than in its stoichiometric form by ≈1.50 eV. Formation of Fe sub-bands between the Fermi energy level and the top of the valence band reveals that encapsulated or substituted C12A7 can be useful for the future applications in catalysis, optics, and electronics.

### ACKNOWLEDGMENTS

Computational facilities and support were provided by the High Performance Computing Centre at Imperial College London.

The authors declare that there is no competing financial interest.

### REFERENCES

1. J. A. Imlach, L. S. Dent Glasser, and F. P. Glasser, Cem. Concr. Res. 1, 57 (1971).
2. S. Watauchi, I. Tanaka, K. Hayashi, M. Hirano, and H. Hosono, J. Cryst. Growth 237-239, 801 (2002).
3. H. Katsuro, H. Masahiro, and H. Hideo, Chem. Lett. 34, 586 (2005).
4. S. Matsuishi, Y. Toda, M. Miyakawa, K. Hayashi, T. Kamiya, M. Hirano, I. Tanaka, and H. Hosono, Science 301, 626 (2003).
5. W. Kim, S. Matsuushi, T. Nomura, Y. Kubota, M. Takata, K. Hayashi, T. Kamiya, M. Hirano, and H. Hosono, Phys. Rev. B 73, 205108 (2006).
6. K. Hayashi, M. Hirano, and H. Hosono, Phys. Rev. B 109, 11900 (2020).
7. M. Miyakawa, H. Kamioka, M. Hirano, T. Kamiya, P. V. Sushko, A. L. Shluger, N. Matsunami, and H. Hosono, Phys. Rev. B 73, 205108 (2006).
8. J. Jeevataram, F. P. Glasser, and L. S. D. Glasser, J. Am. Ceram. Soc. 47, 105 (1964).
9. G. I. Zhmoidin and A. K. Chatterjee, Cem. Concr. Res. 14, 386 (1984).
10. H. Hosono and Y. Abe, Inorg. Chem. 26, 1192 (1987).
11 M. Kitano, S. Kanbara, Y. Inoue, N. Kuganathan, P. V. Sushko, T. Yokoyama, M. Hara, and H. Hosono, Nat. Commun. 6, 6731 (2015).
12 Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P. V. Sushko, and H. Hosono, Nat. Commun. 4, 2378 (2013).
13 N. Kuganathan, A. Chroneos, and R. W. Grimes, Sci. Rep. 9, 13612 (2019).
14 N. Kuganathan, R. W. Grimes, and A. Chroneos, J. Appl. Phys. 125, 165103 (2019).
15 N. Kuganathan, H. Hosono, A. L. Shluger, and P. V. Sushko, J. Am. Chem. Soc. 136, 2216 (2014).
16 N. Kuganathan and A. Chroneos, Nanomaterials 9, 816 (2019).
17 M. I. Bertoni, T. O. Mason, J. E. Medvedeva, Y. Wang, A. J. Freeman, and K. R. Poeppelmeier, J. Appl. Phys. 102, 113704 (2007).
18 S. Matsuishi, H. Muramatsu, and H. Hosono, Chem. Lett. 43, 1371 (2014).
19 M. I. Bertoni, T. O. Mason, J. E. Medvedeva, A. J. Freeman, K. R. Poeppelmeier, and B. Delley, J. Appl. Phys. 97, 103713 (2005).
20 L. Palacios, S. Bruque, and M. A. G. Aranda, Phys. Status Solidi B 245, 666 (2008).
21 S. G. Ebbinghaus, H. Krause, D.-K. Lee, and J. Janek, Cryst. Growth Des. 14, 2240 (2014).
22 J. T. S. Irvine and A. R. West, Solid State Ionics 40–41, 896 (1990).
23 K. Hayashi, H. Muramatsu, S. Matsuishi, T. Kамия, and H. Hosono, Electrochem. Solid-State Lett. 12, J11 (2009).
24 J. Huang, L. Valenzano, and G. Sant, Chem. Mater. 27, 4731 (2015).
25 C. Ruttanapun, P. Srepusharawoot, and S. Maensiri, Chin. J. Phys. 56, 252 (2018).
26 G. Kresse and J. Furthmüller, Phys. Rev. B 54, 11169 (1996).
27 G. Kresse and D. Joubert, Phys. Rev. B 59, 1758 (1999).
28 P. E. Blöchl, Phys. Rev. B 50, 17953 (1994).
29 J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. 77, 3865 (1996).
30 H. J. Monkhorst and J. D. Pack, Phys. Rev. B 13, 5188 (1976).
31 W. H. Press, S. A. Teukolsky, W. T. Vetterling, and B. P. Flannery, Numerical Recipes in C: The Art of Scientific Computing, 2nd ed. (Cambridge University Press, 1992).
32 S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, J. Chem. Phys. 132, 154104 (2010).
33 G. Henkelman, A. Arnaldsson, and H. Jónsson, Comput. Mater. Sci. 36, 354 (2006).
34 P. V. Sushko, A. L. Shluger, Y. Toda, M. Hirano, and H. Hosono, Proc. R. Soc. A 467, 2066 (2011).
35 N. V. Sarlis and E. S. Skordas, Solid State Ionics 335, 82 (2019).