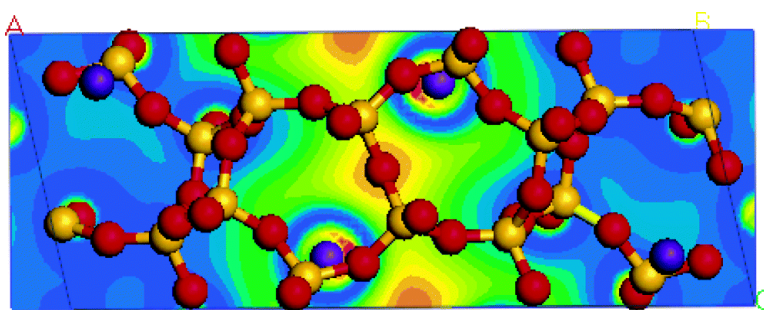Communication

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Inorganic Electride: Theoretical Study on Structural and Electronic Properties

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Electrides[1] are a novel kind of ionic compound in which the "anions" are electrons confined in a complex array of cavities or channels and the cations are nanoscale arrays of alkali metal ions that provide charge balance. With such a unique structure, electrides provide a rich area for theory and have broad or potential applications to chemical synthesis, catalysis, nanodevices, and functional materials.[2] Traditionally, electrides are composed of alkali ions sequestered within cages formed from one or two organic complexants and trapped electrons. Unfortunately, these organic eletrides tend to degrade rapidly at room temperature, which hampers the research and application of them. Recently, a room-temperature stable inorganic electride, with its structure model confirmed by the atomic pair distribution function (PDF) analysis,[3] has been synthesized by intercalating cesium in zeolite ITQ-4.[4]

Although experiments have provided many data on this novel material, which can be correlated with the electride structure model,[3,4] there is no direct information on its electronic structure in the literature. In this communication, we report a density functional theory (DFT) study on this material.

Our calculations are carried out using the local orbital functional method implemented with the DMol[3] package.[5] All-electron calculations with scalar relativistic corrections are used together with the numerical DNP basis set[5] and the generalized gradient approximation (GGA).[6] The structure of the inorganic electride is modeled within a 100-atom unit cell of $Cs_4Si_{32}O_{64}$ with periodic boundary condition.

The geometry optimization starts from optimized zeolite geometry together with randomly located cesium atoms in the zeolite channels. During the optimization, the shape and volume of the unit cell are fixed to the experimental values of the zeolite ITQ-4 cell.[7] As shown in Figure 1, with the geometry of the zeolite being little affected, the doped cesium atoms form zigzag cesium chains within the channels. The optimized positions of cesium atoms agree well with the PDF fitting results,[3] except for some deviations in the coordinates along the channel direction. We obtain variable Cs–Cs distances (5.42 and 5.65 Å alternately) indeed, which match the channel shape better than the PDF fitting results.[3] The inner angles of the zigzag chains are 87.1°. In the optimized geometry, each cesium atom is bound by six Si–O–Si units as proposed by Ichimura et al.,[3] and the Cs–O distances vary from 4.12 to 4.64 Å.

With the optimized geometry, we also calculate the formation energy of the electride by extracting energies of zeolite and bulk cesium atoms from the energy of electride, and we find the insertion of cesium atoms is favorable in energy with the formation energy of −0.11 eV/cesium.

To investigate the electronic structure of the inorganic electride, we calculate the band structure of zeolite ITQ-4 first. As shown in Figure 2a, a manifold of bonding molecular orbitals (valence band) is separated from a manifold of antibonding molecular orbitals
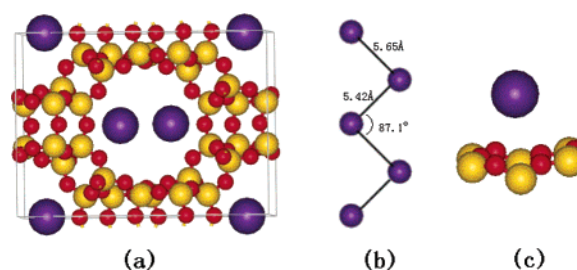

