Low Thermal Expansion of Layered Electrides Predicted by Density-Functional Theory

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Introduction

Electrides are solid-state ionic materials in which the anions are electrons localized within interstitial regions of the crystal lattice. Layered electrides are a subset of these materials that contain anionic electrons bound in 2D interstitial regions between positively charged atomic layers. They are of interest due to their unusual chemical properties and facile electron mobility, which may be exploited in development of new chemical processes and electronic devices.

In this work, density-functional calculations are performed for five layered electrides with two stoichiometries: $[AE_2N]^+e^-$ (Ca_2N, Sr_2N, Ba_2N) and $[M_2C]^{2+}(2e^-)$ (Sc_2C, Y_2C). Crystal structures of these materials have all been well characterized experimentally. We assess the accuracy of density functionals paired with five popular post-SCF dispersion corrections for the structural properties of these layered electrides, and provide the first evaluation of their thermal expansion coefficients.

Computational Methods

Calculations were performed with both FHI-aims and Quantum ESPRESSO (QE). The FHI-aims calculations used the 'tier1' basis of numerical atom-centered orbitals (NAOs), while the QE calculations used a planewave basis and projector augmented-wave (PAW) pseudopotentials. Five dispersion corrections were tested: XDM, D3, D3BJ, MBD-NL, and TS. The PBE functional was paired with all dispersion corrections, while B86bPBE was only paired with XDM.

Cell parameters and atomic positions were fully relaxed at a sequence of positive and negative pressures to produce parabolic volume-energy equation of state curves. Finite-temperature thermodynamic properties, including the out-of-plane lattice parameters, c_{th}, cell volumes, V_{th}, and coefficients of thermal expansion,

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P,$$

were obtained using the gibbs2 program. For all methods, the vibrational Helmholtz free-energy corrections were evaluated from the static lattice parameters and bulk modulus via the Debye approximation. To confirm its accuracy, phonon calculations were performed only for B86bPBE-XDM/PAW using phonopy and the thermodynamic properties re-evaluated with gibbs2 using the quasi-harmonic approximation.

