Inorganic Electrides

Is Mayenite without Clathrated Oxygen an Inorganic Electride?**

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With electrons as their anions, electrides have attracted a much interest recently in broad fields of research.[1] Despite their importance both in fundamental science and industrial

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applications, traditional organic electrides are stable only at cryogenic temperatures and are air- and water-sensitive. It is therefore interesting and important to explore room-temperature stable inorganic electrides.[2] Existing model systems towards this direction include Na_4^{3+} clusters in the sodalite cage of Na^+Y[3] and alkali metals in the channels of zeolite ITQ-4.[4] Recently, Matsuishi et al.[5] removed the clathrated oxygen ions from the crystallographic cages of mayenite $12CaO{\cdot}7Al_2O_3$ (C12A7) through a base-metal oxidation process. They suggested that their treatment inject extra electrons in place of the free O^{2-} with a spherical 1*s* wave function of an F^+-like center, and thus produce an inorganic electride.

To gain insight into the electronic properties of this kind of mayenite with removed clathrated oxygen (C12A7:2e$^-$) and to verify the electride model, it is important to investigate this material theoretically. Unfortunately, the existing theoretical studies give contradictory conclusions. The first theoretical work by Sushko et al.[6] supports the electride model with localized extra electrons, whereas a recent study by Medvedeva and Freeman[7] reveals that the extra electrons are highly delocalized both in the cavities and in the regions occupied by cations, and thus opposes the electride model. We noticed that both studies do not provide a satisfactory conclusion with respect to the real physical picture of the extra electrons in this novel material. Sushko et al.[6] used an embedded cluster model, which is only suitable for the dilute extra electron limit, and Medvedeva and Freeman[7] used the linear muffin-tin orbital (LMTO) method with a simple atomic sphere approximation, which may not be accurate enough to describe the charge-density distribution in this complex system. Moreover, the geometry was not fully optimized in either of the studies. To clarify this issue, we report herein a careful plane-wave pseudopotential study on the geometrical and electronic structure of this material.

The crystal structure of C12A7, with two formula units per unit cell, is characterized by a positively charged lattice framework $[Ca_{24}Al_{28}O_{64}]^{4+}$ that forms twelve crystallographic cages per unit cell ($I\bar{4}3d$ space group). The remaining two oxygen ions are clathrated in the cages to maintain charge neutrality. We optimized the geometry of C12A7 with its lattice parameter fixed to the experimental value (11.989 Å).[8] As shown in Figure 1, cages with free oxygen inside have a relatively large distortion after optimization, where it can be clearly seen that two opposite Ca atoms at the cage wall are strongly pulled towards the center of the cage. Therefore, after optimization, the cages in C12A7 are no longer identical.

When considering the geometry of the system without clathrated oxygen, one must take special care. In the work of Medvedeva and Freeman,[7] they simply assumed that all cages in C12A7:2e$^-$ are identical. But considering the possibility that the extra electrons may be captured in some cages with other cages being kept empty,[5,6] this assumption is far from obvious. In this work, we optimized the geometry of C12A7:2e$^-$ from two initial configurations. The first optimization starts from a framework of undistorted cages, and the second starts from the previously relaxed distorted framework, but without clathrated oxygen. Within numerical

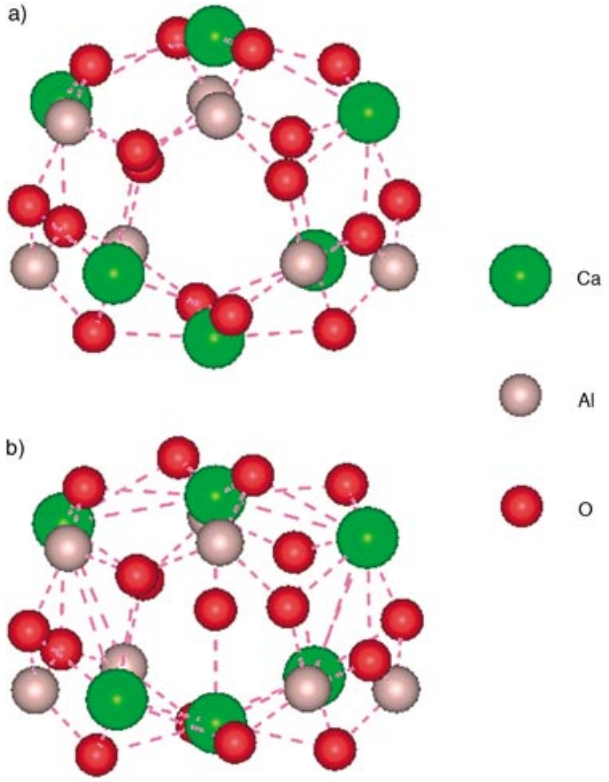

Figure 1. Perspective view of a) an undistorted cage and b) a distorted cage in mayenite. There is a clathrated oxygen inside the distorted cage, and the upper and lower Ca (green) at the cage wall are strongly pulled towards the center O (red).

precision, both optimizations led to the same final structure, and the distortion of the second initial geometry finally disappeared. Therefore, the simple assumption of Medvedeva and Freeman[7] turns out to be correct, but it must be emphasized that we can only be confident with the following calculations on electronic structure after such a careful examination of the geometry.