Figure 1. Optimized atomic structure of the inorganic electride. (a) Perspective view of the unit cell of $Cs_4Si_{32}O_{64}$. Cesium atoms (purple circles) are in the nanopores. Oxygen atoms are in red, and silicon is in yellow. (b) Zigzag cesium chain of the inorganic electride. (c) Picture of a binding Cs atom.
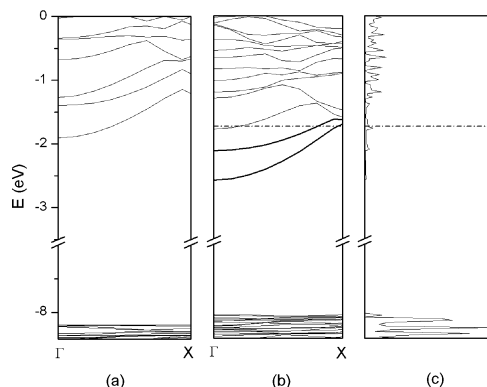

Figure 2. (a) Band structure of zeolite ITQ-4. The *x*-axis stands for a k-point sampling along the zeolite channel direction in the Brillouin zone. (b) Band structure of the inorganic electride with the Fermi level marked by a dot−dash line. (c) Density of states of the inorganic electride. The horizontal axis is in units of states/eV·cell and ranges from 0 to 135 states/eV·cell.

(conduction band) by an energy gap of about 6.5 eV. The valence band, with a width of about 3.6 eV, is very dense and flat, while the conduction band is relatively coarse and has big dispersions along the *c*-axis.

When doping with cesium, two interstitial electride energy bands (both spin-degenerated), which mainly originate from the Cs 6s electrons, appear in the energy gap near the bottom of conduction band. In Figure 2b, we can clearly see an interaction between the two electride bands and the zeolite conduction band. An upward shift about 0.1 eV of the whole zeolite band can be recognized. Including the two electride bands, there are three energy bands crossing the Fermi level. Thus, unlike the previously studied organic electrides such as $Cs^+(15\text{-crown-}5)_2 \cdot e^-$,[8] the inorganic electride has a metallic DFT band structure.

Figure 2c shows the density of states (DOS) of this inorganic electride, which is obtained from the tetrahedron method with a 1 × 1 × 15 k points sampling. The DOS at the electride Fermi level

(-1.7 eV) is 7.09 states/eV·cell, with a distinct enhancement comparing with the zeolite. This enhancement corresponds to the interstitial electride bands.

Traditionally, electrides are considered as Mott insulators,[1,8] in which a narrow electride band exists and the electron−electron interactions are important. The Hubbard model, with an atomic-like state at each lattice site, is usually invoked to describe the correlation effect in such systems. The key parameter in Hubbard model is B/U, where B is the bandwidth and U is the additional energy cost for occupying an atomic state with two electrons.

For this new inorganic electride, the total width of the two elctride bands, with dispersions up to 0.88 eV along the c-axis, is 0.95 eV, which is much larger than the value of 0.15 eV in the organic electride $Cs^+(15\text{-crown-}5)_2 \cdot e^-$.[8] If we simply suppose these two electrides have the same U value (~ 0.15 eV),[8] the electron correlation should not be so strong in the inorganic electride, and the DFT description is valid for this electride.

The experimental doping rates range from 1.0 to 4.8 Cs per cell. So, we also calculate band structures of $Cs_x Si_{32} O_{64}$ ($x = 1, 2, 3$). The number of electride band decreases to one for $x = 1$. In both the $x = 1$ and $x = 3$ cases, there is a half-occupied electride band, which indicates a high-quality metal of the inorganic electride. The $x = 2$ case is relatively complex. There are several possibilities to put the two Cs in the two nanopores within the electride unit cell. Accordingly, there can be one or two electride bands in this case. The energetically favorable geometry is found to be the one with two Cs in one nanopore, leaving the other nanopore empty, which gives one electride band. Regardless of this complexity, metallic inorganic electrides are predicted by our GGA band structures in all the cases studied here. The metallic properties promise a broad application of this material in areas such as nanodevices.

