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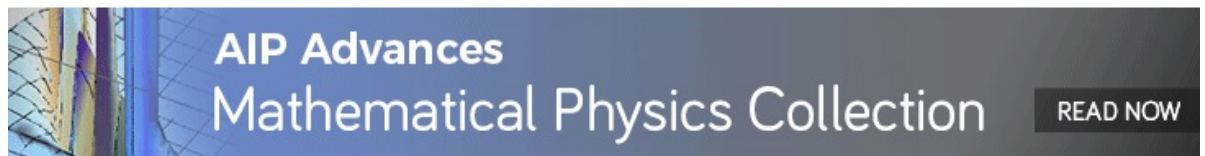
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ABSTRACT

The storage of atomic fluorine anions (F^-) is an important issue in the development of emission materials that have numerous technological applications including catalysis. Using density functional theory simulations, we examine the formation of F^- ions from gaseous F_2 in the nanoporous complex oxide $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7). Both stoichiometric and electrified forms of C12A7 strongly encapsulate fluorine atoms, and the formation of F^- ions is confirmed from the charge analysis. There is a significant enhancement in the encapsulation in the electrified form of C12A7 due to the presence of electrons in its nanocages. Successive encapsulation of multiple F atoms is also energetically favorable in both forms of C12A7. The formation of molecular fluorine (F_2) in the nanocages of both forms is unfavorable due to the strong electronegativity of fluorine.

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I. INTRODUCTION

Atomic fluorine anion (F^-) has attracted considerable research interest due to its potential applications in many areas including semiconductor etching, filming, and material engineering.^{1–6} However, production and storage of pure F^- ions are generally complicated due to the formation of impurities.⁷ Recent development of synthesizing anionic storage emission materials to incorporate a variety of anions such as H^- , OH^- , and O^- has led to the discovery of new nanoporous materials that can efficiently confine F^- ions from F_2 gas.^{8–14}

The nanoporous crystal $12\text{CaO}\cdot 7\text{Al}_2\text{O}_3$ (C12A7) has been considered as a candidate material for encapsulating many anions including Au^- , NH_2^- , and O_2^- .^{15–19} C12A7 is cubic with a lattice constant of 11.989 Å,²⁰ and its stoichiometric form ($\text{C12A7}\cdot\text{O}^{2-}$) can be considered as a positively charged framework $[\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}]^{4+}$ compensated by two extra-framework O^{2-} ions occupied by 2 out of 12 empty cages. In the electrified form of C12A7 ($\text{C12A7}\cdot\text{e}^-$), a positively charged framework is compensated by four electrons. Owing to the porous nature of C12A7 with subnanometer sized cages, it is expected that this material would have unique anion storage and emission features required for the applications in many areas

including catalysis. In previous experimental and theoretical studies, this material has been examined for the activation of small molecules such as N_2 and CO_2 .^{21–23}

The fluoride derivative of C12A7 was first synthesized by Jeevaratnam *et al.*,²⁴ and the final composition was determined to be $\text{Ca}_{24}\text{Al}_{28}\text{O}_{64}\text{F}_4$. Fluorinated C12A7 compounds were shown to be promising materials in the setting and hardening of fluoride-bearing cement.^{25,26} Song *et al.*⁶ used a novel approach to produce gas phase F^- ions in $\text{C12A7}\cdot\text{O}^{2-}$. In this approach, CaCO_3 , CaF_2 , and $\gamma\text{-Al}_2\text{O}_3$ were used in the solid-state reaction to produce $(\text{Ca}_{24}\text{Al}_{28}\text{O}_{64})^{4+}\cdot(\text{O}^{2-})_{0.35}(\text{F}^-)_{3.30}$. The final composition is proposed to be applicable in fields such as atmospheric chemistry, particle accelerators, and material modifications.⁶ Furthermore, the formation of F^- ions in the nanocages of C12A7 is of great interest in the fluoride ion batteries as fluoride is the most stable anion with high mobility.²⁷

In this study, we use density functional theory together with dispersion corrections (DFT + D) to examine the thermodynamic stability of F^- ions in both stoichiometric and electrified forms of C12A7. This simulation technique allowed us to elucidate the structures, electronic structures, and charge transfer between C12A7 and F atoms.

