

## Electronic Supplementary Information

### **NaMgX<sub>3</sub> (X=Cl, Br) for Solid Electrolyte Interfaces: Atomistic Insights into Defects, Surfaces, and Doping Strategies**

**Yohandys A. Zulueta,<sup>a</sup> Bao-Ngan Nguyen-Ha,<sup>b,c</sup> and Minh Tho Nguyen<sup>b,c,\*</sup>**

<sup>a</sup> *Departamento de Física, Facultad de Ciencias Naturales y Exactas, Universidad de Oriente, CP 90500, Santiago de Cuba, Cuba*

<sup>b</sup> *Laboratory for Chemical Computation and Modeling, Institute for Computational Science and Artificial Intelligence, Van Lang University, Ho Chi Minh City, 70000 Vietnam*

<sup>c</sup> *Faculty of Applied Technology, Van Lang School of Technology, Van Lang University, Ho Chi Minh City, 70000 Vietnam, Email: minhtho.nguyen@vlu.edu.vn*

#### **1. Metrics describing the octahedral geometry**

**Octahedral volume (V):** The three-dimensional volume enclosed by the six coordinating anions around the central cation. It reflects the spatial size of the octahedron and scales with the ionic radii of the ligands.

**Average bond length (L):** The mean distance between the central atom and its six coordinating anions. It provides a measure of the overall bond strength and compactness of the octahedron.<sup>1</sup>

**Bond angle variance (Ω):** A statistical measure of how much the bond angles deviate from the ideal octahedral value (90°):

$$\Omega = \frac{1}{n} \sum_{i=1}^n (\theta_i - 90^\circ)^2$$

Larger values indicate stronger angular distortions.<sup>1</sup>

**Distortion index (<sup>d</sup><sub>i</sub>):** Quantifies the deviation of individual bond lengths (<sup>l</sup><sub>i</sub>) from the average bond length (L):

$$d_i = \frac{1}{n} \sum_{i=1}^n \frac{|l_i - L|}{L}$$

Higher values mean greater bond-length asymmetry.<sup>1</sup>

**Quadratic elongation (Q):** A measure of polyhedral distortion based on the ratio of observed bond lengths (<sup>l</sup><sub>i</sub>) to those in an ideal polyhedron (<sup>l</sup><sub>0</sub>):

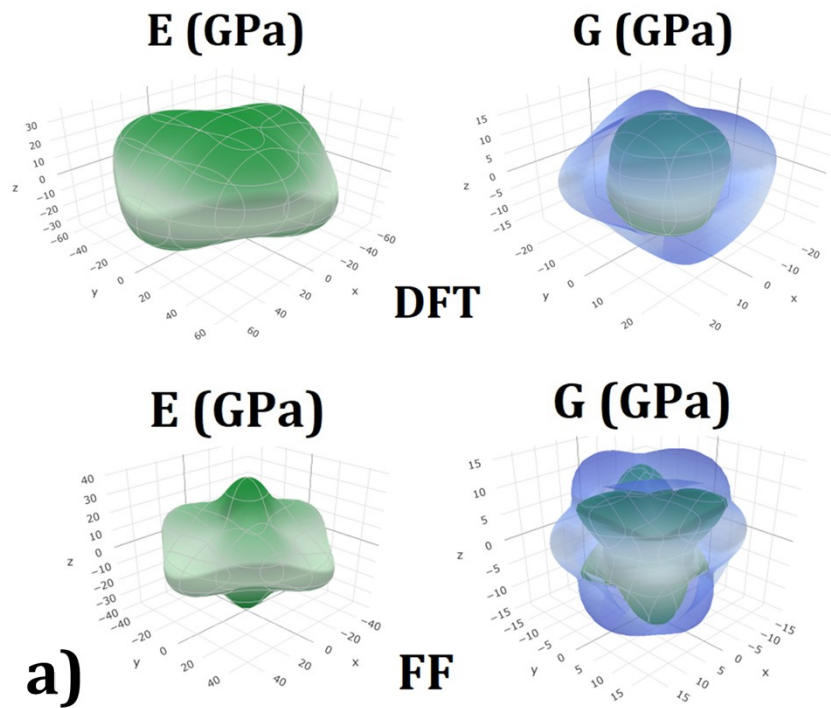
$$Q = \frac{1}{n} \sum_{i=1}^n \left( \frac{l_i}{l_0} \right)^2$$

