Sr₃CrN₃: A New Electride with a Partially Filled d-Shell Transition Metal

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Supporting Information

ABSTRACT: Electrides are ionic crystals in which the electrons prefer to occupy free space, serving as anions. Because the electrons prefer to be in the pockets, channels, or layers to the atomic orbitals around the nuclei, it has been challenging to find electrides with partially filled d-shell transition metals, since an unoccupied d-shell provides an energetically favorable location for the electrons to occupy. We recently predicted the existence of electrides with partially filled d-shells using high-throughput computational screening. Here, we provide experimental support using X-ray absorption spectroscopy and X-ray and neutron diffraction to show that Sr₃CrN₃ is indeed an electride despite its partial d-shell configuration. Our findings indicate that Sr₃CrN₃ is the first known electride with a partially filled d-shell transition metal, in agreement with theory, which significantly broadens the criteria for the search for new electride materials.

Only a handful of electrides have to date been discovered:1 organic crown ether-alkalis2 and a series of inorganic materials—mayenite Ca₁₁₂Al₁₄O₃₂,3 Ca₂N₄,4 Y₄Si₃,5 Y₂C,6 or LaH₂.7 Yet, in this limited materials set, many fascinating and unusual behaviors have already been uncovered in terms of their chemical, transport, optical, and catalytic properties.8−11 We recently identified >60 new electrides from a database of 40,000 inorganic materials using high-throughput computational screening.12 Among the predicted compounds, Sr₂³Cr₄⁺N₃⁻ and Ba₂⁺Cr₄⁺N₃⁻ stood out as electrides that had transition metals with partially filled 3d-shells. This observation is unusual considering that the redox active chromium could accept the excess electron with a decrease in the formal oxidation state from +4 to +3. Instead, for these Cr-containing nitrides, the valence electron prefers to occupy an off-nuclei site. In fact, of the 60 electrides predicted by Burton et al. and all known electrides, only Sr₃CrN₃ and Ba₃CrN₃ contain partially filled d-shell transition metals.12 Combining the specific electronic/magnetic or catalytic properties of transition metals and electrides within one material could lead to unique emerging properties. We experimentally demonstrate herein that Sr₃CrN₃ is indeed an electride. Our result verifies not only the validity of our high-throughput screening, but additionally that electrides containing partially filled d-shell transition metal are possible and the electrostatics within the crystal structure can ionize even the closely spaced, partially filled d-shells.

Sr₃CrN₃ was identified in our high-throughput computational screening as presenting off-nuclei electrons and an electride behavior.12 Figure 1A shows the crystal structure of Sr₃CrN₃ with the electron density around the Fermi level obtained by Density functional theory (DFT) computations

Figure 1. (A) Crystal structure of Sr₃CrN₃ with the partial charge density of electrons near the Fermi level. (B and C) Electron density of the 1D channel. All partial charge densities have been computed by integrating from 0.5 eV below to the Fermi level. (D) Band structure of Sr₃CrN₃. Density of states and projections on Sr, Cr, and N are also provided. All computations are performed within DFT-GGA-PBE.

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within the generalized gradient approximation (GGA) and Perdew–Burke–Ernzerhoff (PBE) functional. Integration of the electron density in the channel indicates an occupation of around one electron per formula unit. While DFT can have shortcomings when modeling transition metals, techniques beyond DFT such as quasiparticle self-consistent GW provide a similar localization of electrons in the channel. In this structure, Cr is surrounded by nitrogen in a trigonal environment. This is an unusual local environment for Cr that is present only in a handful of structures.

The structure of Sr$_3$CrN$_3$ shows that a series of Sr atoms organize in a way that form a cavity that maintains the 1D electron channel (see Figure 1B and C). Figure 1D plots the band structure of Sr$_3$CrN$_3$. The compound is metallic with a parabolic behavior along the Γ-A direction indicating favorable transport in the direction of the 1D channel. Parabolic bands have also been observed in 2D electrides such as Ca$_2$N. This 1D channel electron could present interesting transport behavior warranting further investigations, especially in the area of low-dimensional physics.

From the theoretical perspective, Sr$_3$CrN$_3$ is clearly an electride. To provide experimental evidence to support this assignment, we synthesized Sr$_3$CrN$_3$ by reacting Sr$_3$N with Cr. Sr$_3$N was prepared by heat-treating Sr$_2$N$_3$ at 600 °C for 18 h. Then, a mixture of Sr$_3$N$_3$ and Cr was heat-treated under N$_2$ at 1050 °C for 96 h. The synthesized nitrides were hygroscopic and thus all the preparation steps were in an N$_2$-filled glovebox. Figure 2 shows the X-ray diffraction of the synthesized sample, verifying the Sr$_3$CrN$_3$ structure with 2 wt % of SrO and 15 wt % of metallic Cr ($\overline{I}m\overline{3}m$, 10 wt %, 3rd row), and Cr ($Fm\overline{3}m$, 5 wt %, 4th row).