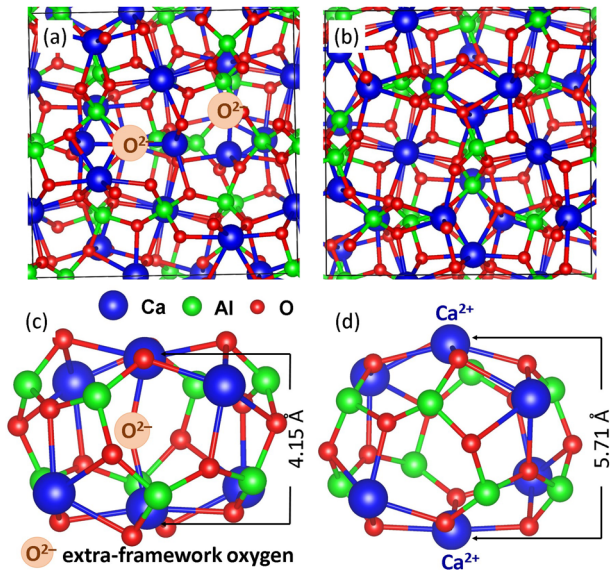


FIG. 1. Relaxed structures of (a) C12A7:O²⁻ and (b) C12A7:e⁻, corresponding cage structures containing extra-framework (c) O²⁻ and (d) e⁻.

II. COMPUTATIONAL METHODS

Spin polarized DFT calculations were performed using the VASP (Vienna *ab initio* simulation program) code²⁸ in order to obtain energy minimized configurations and electronic structures. Projected augmented wave (PAW) potentials²⁹ were used for Ca, Al, O, and F. Stoichiometric and electroneutral forms of C12A7 were modeled using a supercell containing 118 and 116 atoms, respectively. Further increase in the size of the cell resulted in a total energy difference of 1 meV/atom showing the appropriateness of the size of the simulation box. A plane wave basis set with a cut-off of 500 eV was used in all calculations. A $2 \times 2 \times 2$ Monkhorst Pack³⁰ k -point mesh was used to sample the Brillouin zone. Further increase in the k -points resulted in a total energy difference of 0.5 meV/atom. The generalized gradient approximation (GGA) as implemented by Perdew, Burke, and Ernzerhof (PBE)³¹ was used to describe the exchange–correlation effects. All geometries were

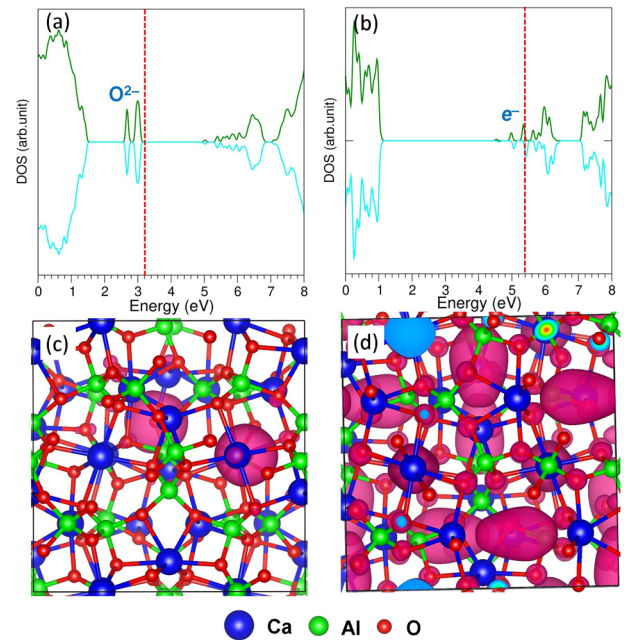


FIG. 2. DOS plots of (a) C12A7:O²⁻ and (b) C12A7:e⁻, band decomposed charge density plots associated with (c) extra-framework oxygen in C12A7:O²⁻ and (d) extra-framework electrons in C12A7:e⁻. Red dot lines correspond to the Fermi energy level.

minimized using a conjugate gradient (CG) algorithm.³² Forces on the atoms were less than 0.001 eV/Å in all optimized structures. Short range dispersive interactions were included using a semi-empirical method (DFT + D3) as implemented by Grimme *et al.*³³ Encapsulation energy of a fluorine atom with respect to the fluorine molecule in C12A7:e⁻ was calculated using the following equation:

$$E_{\text{enc}} = E(\text{F@C12A7} : \text{e}^-) - E(\text{C12A7} : \text{e}^-) - E(1/2 \text{F}_2), \quad (1)$$

where $E(\text{F@C12A7} : \text{e}^-)$ is the total energy of a fluorine atom encapsulated in one of the empty cages of C12A7:e⁻, $E(\text{C12A7} : \text{e}^-)$ is the total energy of C12A7:e⁻, and $E(1/2 \text{F}_2)$ is half the energy of an

TABLE I. Calculated lattice parameters of C12A7:O²⁻ and C12A7:e⁻. Available experimental values are also reported.

