Sr$_3$CrN$_3$: 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 Sr$_3$CrN$_3$ is indeed an electride despite its partial $d$-shell configuration. Our findings indicate that Sr$_3$CrN$_3$ 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.

Figure 1. (A) Crystal structure of Sr$_3$CrN$_3$ with the partial charge density of electrons near the Fermi level. (B and C) Electron density obtained by Density functional theory (DFT) computations integrating from 0.5 eV below to the Fermi level. (D) Band structure of Sr$_3$CrN$_3$. Density of states and projections on Sr, Cr, and N are also provided. All computations are performed within DFT-GGA-PBE.
The synthesized sample, verifying the Sr₃CrN₃ structure with 2 wt % of SrO and 15 wt % of metallic Cr (I/a3m and Fm3m phases). In comparison to the previously reported literature, the structure of the obtained Sr₃CrN₃ compound agrees well, with the space group P6₃/m (lattice constants, a = 7.71678(20) Å and c = 5.2783(2) Å).¹⁴

Considering the Sr₃CrN₃ formula, a natural assignment of the formal oxidation state is Cr(III) (i.e., Sr²⁺Cr⁴⁺N₃⁻⁻). In fact, Barker et al. described the material in this manner when they first reported the synthesis.¹² However, our computation supports a Sr²⁺Cr⁴⁺N₃⁻⁻ 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.¹² Demonstrating the Cr(IV) state is therefore central to verifying the electride nature of Sr₃CrN₃.

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 a hydride and that most of the tunnel is filled by electrons with a tentative composition of Sr²⁺₃Cr⁴⁺N₃⁻⁻H⁺₀.₂₂e⁻₀.₅₈. It is important to note that the

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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 electrode nature of Sr₃CrN₃. 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 Ba₃CrN₃H reported the presence of a stoichiometric amount of hydrogen in the channel using NMR spectroscopy. The authors also reported a higher c/a ratio measured by XRD compared to the previous work from Barker et al. on Ba₃CrN₃ 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 BaH₂ as a hydrogen source. The possibility to form hydrogenated and non-hydrogenated versions of an electride has been observed in other systems such as Y₃Si₃ or mayenite. 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. Finally, we note that other compounds such as Ca₃CrN₃ and Sr₃FeN₃ crystallize in the same crystal structure as Sr₃CrN₃ and Ba₃CrN₃ and could potentially also form electrides.

In conclusion, our theoretical analysis combined with XRD, XANES, and NPD show that Sr₃CrN₃ is an electride, which can be described as a nominally Cr(IV) compound, SrCr⁵⁺N³⁻: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 transition metals. Our work shows that the electride nature of Sr₃CrN₃ and could potentially also form electrides.

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■ REFERENCES