The identical-cage geometry strongly suggests that the picture[5,6] of two types of cages (electron trapping and empty) in C12A7:2e$^-$ may be incorrect. We noticed that in the embedded cluster calculation[6] the two quantum-mechanical (QM) cages are geometrically different on account of different classical neighboring cages. This artificial difference between the two QM cages may be the reason that leads to the extra electron being localized in only one of the two cages.

Based on the optimized geometries, we calculated the band structures of C12A7 and C12A7:2e$^-$, and the result is shown in Figure 2. For C12A7, there are two very narrow bands below the Fermi level, which mainly come from the *p* orbitals of the clathrated oxygen, as suggested by Medvedeva and Freeman.[7] Above these two interstitial bands, there is a band manifest (from about 2.0 to 3.8 eV) that corresponds to the cavities. After the clathrated oxygen is removed, the interstitial bands disappear, and the cavity bands become partially occupied by the extra electrons. Because of the disappearance of the distortion, the cavity bands become more degenerate for C12A7:2e$^-$.

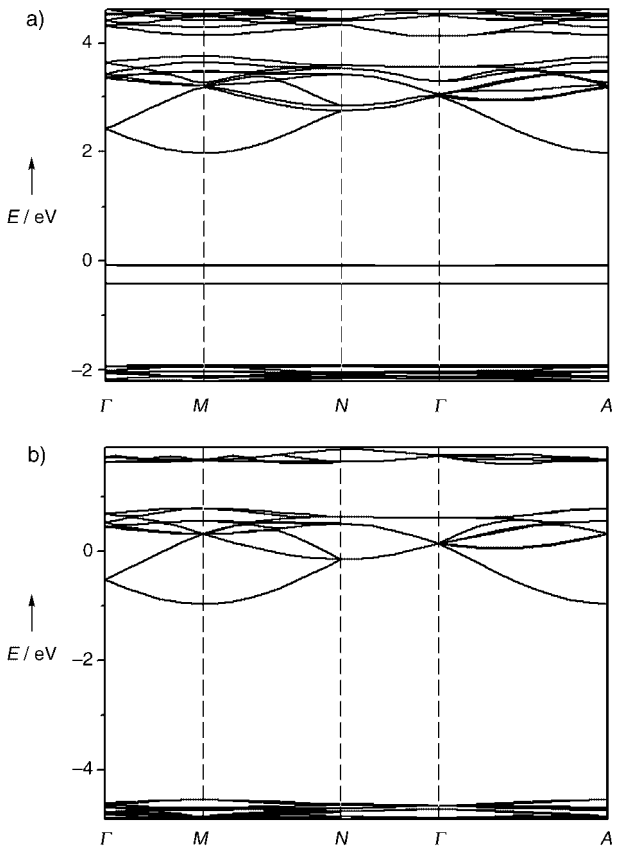

Figure 2. Band structures of a) C12A7 and b) C12A7:2e$^-$. The Fermi energy is at 0. $\Gamma = (0,0,0)$, $M = (1/2,0,0)$, $N = (1/2,1/2,0)$, and $A = (0,0,1/2)$.

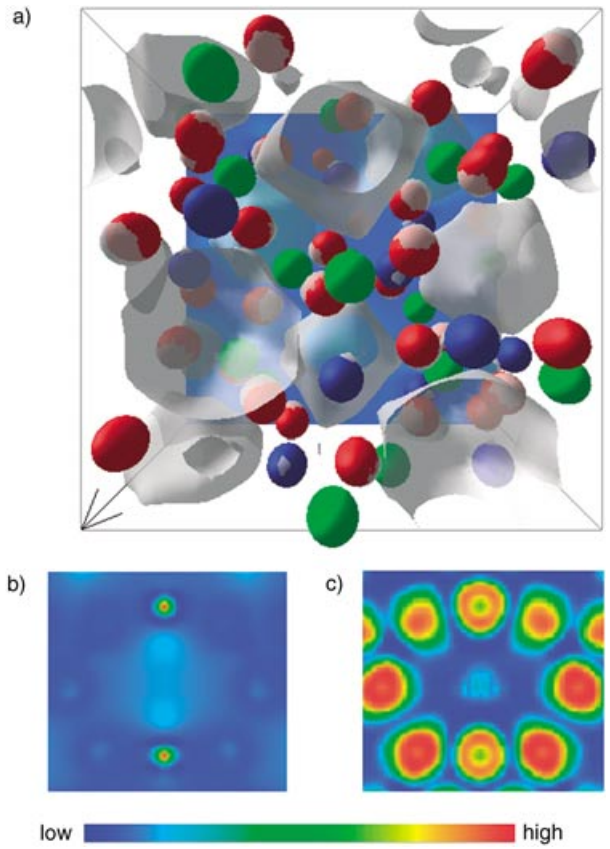

Figure 3. a) Isosurface and b) contour map of the charge density of extra electrons in C12A7:2e$^-$, and c) contour map of the C12A7:2e$^-$ electron-localization function. The isosurface is plotted within a unit cell, and the contour maps are plotted on a profile crossing one cage. The value of the isosurface is 7.0 electrons per unit cell.