To this end, we use X-ray absorption near-edge spectroscopy (XANES) to probe the electronic structure of Cr. Figure 3A shows the Cr K-edge spectra of Sr$_3$CrN$_3$ and Cr$_2$O$_3$. For Sr$_3$CrN$_3$, the presence of a strong prepeak indicates that the formal oxidation state of Cr is likely higher than Cr(III). (B) Experimental vs computed Cr K-edge XANES spectra of Sr$_3$CrN$_3$ (the computed spectra was shifted in energy to align with the experimental spectra). All spectra were normalized to the same value at high energy. We observe a good agreement between the theoretical computation and the experimental measurement, thus supporting the validity of the computed electronic structure of Sr$_3$CrN$_3$.

Having established the nominal Cr(IV) formal oxidation state in Sr$_3$CrN$_3$, we next examine whether there are hydrogen atoms in the channel. The presence of hydrogen in the channel could also lead to the Cr(IV) observation, where the hydrogen atoms serve as hydride anions (H$^\text{-}$). The possibility that the electrons in free space are instead hydrides has been discussed for many electrides, with the weak hydrogen scattering disallowing the direct use of XRD to identify the presence of the hydrogen atoms. However, the presence of hydrogen can affect the lattice parameter of the material. Our DFT computation using the PBEsol functional, known to reproduce lattice parameters well, reveals that hydrogenated Sr$_3$CrN$_3$H$_x$ and non-hydrogenated Sr$_3$CrN$_3$ support our prediction that Sr$_3$CrN$_3$ is an electride with the electrons in free space are instead hydrides has been discussed for many electrides, with the weak hydrogen scattering disallowing the direct use of XRD to identify the presence of the hydrogen atoms. However, the presence of hydrogen can affect the lattice parameter of the material. Our DFT computation using the PBEsol functional, known to reproduce lattice parameters well, reveals that hydrogenated Sr$_3$CrN$_3$H$_x$ and non-hydrogenated Sr$_3$CrN$_3$ have a significant difference in $c/a$ ratio (see Supporting Information). The experimental $c/a$ ratio (0.68) obtained by XRD is consistent with the non-hydrogenated structure ($c/a = 0.67$), suggesting that our synthesized Sr$_3$CrN$_3$ is unlikely a hydride.

To estimate the hydrogen content, we turn to neutron powder diffraction (NPD), which is more sensitive to hydrogen than XRD. Our NPD refinement indicates a hydrogen content around 0.22 ± 0.11 (see Supporting Information). This indicates also that the sample is unlikely to be a hydride and that most of the tunnel is populated by electrons with a tentative composition of Sr$_3$Cr$_{4+}$Cr$^{3+}$N$_{3-}$H$_{0.22}^-$e$^{-0.88}$. It is important to note that the
work from Barker et al. on Ba3CrN3 suggesting a higher shell transition metals. Our work shows that the electride *a higher presence of a stoichiometric amount of hydrogen in the content in our sample likely stems from our strict experimental hydrogen content for their sample. The relatively low hydrogen X-ray reSr2+ can be described as a nominally Cr(IV) compound, materials chemistry for identifying unique materials. demonstrates the growing power of computational screening in hydrogenated and non-hydrogenated versions of an electride mayenite.5,21 In fact, the ability to capture and release hydrogen is one of the hypotheses underlying why electrides are an excellent support for ammonia-synthesis catalysts.10

In conclusion, our theoretical analysis combined with XRD, XANES, and NPD show that Sr3CrN3 is an electrode, which can be described as a nominally Cr(IV) compound, Sr23Cr14N38−3e−, with the free electron occupying the one-dimensional channels in the material. The tendency for the electron to dissociate from Cr(III) to occupy one-dimensional channels is unique, since no other electrodes have so far exhibited this type of behavior, i.e., containing partially filled d-shell transition metals. Our work shows that the electrode chemistry is not restricted to only closed shell materials and identifies a new class of electrodes that could be of interest for further fundamental characterisation such as transport and catalytic activity. The confirmation of Sr3CrN3 as an electrode demonstrates the growing power of computational screening in materials chemistry for identifying unique materials.

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