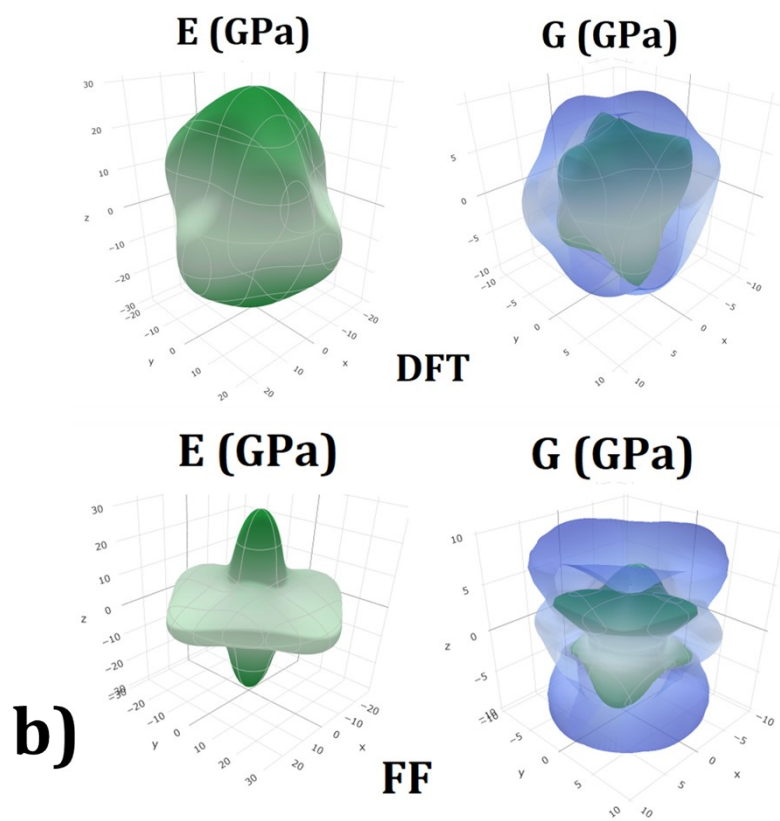
A perfect octahedron has Q = 1; values > 1 indicate elongation/distortion.<sup>1</sup>

Further details concerning these metrics are discussed in the literature.<sup>1</sup> These metrics are computed by simply open the optimized crystallographic information file in VESTA code.<sup>2</sup>

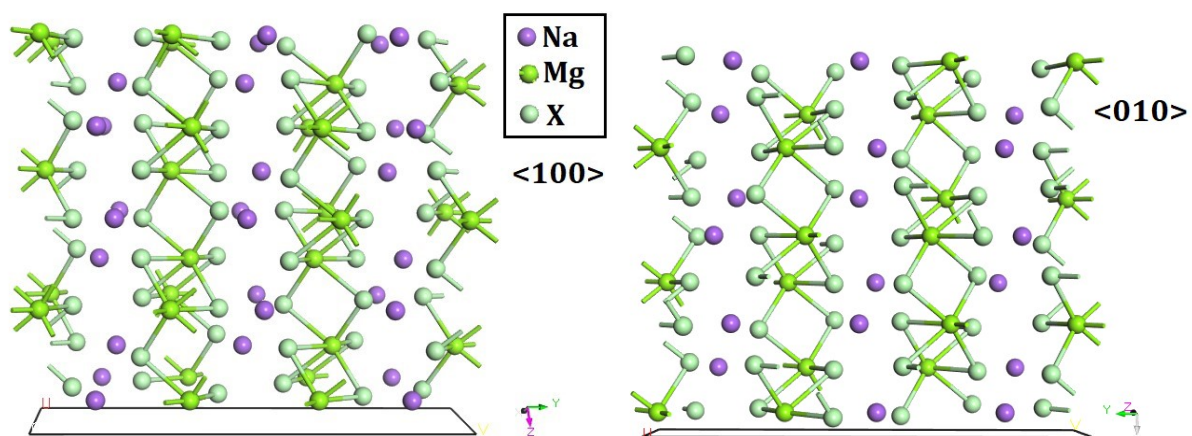
## 2. Elastic constant and mechanical anisotropy

