

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 Ca₁₂Al₁₄O₃₂,³ Ca₂N,⁴ Y₅Si₃,⁵ 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, Sr²⁺₃Cr⁴⁺N³⁻₃ and Ba²⁺₃Cr⁴⁺N³⁻₃ stood out as electrides that had transition metals with partially filled 3*d*-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

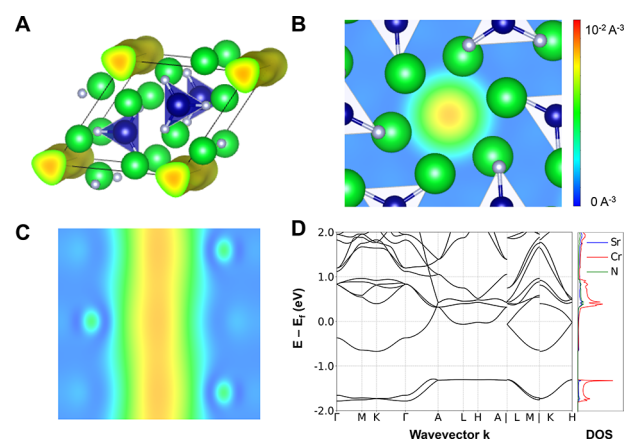


Figure 1. (A) Crystal structure of Sr₃CrN₃ with the partial charge density of electrons near the Fermi level. (B and C) Electron density of the 1D channel. All partial charge densities have been computed by integrating from 0.5 eV below to the Fermi level. (D) Band structure of Sr₃CrN₃. Density of states 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.¹² 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_3CrN_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_3CrN_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_2N .¹¹ This 1D channel electron could present interesting transport behavior warranting further investigations, especially in the area of low-dimensional physics.^{5,13}

From the theoretical perspective, Sr_3CrN_3 is clearly an electride. To provide experimental evidence to support this assignment, we synthesized Sr_3CrN_3 by reacting Sr_2N with Cr. Sr_2N was prepared by heat-treating Sr under N_2 at 600 °C for 18 h. Then, a mixture of Sr_2N 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

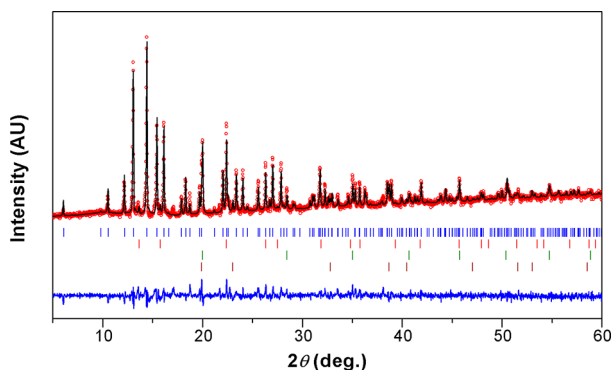


Figure 2. X-ray diffraction of Sr_3CrN_3 . The main phase (Bragg positions marked by the 1st row of vertical lines) represents 83 wt %; the impurities are SrO (2 wt %, 2nd row), Cr ($Im\bar{3}m$, 10 wt %, 3rd row), and Cr ($Fm\bar{3}m$, 5 wt %, 4th row).

synthesized sample, verifying the Sr_3CrN_3 structure with 2 wt % of SrO and 15 wt % of metallic Cr ($Im\bar{3}m$ and $Fm\bar{3}m$ phases). In comparison to the previously reported literature, the structure of the obtained Sr_3CrN_3 compound agrees well, with the space group $P6_3/m$ (lattice constants, $a = 7.71678(20)$ Å and $c = 5.2783(2)$ Å).¹⁴

Considering the Sr_3CrN_3 formula, a natural assignment of the formal oxidation state is Cr(III) (i.e., $\text{Sr}^{2+}_3\text{Cr}^{3+}\text{N}^{3-}_3$). In fact, Barker et al. described the material in this manner when they first reported the synthesis.¹⁴ However, our computation supports a $\text{Sr}^{2+}_3\text{Cr}^{4+}\text{N}^{3-}_3\cdot e^-$ assignment, indicating that Cr(III) is ionized to Cr(IV) with the extra electron residing in the one-dimensional channel. The Cr(IV) state is in better agreement with the bond valence analysis as pointed out already by Barker et al.¹⁴ Demonstrating the Cr(IV) state is therefore central to verifying the electride nature of Sr_3CrN_3 .