To address the validity of the electride model, we calculated the charge density in a 1.5 eV window below E_F, which gives the spatial distribution of the extra electrons. We found that the density is equally distributed in the twelve cages and that most of the charge density is inside the cages (Figure 3a,b). Although it is still not perfectly localized, our charge density is already different from that of Medvedeva and Freeman.[7] To evaluate the degree of localization quantitatively, we integrated the charge density inside the cage with the ionic radii of Ca, Al, and O set to 0.99, 0.51, and 1.32 Å, respectively. We found that 75% of the extra electron density is distributed in the twelve cages. Although this value is not very high, it is comparable to those of organic electrides. For example, in $Cs^+([15]crown\text{-}5)_2{\cdot}e^-$,[9] a well-studied electride, we determined the ratio of the in-cavity extra electron as 83% by performing a similar analysis. Therefore, our pseudopotential plane-wave calculations show that the extra electrons are generally localized in the cages, and thus support an electride model for C12A7:2e$^-$.

Further important theoretical evidence for the electride model comes from the types of chemical bond between the extra electrons and the positively charged lattice framework. Ionic bonding would support the electride model, whereas metallic bonding would lead to the opposite conclusion. Following the seminal work of Silvi and Savin,[10] we used the topological analysis of electron-localization functions (ELF)[11] to classify chemical bonds rigorously. The key topological character of ELF is its local maxima, namely the localization attractors. There are three types of attractors: bonding, nonbonding, and core. For systems with shared-electron interactions (covalent, dative, and metallic bonds), there is always a point or ring bonding attractor on the bond path, whereas for the unshared-electron interactions (ionic, hydrogen, electrostatic, and van der Waals bonds) there is nothing between the core attractors. A previous study also showed that ELF topological analysis of metallic bonds is characterized by di- or polysynaptic bonding attractors and a tridimensional network of channels.[12] For F or F^+ centers, which are chemically bonded (ionic type) to the host lattice as a quantum-mechanical subsystem, the ELF topology is characterized by a localization attractor at the vacancy site.[13]

As shown in Figure 3c, the calculated ELF for C12A7:2e$^-$ gives only one localization attractor at the center of the cavity, which is very different from the case of the typical metallic bond,[12] but similar to the ELF topology for F or F^+ centers.[13] Therefore our ELF topological analysis supports the fact that the extra electrons act as coreless anions, and there is ionic bonding between these anionic electrons and the positively charged host lattice. The electride model of C12A7:2e$^-$ is thus also supported by the criterion of the bond type. This new criterion based on powerful ELF topological analysis is much

more conclusive and easy to use than the previous charge-density criterion, which is more frequently used in the literature. In fact, the charge-density criterion may be difficult to apply even for some classical organic electrides that contain delocalized electrons.[1]

Although C12A7:2e$^-$ should be considered as an inorganic electride based on the above discussions, it is very different from the originally suggested electride model.[5,6] The integrated extra electron density within the cavity only approaches 1/3 instead of one electron, and the ELF value of the corresponding localization attractor is also relatively small (about 0.45). Therefore, C12A7:2e$^-$ can be considered as a nonstoichiometric (between extra electrons and cages) electride with only 1/3 of the electron localized in a cage. Accordingly, the chemical formula can be written as $[Ca_{24}Al_{28}O_{64}]^{4+}\cdot(1/3e^-)_{12}$. We point out that before a stoichiometric inorganic electride can be found, it is essential to obtain a stoichiometric ratio between cavities and extra electrons.

In conclusion, by carefully checking the distribution of the extra electron density and the type of bonding between these extra electrons and the host lattice, we obtained a conclusive result on whether mayenite without clathrated oxygen is an electride. This study is useful for pursuing a rigorous definition of electrides in future, and demonstrates that ELF topological analysis may play an important role in this topic. The results presented herein may also shed light on the behavior of a confined electron gas of different topology and suggest new designs for stoichiometric inorganic electrides and related functional materials.

Experimental Section

Computational methodology: Electronic-structure calculations were performed with a pseudopotential plane-wave method within the generalized gradient approximation (GGA) for exchange and correlation. A projector-augmented wave (PAW) pseudopotential[14] for electron–ion interactions and the Perdew–Wang form[15] of the GGA functional were used. A plane-wave kinetic-energy cutoff of 500 eV and a $6\times6\times6$ Monkhorst–Pack *k*-mesh were used to calculate the total energy and charge density. The calculations were performed with the Vienna Ab initio Simulation Package (VASP)[16] on an HP RX2600 cluster and an HP superdome server of the USTC-HP Laboratory for High-Performance Computing.

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