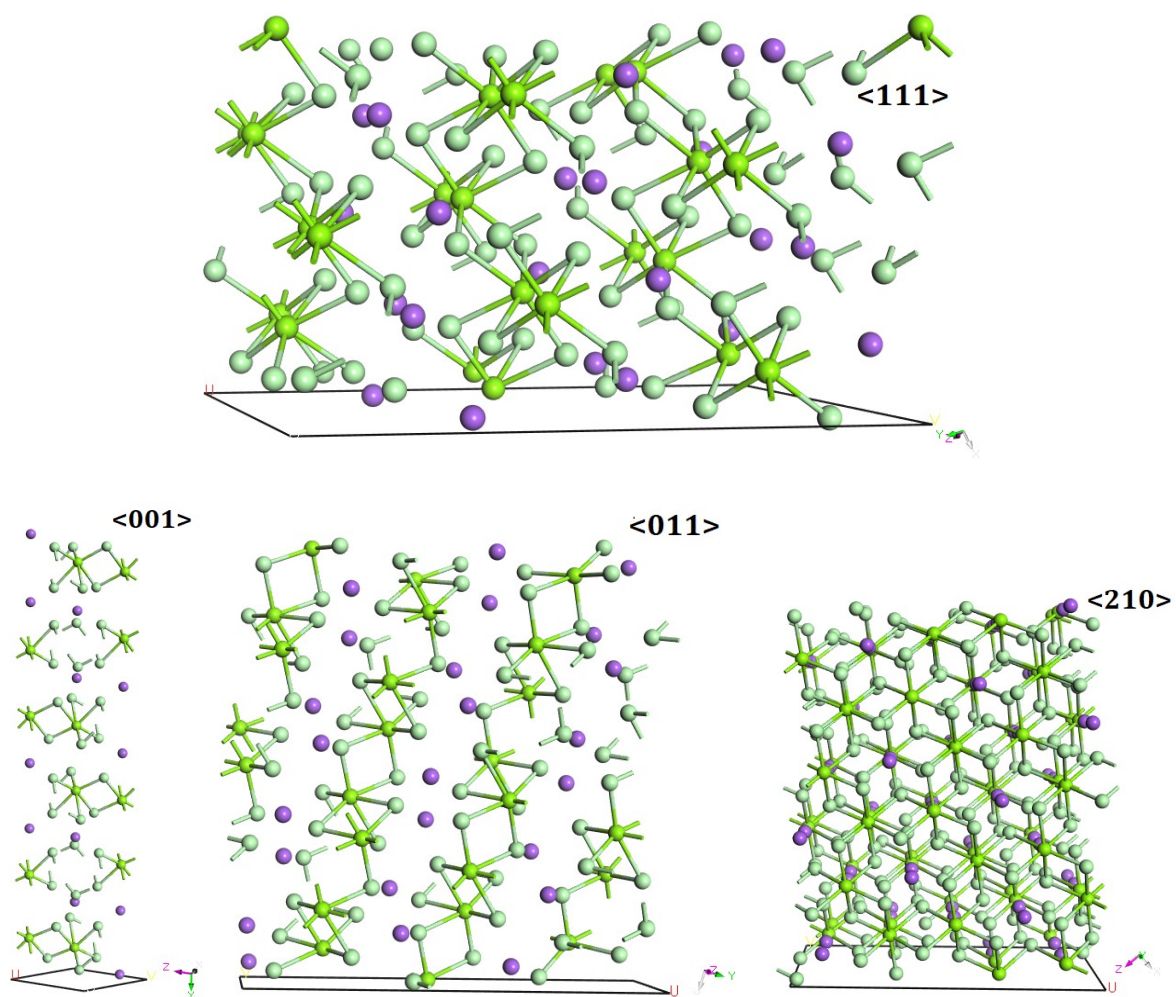
	NaMgCl <sub>3</sub>		NaMgBr <sub>3</sub>	
	DFT	FF	DFT	FF
$C_{11}$	76.54	69.38	30.33	40.00
$C_{12}$	22.62	35.18	16.39	21.48
$C_{13}$	21.77	17.81	9.16	8.52
$C_{14}=C_{56}$	0.16	1.42	-0.15	1.41
$C_{15}$	-3.43	-3.08	-2.00	-0.42
$C_{33}$	43.22	44.58	32.82	31.85
$C_{25}$	3.43	3.08	2.00	0.42
$C_{44}=C_{55}$	15.99	9.81	9.42	4.47
$C_{66}$	26.96	17.10	6.97	9.26