Layered Electride Structures and ILDOS

Ca$_2$N — Sr$_2$N — Ba$_2$N — Sc$_2$C — Y$_2$C
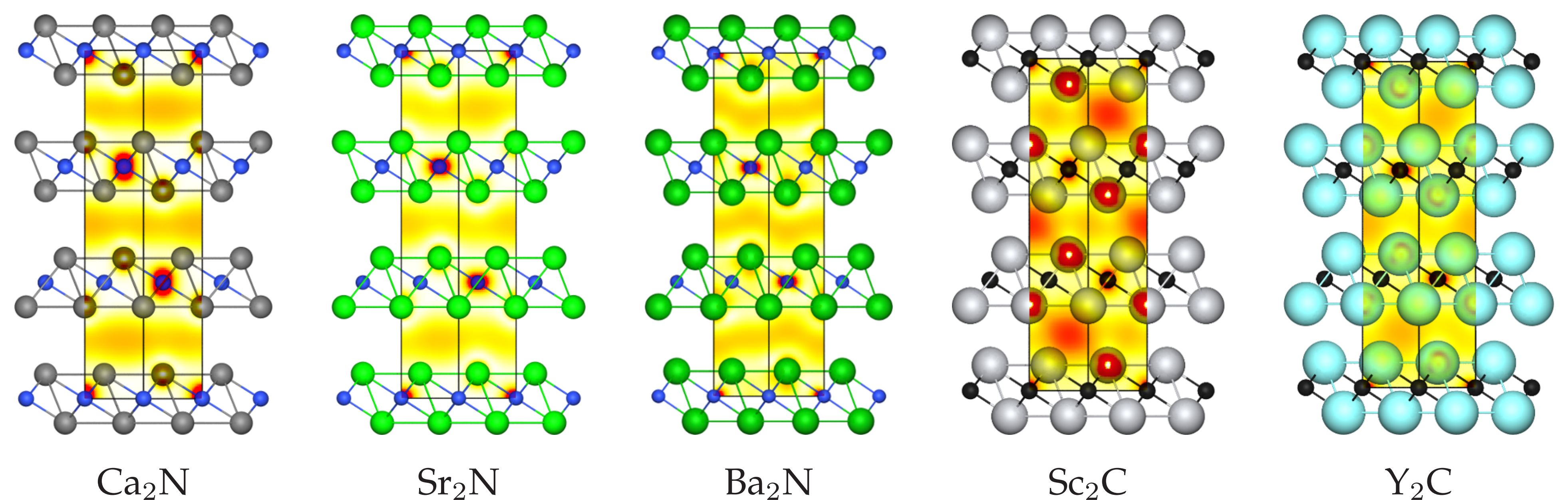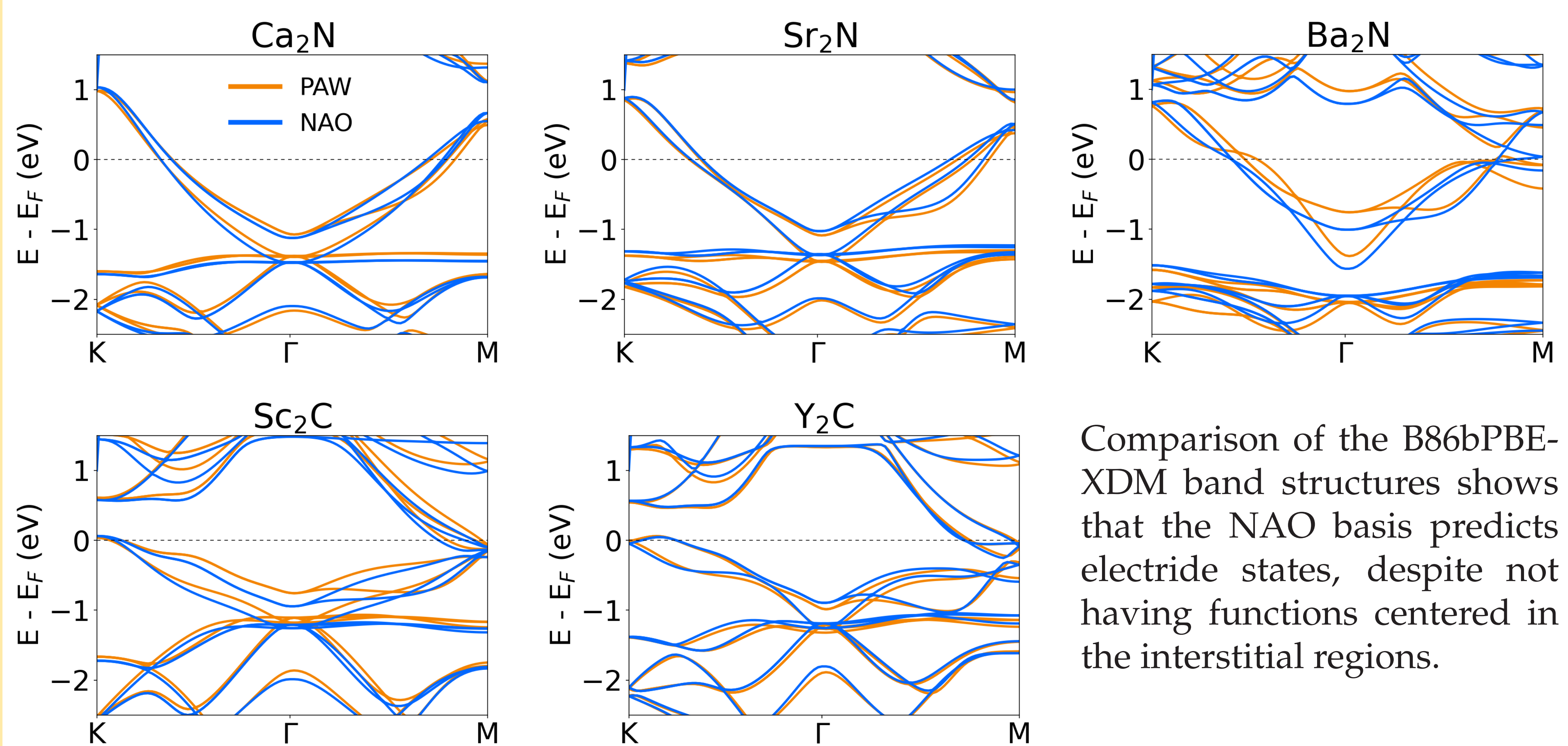
Band Structures

Comparison of the B86bPBE-XDM band structures shows that the NAO basis predicts electride states, despite not having functions centered in the interstitial regions.

Lattice Constants, Cell Volumes, Thermal Expansion

Mean absolute errors in the thermally corrected c-lattice parameters and unit-cell volumes of the five electrides, relative to experimental data collected at 298 K:

Method	Basis	c_{th} (Å)	V_{th} (Å^3)
B86bPBE-XDM	PAW	0.34	7.7
B86bPBE-XDM	NAO	0.40	10.4
PBE-XDM	PAW	0.40	11.0
PBE-XDM	NAO	0.43	11.4
PBE-D3BJ	PAW	0.47	7.9
PBE-D3	PAW	0.59	9.5
PBE-MBD-NL	NAO	0.43	11.4
PBE-TS	NAO	0.58	14.5