Parameters	C12A7:O ²⁻			C12A7:e ⁻		
	Calc.	Expt.	$ \Delta (\%)$	Calc.	Expt.	$ \Delta (\%)$
a (Å)	12.05	11.99 ²⁰	0.50	12.06	12.00 ³³	0.50
b (Å)	12.01	11.99 ²⁰	0.17	12.06	12.00 ³³	0.50
c (Å)	12.02	11.99 ²⁰	0.25	12.06	12.00 ³³	0.50
α (°)	90.0	90.0	0.00	90.0	90.0	0.00
β (°)	90.0	90.0	0.00	90.0	90.0	0.00
γ (°)	89.9	90.0	0.11	90.0	90.0	0.00
V (Å ³)	1738.66	1727.38	0.65	1754.05	1728.00	1.51

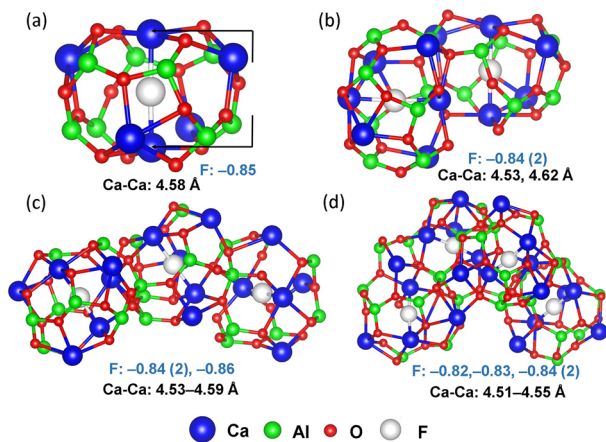


FIG. 3. Relaxed cages containing F^- ions in (a) $F@C12A7:O^{2-}$, (b) $2F@C12A7:O^{2-}$, (c) $3F@C12A7:O^{2-}$, and (d) $4F@C12A7:O^{2-}$.

isolated gas phase F_2 molecule. A similar equation was used to calculate the encapsulation energy for the subsequent encapsulation of F atoms.

III. RESULTS AND DISCUSSION

A. Structures of stoichiometric and electride forms of C12A7

Crystal structures of both forms of C12A7 were relaxed under constant pressure to obtain equilibrium lattice constants to validate the quality of the basis sets and pseudopotentials of Ca, Al, and O. Figure 1 shows the relaxed configurations together with the cages containing an extra-framework O^{2-} ion in $C12A7:O^{2-}$ and an extra-framework electron in $C12A7:e^-$. Table I reports the calculated lattice parameters together with experimental values^{20,34} and demonstrates that there is a good agreement.

The calculated density of states (DOS) plot shows that the $C12A7:O^{2-}$ is an insulator, as reported in previous simulation studies.^{35,36} The peaks associated with the extra-framework O^{2-} ions appear at 2.70 eV [refer to Fig. 2(a)]. The electride form of C12A7 is metallic [refer to Fig. 2(b)] in agreement with previous DFT

studies.^{35,36} This is because of the extra-framework electrons occupying the nanocages. Band decomposed charge density associated with the extra-framework O^{2-} ions and electrons is shown in Figs. 2(c) and 2(d), respectively. In $C12A7:e^-$, electrons are equally distributed ($\frac{1}{3}e^-$ per cage), as shown in Fig. 2(d).

B. Encapsulation of fluorine atoms in $C12A7:O^{2-}$

The encapsulation of four F atoms was considered consequently in the empty cages of $C12A7:O^{2-}$. The relaxed cage structures containing F^- ions are shown in Fig. 3. There is a significant contraction in the Ca–Ca cage pole distances due to the strong attraction between F^- ions and cage pole Ca^{2+} ions in comparison with the Ca–Ca distance of 5.76 Å calculated in an empty cage in $C12A7:O^{2-}$. The formation of F^- is confirmed by the negative Bader charges on the F atoms (refer to Fig. 3). Furthermore, negative charges on the F atoms are gained from cations mainly from cage pole Ca^{2+} ions.

The encapsulation energies and total Bader charges on the encapsulated F atoms are shown in Fig. 4. Encapsulation energies are exothermic in all cases [refer to Fig. 4(a)]. Encapsulation energies calculated using $\frac{1}{2}F_2$ as a reference are less negative compared to those calculated using atomic F as a reference. In our previous simulation,¹⁹ encapsulation energies calculated for Br and I using F atom as a reference are -2.73 eV and -1.56 eV, respectively. These values are less negative than that calculated for F (~ -4.60 eV) inferring its strong electronegativity. This is due to the energy needed to dissociate $\frac{1}{2}F_2$ to form atomic F. Encapsulation energy decreases slightly upon consecutive encapsulation. This can be due to the structural changes introduced by the pre-encapsulated F atoms. The total Bader charges on F atoms increase linearly with the addition of F atoms [refer to Fig. 4(b)]. A negative Bader charge of ~ -0.85 on each F atom confirms the formation of F^- ions. The Bader charge calculated for F is higher than those calculated for Br (-0.75) and I (-0.68).¹⁹

The calculated DOS plots for the encapsulated configurations are shown in Fig. 5. The Fermi energy is reduced upon encapsulation of up to three F atoms [refer to Figs. 5(a)–5(c)]. Encapsulation of the fourth F atom did not affect the Fermi energy [refer to Fig. 5(d)]. Peaks associated with the s states of F appear in the deeper level (~ 20 eV). Additional states arising from the p states of F are located just below the Fermi level [refer to Figs. 5(e)–5(h)]. The encapsulated compounds are still insulator.