**Figure S1:** Young's (E) and Shear (G) modulus anisotropic behavior of **a)** NaMgCl<sub>3</sub> and **b)** NaMgBr<sub>3</sub> by using Elastic Local Anisotropy Tool (ELATE).<sup>3</sup>

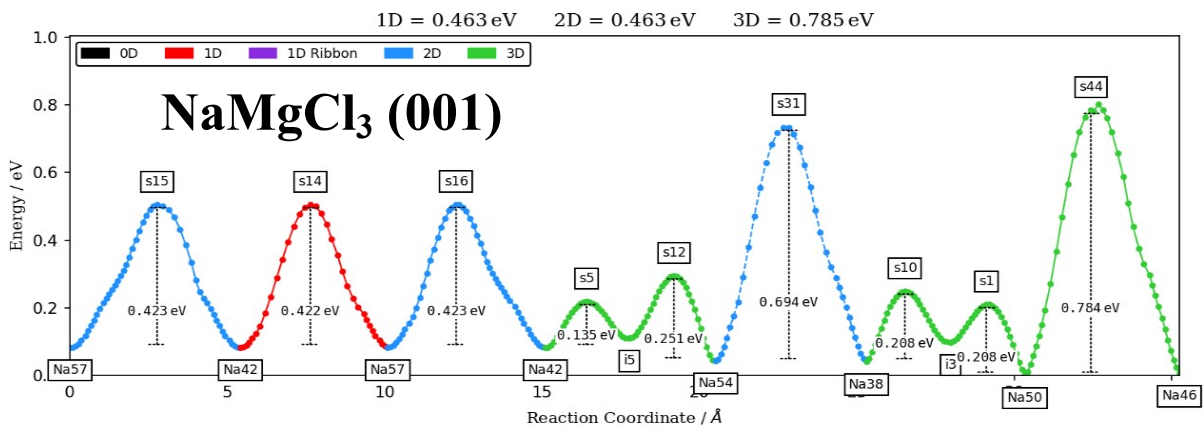