As expected, our electronic structure calculations also strongly support the electride model of this material. The doping cesium is found to be ionized to yield Cs^+. First, the Mulliken population analysis assign about $+0.3e$ to cesium. And, second, we can find addtionial evidence for cationic cesium from the band structure of the individual cesium chains. We construct fictitious cesium chains by removing the silicon and oxygen atoms from the optimized geometry of the inorganic electride and calculate the band structure of these fictitious chains of cesium atoms or cations. When comparing their 6s bands with the interstitial electride bands, we get similar energy dispersions in both cases, but only the locations of cationic chains bands are close to the electride bands. The atomic chains have much higher 6s bands.

Another prominent characteristic of electrides is that the donated electrons from alkali metal ions are confined within cavities or channels in the host matrix. To explore the real space distribution of the interstitial electride bands, we plot the charge density in Figure 3 for one of these two bands. We get similar results for the other band. The density is obtained from the wave function at the center of the Brillouin zone, and minor differences are seen at other points. We can clearly see that the charge density distributes mainly within the zeolite channel and is delocalized from the cesium cations. In the isosurface image with the isovalue being a little larger than the mean value, we can find chains of connected charge density maxima, which are very similar to those of the organic electride.[1,8]

The two electride bands make the Fermi level relatively high. Compared with the zeolite, the Fermi level of the inorganic electride increases about 3 eV, which makes it shift from below the Fermi
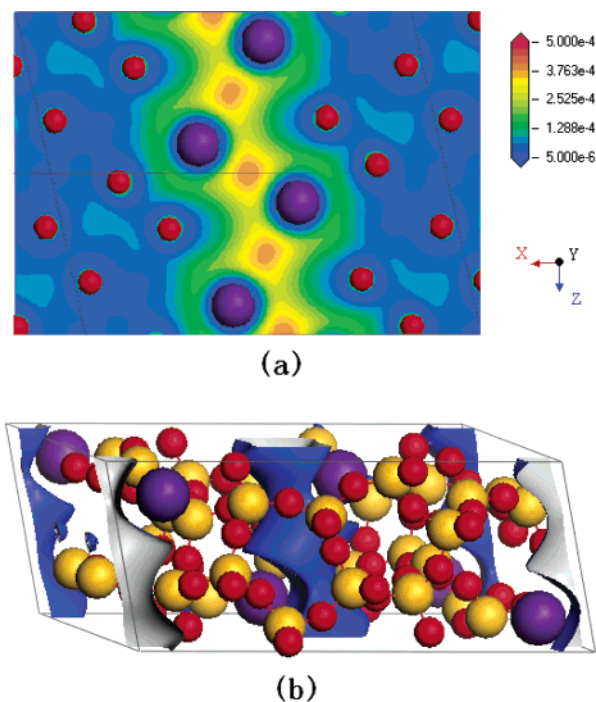

(a)

(b)

Figure 3. Charge density of an electride state at the Γ point in Brillouin zone. (a) Contour map of the charge density within a slice parallel to the a- and c-axes. The purple and red circles are Cs and O, respectively. (b) Isosurface of the charge density with the isovalue of 2.0×10^{-4} e/Å^3. The mean value of the charge density is 8.0×10^{-5} e/Å^3.

levels of some molecules such as benzene and water to above them. According to its relatively high Fermi energy and the delocalization of the donated-electron density, the inorganic electride as a powerful reducing agent[3] has very active channel sites.

Supporting Information Available: Stucture file of the inorganic electride (TXT) and DOS of zeolite ITQ-4 and the electride (PDF). This material is available free of charge via the Internet at http://www.acs.org.

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