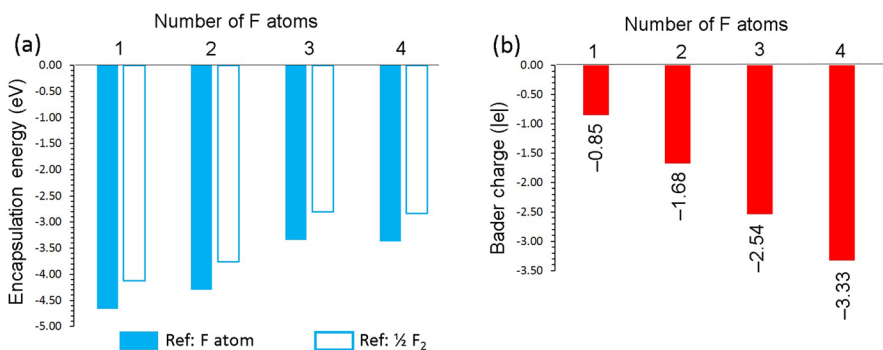


FIG. 4. (a) Encapsulation energies calculated for the formation of $xF@C12A7:O^{2-}$ ($x = 1-4$) using atomic F and F_2 gas as references and (b) total Bader charges on the encapsulated F atoms.

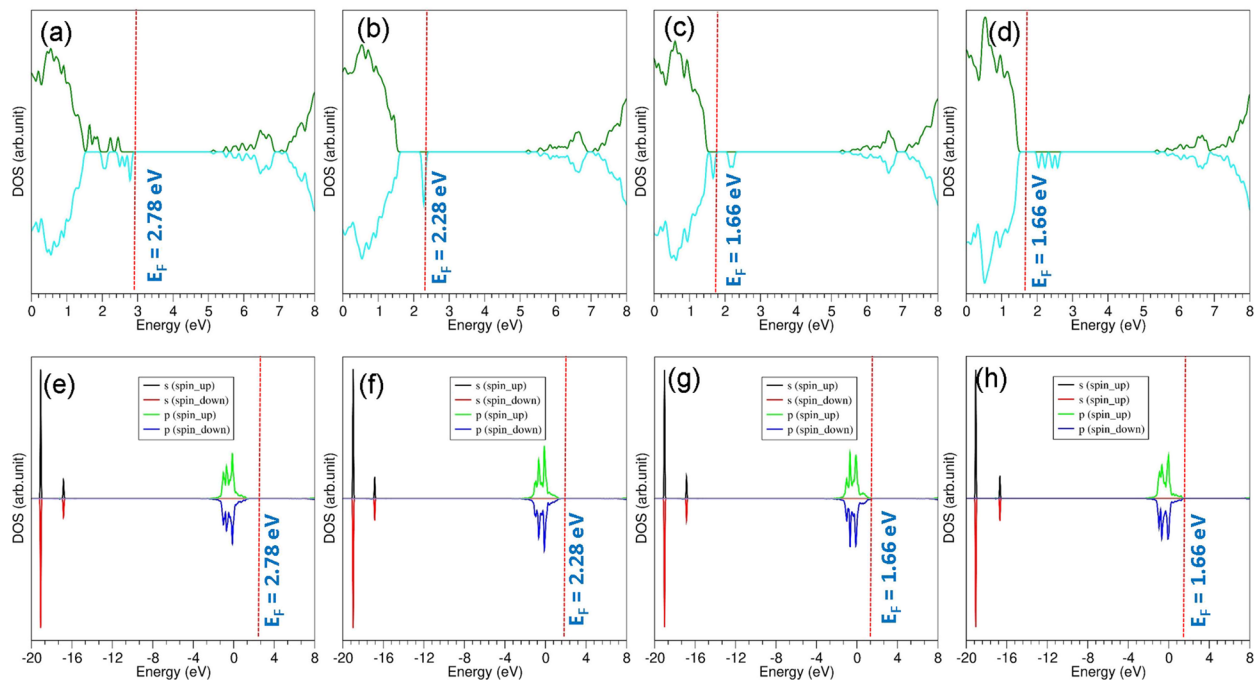


FIG. 5. DOS plots calculated for (a) $F@C12A7:O^{2-}$, (b) $2F@C12A7:O^{2-}$, (c) $3F@C12A7:O^{2-}$, and (d) $4F@C12A7:O^{2-}$. The corresponding atomic DOS plots calculated for F are shown in (e)–(h).