Comparison of results from the Debye approximation versus the quasi-harmonic approximation (QHA) using B86bPBE-XDM/PAW:

	c_{th} (Å)		V_{th} (Å^3)	
	Debye	QHA	Debye	QHA
MAE (wrt QHA)	0.05	—	1.2	—
MAE (wrt Expt)	0.34	0.36	7.7	7.4
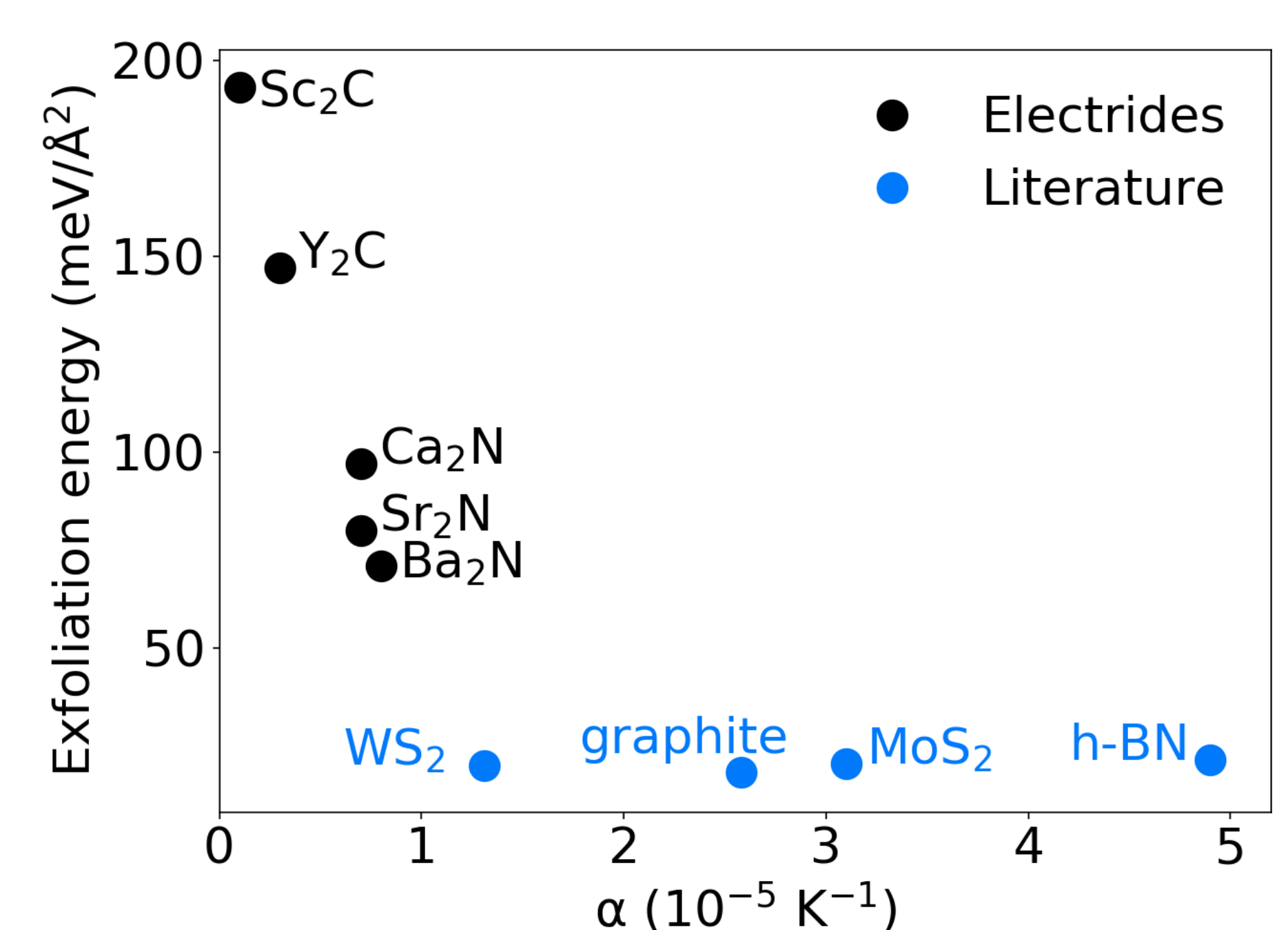
Comparing values computed using B86bPBE-XDM/PAW and the QHA, the ionically bound layered electrides have both much stronger exfoliation energies and lower thermal expansion coefficients than common dispersion-bound layered materials. Materials with more comparable thermal expansion coefficients are SiC and borosilicate glasses, which have $\alpha \approx 1.0 \times 10^{-5}$ K^{-1} at 298.15 K.

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Further Reading

A. F. Rumson, E. R. Johnson, Low Thermal Expansion of Layered Electrides Predicted by DFT. *J. Chem. Phys.* **159**, 174701 (2023). https://doi.org/10.1063/5.0171959