To this end, we use X-ray absorption near-edge spectroscopy (XANES) to probe the electronic structure of Cr. Figure 3A

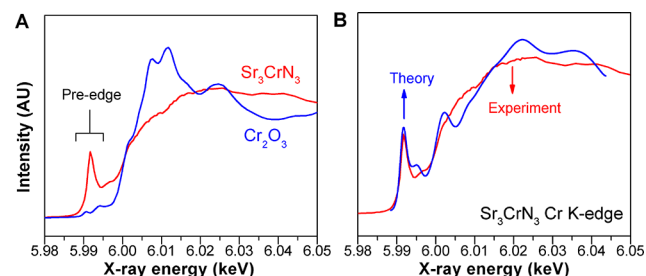


Figure 3. (A) Cr K-edge XANES of Sr_3CrN_3 and Cr_2O_3 . For Sr_3CrN_3 , the presence of a strong prepeak indicates that the formal oxidation state of Cr is likely higher than Cr(III). (B) Experimental vs computed Cr K-edge XANES of Sr_3CrN_3 (the computed spectra was shifted in energy to align with 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_3CrN_3 .

shows the Cr K-edge spectra of Sr_3CrN_3 . A comparison between Sr_3CrN_3 and Cr_2O_3 as a Cr(III) reference shows that Sr_3CrN_3 exhibits a significantly more pronounced pre-edge peak than Cr_2O_3 . It is well reported in the literature that the presence of a pre-edge peak in Cr K-edge XANES spectra is associated with chromium oxidation states higher than +3 as one would expect from the lower occupation of low-lying 3d orbitals (see Supporting Information).^{15–18} Thus, our XANES data imply that Cr are unlikely Cr(III) in Sr_3CrN_3 and supports our prediction that Sr_3CrN_3 is an electride with the electronic structure of $\text{Sr}^{2+}_3\text{Cr}^{4+}\text{N}^{3-}_3\cdot e^-$. Figure 3B shows the theoretically predicted spectra of Sr_3CrN_3 computed using DFT and FEFF. The very good agreement, especially the comparable area under the pre-edge peak, further supports the connection between the electride behavior observed theoretically and experimentally measured.

Having established the nominal Cr(IV) formal oxidation state in Sr_3CrN_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^-). 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 $\text{Sr}_3\text{CrN}_3\text{H}_x$ and non-hydrogenated Sr_3CrN_3 have a significant difference in c/a ratio (see Supporting Information).¹⁹ 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_3CrN_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 filled by electrons with a tentative composition of $\text{Sr}^{2+}_3\text{Cr}^{4+}\text{N}^{3-}_3\text{H}^-_{0.22}\cdot e^-_{0.88}$. It is important to note that the

sample was briefly exposed to ambient air before the NPD measurement. Thus, the sample likely has reacted to the moisture prior to the NPD. In fact, the c/a ratio from the NPD is higher (0.7) than that from the XRD (0.68). This higher c/a indicates a higher hydrogen content in the NPD sample, which has been exposed to ambient air, than the XRD sample (processed under vacuum). Nonetheless, both NPD and XRD combined with our XANES assignment of the Cr(IV) state and our theoretical results demonstrate conclusively the electride nature of Sr_3CrN_3 . Additionally, we note that both neutron and X-ray refinements of the chromium occupancy indicate an occupancy close to one (see [Supporting Information](#)). This excludes the possibility for chromium vacancies to “compensate” the electrons present in the channel.

A recent report from Falb et al. on $\text{Ba}_3\text{CrN}_3\text{H}$ reported the presence of a stoichiometric amount of hydrogen in the channel using NMR spectroscopy.²⁰ The authors also reported a higher c/a ratio measured by XRD compared to the previous work from Barker et al. on Ba_3CrN_3 suggesting a higher hydrogen content for their sample. The relatively low hydrogen content in our sample likely stems from our strict experimental control to prevent the sample from any exposure to moisture. Falb et al. on the contrary intentionally added hydrogen using BaH_2 as a hydrogen source. The possibility to form hydrogenated and non-hydrogenated versions of an electride has been observed in other systems such as Y_5Si_3 or 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 Finally, we note that other compounds such as Ca_3CrN_3 ²² and Sr_3FeN_3 ²³ crystallize in the same crystal structure as Sr_3CrN_3 and Ba_3CrN_3 and could potentially also form electrides.

In conclusion, our theoretical analysis combined with XRD, XANES, and NPD show that Sr_3CrN_3 is an electride, which can be described as a nominally Cr(IV) compound, $\text{Sr}^{2+}_3\text{Cr}^{4+}\text{N}^{3-}_3\text{:e}^-$, 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 electrides have so far exhibited this type of behavior, i.e., containing partially filled d -shell transition metals. Our work shows that the electride chemistry is not restricted to only closed shell materials and identifies a new class of electrides that could be of interest for further fundamental characterization such as transport and catalytic activity. The confirmation of Sr_3CrN_3 as an electride demonstrates the growing power of computational screening in materials chemistry for identifying unique materials.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/jacs.9b03472](https://doi.org/10.1021/jacs.9b03472).

Computational and experimental methods and results; additional figures ([PDF](#))

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Notes

The authors declare no competing financial interest.

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