C. Encapsulation of fluorine atoms in $C12A7:e^-$

Next, the encapsulation of F atoms was considered in $C12A7:e^-$. The relaxed configurations of single F atoms occupying a

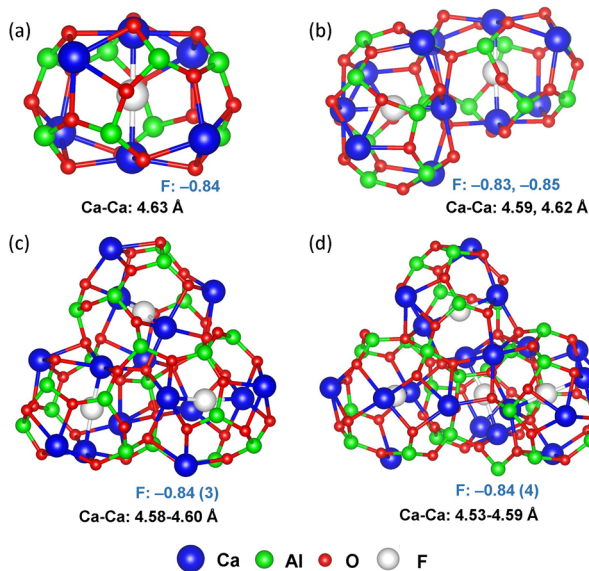


FIG. 6. Relaxed cages containing F^- ions in (a) $F@C12A7:e^-$, (b) $2F@C12A7:e^-$, (c) $3F@C12A7:e^-$, and (d) $4F@C12A7:e^-$.

cage are shown in Fig. 6. In all cases, F atoms occupy the center of the cage. Deformation of the occupied cage is evidenced by the shorter Ca–Ca cage pole distances (4.53 Å–4.62 Å) compared to those calculated in the unoccupied cage: the distance in the unoccupied cage is 5.71 Å. As discussed earlier, the distortion is due to the F^- ions sandwiched by the two cage pole Ca^{2+} ions. The Bader charges confirmed the formation of F^- ions.

The encapsulation energies are highly exothermic in comparison with those calculated in $C12A7:O^{2-}$ [refer to Fig. 7(a)]. This is due to the availability of the extra-framework electrons in the lattice. Encapsulation energies calculated for Br (−5.17 eV) and I (−3.99 eV) using F atom as a reference are less negative than that calculated for F (−7.20 eV).¹⁹ Successive encapsulation is also exoergic though encapsulation energies are less negative compared to the first encapsulation. The Bader charge analysis confirms the formation of F^- ions. The Bader charge on F (−0.84) is higher than those calculated on Br (−0.76) and I (−0.69).¹⁹ The total Bader charge increases with the addition of F atoms [refer to Fig. 7(b)]. In both $C12A7:O^{2-}$ and $C12A7:e^-$, the amount of total charge on the encapsulated F atoms is the same. It should be noted, however, that the encapsulation efficacy is higher in $C12A7:e^-$ than in $C12A7:O^{2-}$.

The DOS plots calculated for the encapsulated complexes are shown in Fig. 8. The Fermi energy level is not affected significantly by the encapsulation of F atoms up to three, and the resultant complexes are still metallic [refer to Figs. 8(a)–8(c)]. The addition of the fourth F atom significantly shifts the Fermi energy level toward the valence band. This is because of the absence of extra-framework electrons as four F atoms gained all four electrons to form F^- ions, and

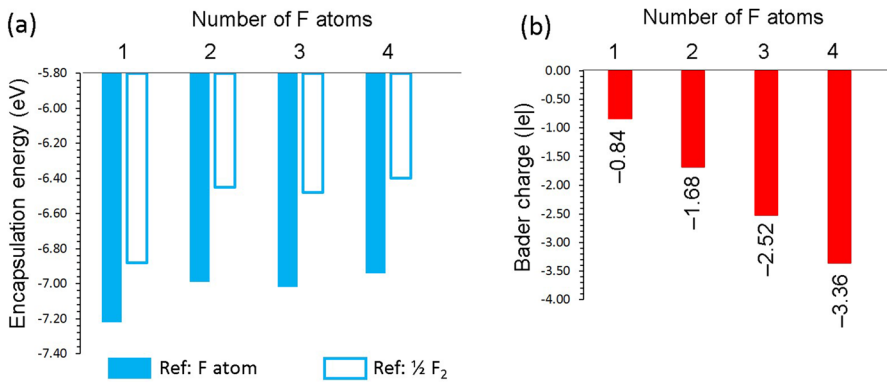


FIG. 7. (a) Encapsulation energies calculated for the formation of $x\text{F}@C12A7:e^-$ ($x = 1-4$) using atomic F and F_2 gas as references and (b) total Bader charges on the encapsulated F atoms.

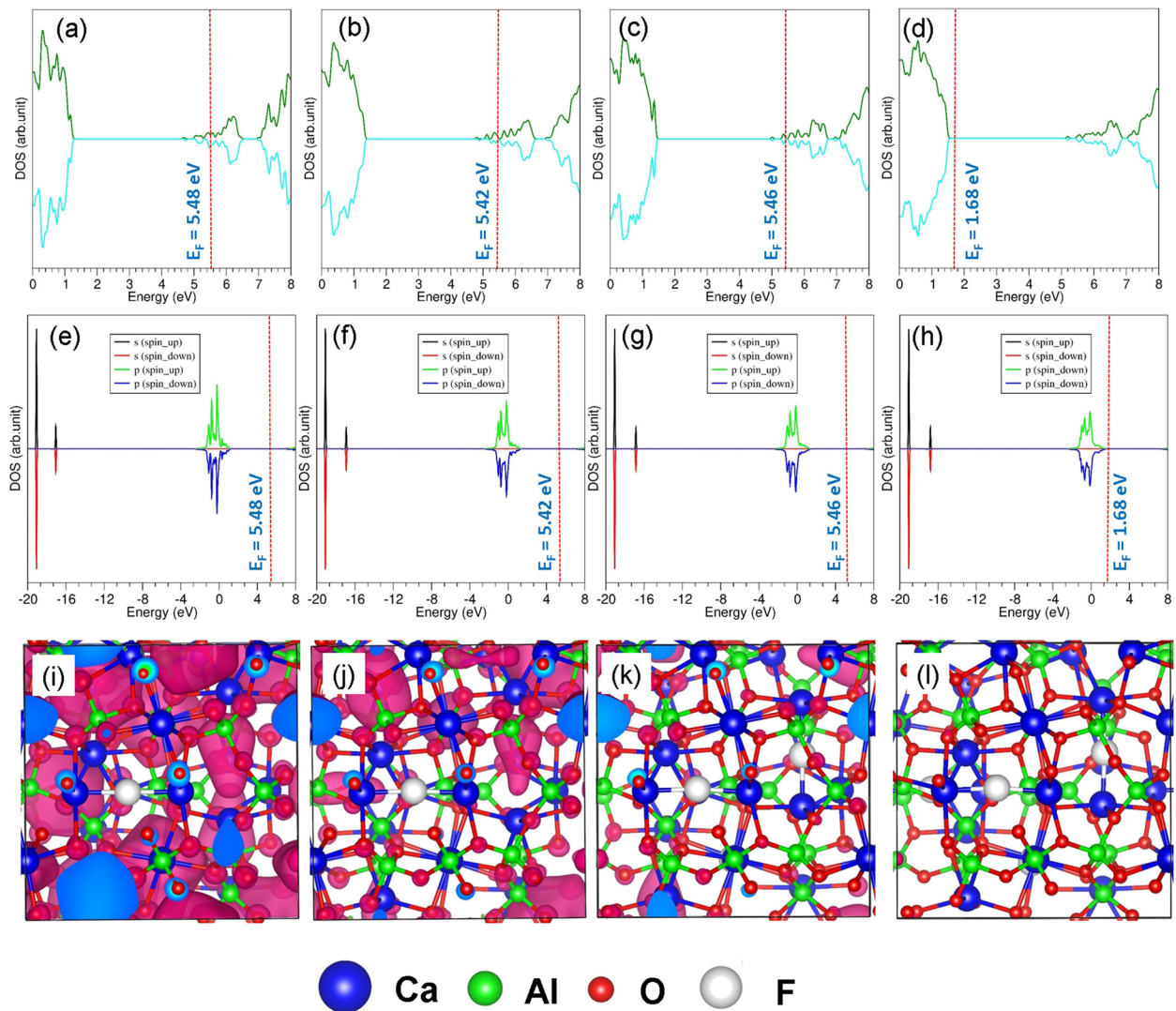


FIG. 8. DOS plots calculated for (a) $\text{F}@C12A7:e^-$, (b) $2\text{F}@C12A7:e^-$, (c) $3\text{F}@C12A7:e^-$, and (d) $4\text{F}@C12A7:e^-$. The corresponding atomic DOS plots calculated for F (e)–(h) and band decomposed charge density plots associated with extra-framework electrons (i)–(l) are also shown.

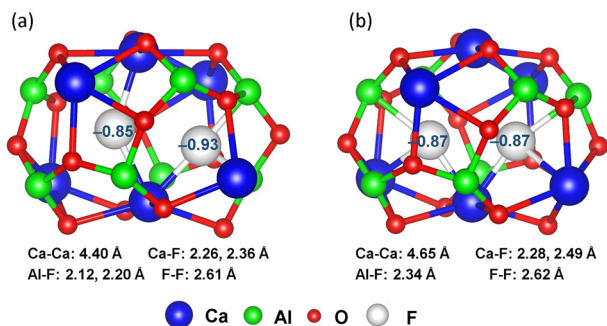


FIG. 9. Optimized structures of F_2 encapsulated in (a) C12A7:O^{2-} and (b) C12A7:e^- .

the resultant compound is an insulator [refer to Fig. 8(d)]. Atomic DOS plots calculated for F atoms show that p states of F appear just below the Fermi level [refer to Figs. 8(e)–8(h)]. Band decomposed charge density plots associated with the remaining electrons show the gradual decrease in electrons upon subsequent encapsulation [refer to Figs. 8(i)–8(l)]. In the case of four F atoms, there is no electron left in the lattice as confirmed by the charge density plot shown in Fig. 8(l).

D. Encapsulation of dimers in C12A7:O^{2-} and C12A7:e^-

We investigated the formation of F_2 dimers within a single cage of C12A7:O^{2-} and C12A7:e^- . The relaxed structures are shown in Fig. 9. The F_2 bond distance is calculated to be 2.61 Å in C12A7:O^{2-} , considerably longer than its corresponding gas phase dimer of 1.77 Å [refer to Fig. 9(a)]. The Bader charges on F atoms confirm the formation of F^- ions and the unfavorability of the formation of F_2 dimers in a single cage. The distortion in the cage is reflected in the shorter Ca–Ca cage pole distance of 4.40 Å compared to that calculated in the empty cage of C12A7:O^{2-} . The encapsulated F^- ions are oriented asymmetrically, as shown in Fig. 9(a). This is further confirmed by the unequal Bader charges on F atoms, one F atom forming Ca–F bonds only, and the other F atom forming both Ca–F and Al–F bonds. In the case of C12A7:e^- , distortion is small as evidenced by the symmetrical orientation of the dimer, equal Bader charges on the F atoms, and a cage pole distance of 4.61 Å, which is close to the values calculated in single F atoms occupied in C12A7:e^- [refer to Fig. 9(b)]. The relative energies between two single F atoms occupying adjacent cages and a dimer occupying a single cage in C12A7:O^{2-} and C12A7:e^- were compared (refer to Table II). The configuration consisting of two single F atoms occupied in adjacent

TABLE II. Relative energies between two single F atoms occupying adjacent cages and a dimer occupying a single cage in C12A7:O^{2-} and C12A7:e^- .

Structures	Relative energy (eV)
2F@C12A7:O^{2-}	0
$\text{F}_2\text{@C12A7:O}^{2-}$	1.60
2F@C12A7:e^-	0
$\text{F}_2\text{@C12A7:e}^-$	1.14

cages is more favorable than the configuration consisting of a dimer in a single cage (refer to Table II).

IV. CONCLUSIONS

DFT simulations were employed to examine the formation and stability of F^- ions in C12A7 . Both stoichiometric and electroneutral forms of C12A7 can accommodate F atoms from the gas phase F_2 molecule in the form of F^- ions exothermically. The electroneutral form of C12A7 exhibits a significant enhancement in the encapsulation. Successive encapsulation of multiple F atoms is also energetically favorable, and the encapsulation of dimers in a single cage is unfavorable in both C12A7:O^{2-} and C12A7:e^- . The current results can be of interest in the development of C12A7 based anion storage materials.

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The authors declare that there is no competing financial interest.

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

- T. Shibayama, H. Shindo, and Y. Horiike, *Plasma Sources Sci. Technol.* **5**, 254 (1996).
- H. Shindo, Y. Sawa, and Y. Horiike, *Jpn. J. Appl. Phys.* **34**, L925 (1995).
- W. M. Lau, I. Bello, M. Sayer, and L. Zou, *Appl. Phys. Lett.* **64**, 300 (1994).
- C. M. S. Rauthan, G. S. Viridi, B. C. Pathak, and A. Karthigeyan, *J. Appl. Phys.* **83**, 3668 (1998).
- J. Ishikawa, *Rev. Sci. Instrum.* **67**, 1410 (1996).
- C. Song, J. Sun, S. Qiu, L. Yuan, J. Tu, Y. Torimoto, M. Sadakata, and Q. Li, *Chem. Mater.* **20**, 3473 (2008).
- Q. X. Li, Y. Torimoto, and M. Sadakata, patent WO/2005/115913, 2005.
- Q. X. Li, Y. Torimoto, and M. Sadakata, Japan patent JP2004–160374, 2004.
- Q. X. Li, K. Hayashi, M. Nishioka, H. Kashiwagi, M. Hirano, Y. Torimoto, H. Hosono, and M. Sadakata, *Appl. Phys. Lett.* **80**, 4259 (2002).
- Q. Li, H. Hosono, M. Hirano, K. Hayashi, M. Nishioka, H. Kashiwagi, Y. Torimoto, and M. Sadakata, *Surf. Sci.* **527**, 100 (2003).
- J. Li, F. Huang, L. Wang, S. Q. Yu, Y. Torimoto, M. Sadakata, and Q. X. Li, *Chem. Mater.* **17**, 2771 (2005).
- J. Li, F. Huang, L. Wang, Z. Wang, S. Yu, Y. Torimoto, M. Sadakata, and Q. Li, *J. Phys. Chem. B* **109**, 14599 (2005).
- F. Huang, J. Li, H. Xian, J. Tu, J. Q. Sun, S. Q. Yu, Q. X. Li, Y. Torimoto, and M. Sadakata, *Appl. Phys. Lett.* **86**, 114101 (2005).
- F. Huang, J. Li, L. Wang, T. Dong, J. Tu, Y. Torimoto, M. Sadakata, and Q. Li, *J. Phys. Chem. B* **109**, 12032 (2005).
- 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).
- F. Hayashi, Y. Tomota, M. Kitano, Y. Toda, T. Yokoyama, and H. Hosono, *J. Am. Chem. Soc.* **136**, 11698 (2014).
- R. W. Nurse, J. H. Welch, and A. J. Majumdar, *Trans. Br. Ceram. Soc.* **64**, 323 (1965).
- H. Hosono and Y. Abe, *Inorg. Chem.* **26**, 1192 (1987).

- ¹⁹N. Kuganathan, A. Chroneos, and R. W. Grimes, *Sci. Rep.* **9**, 13612 (2019).
- ²⁰M. Miyakawa, N. Ueda, T. Kamiya, M. Hirano, and H. Hosono, *J. Ceram. Soc. Jpn.* **115**, 567 (2007).
- ²¹N. Kuganathan, H. Hosono, A. L. Shluger, and P. V. Sushko, *J. Am. Chem. Soc.* **136**, 2216 (2014).
- ²²M. Kitano, S. Kanbara, Y. Inoue, N. Kuganathan, P. V. Sushko, T. Yokoyama, M. Hara, and H. Hosono, *Nat. Commun.* **6**, 6731 (2015).
- ²³Y. Toda, H. Hirayama, N. Kuganathan, A. Torrisi, P. V. Sushko, and H. Hosono, *Nat. Commun.* **4**, 2378 (2013).
- ²⁴J. Jeevaratnam, F. P. Glasser, and L. S. D. Glasser, *J. Am. Ceram. Soc.* **47**, 105 (1964).
- ²⁵I. Odler and S. Abdul-Maula, *J. Am. Ceram. Soc.* **63**, 654 (1980).
- ²⁶C.-K. Park, *Cem. Concr. Res.* **28**, 1357 (1998).
- ²⁷D. R. Lide, *CRC Handbook of Chemistry and Physics Internet Version 2005 Edition* (CRC Press, 2005).
- ²⁸G. Kresse and J. Furthmüller, *Phys. Rev. B* **54**, 11169 (1996).
- ²⁹P. E. Blöchl, *Phys. Rev. B* **50**, 17953 (1994).
- ³⁰H. J. Monkhorst and J. D. Pack, *Phys. Rev. B* **13**, 5188 (1976).
- ³¹J. P. Perdew, *Int. J. Quantum Chem.* **28**, 497 (1985).
- ³²W. 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).
- ³³S. Grimme, J. Antony, S. Ehrlich, and H. Krieg, *J. Chem. Phys.* **132**, 154104 (2010).
- ³⁴L. Palacios, Á. G. De La Torre, S. Bruque, J. L. García-Muñoz, S. García-Granda, D. Sheptyakov, and M. A. G. Aranda, *Inorg. Chem.* **46**, 4167 (2007).
- ³⁵P. V. Sushko, A. L. Shluger, Y. Toda, M. Hirano, and H. Hosono, *Proc. R. Soc. A* **467**, 2066 (2011).
- ³⁶P. V. Sushko, A. L. Shluger, M. Hirano, and H. Hosono, *J. Am. Chem. Soc.* **129**, 942 (2007).