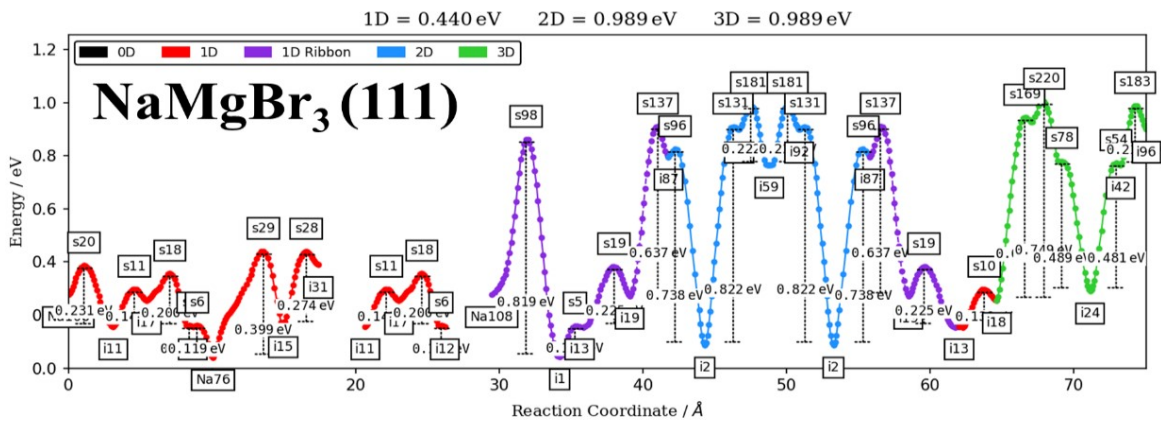
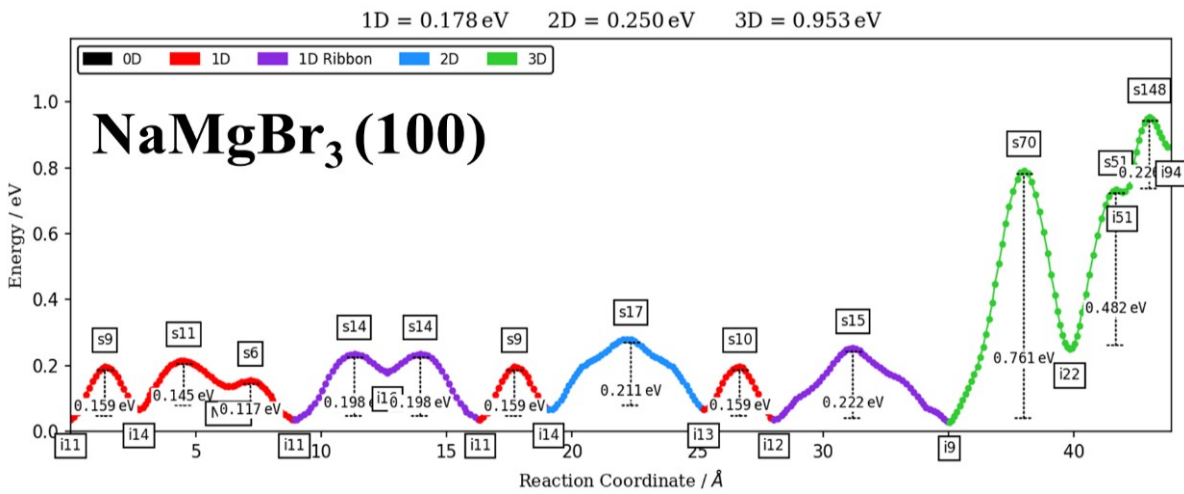
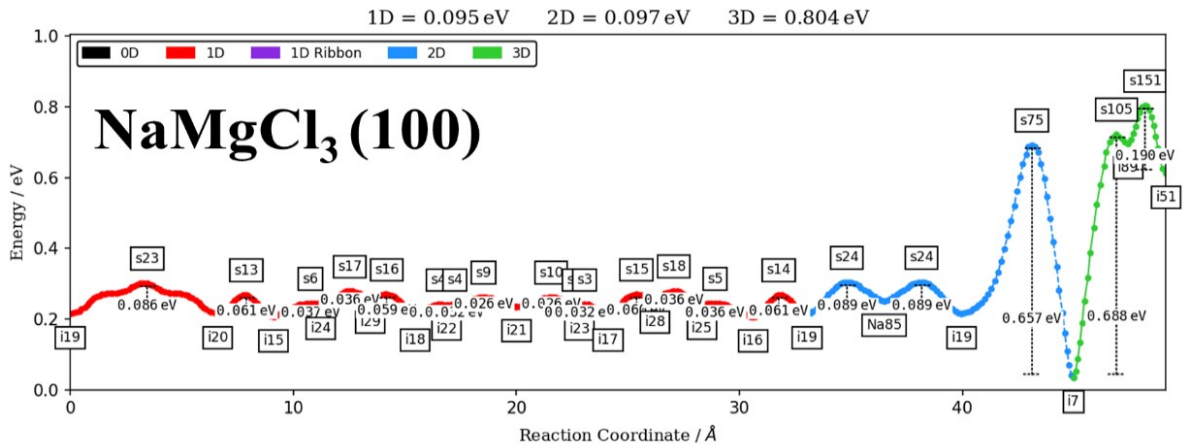




**Figure S2:** Atomic views of the  $\text{NaMgX}_3$  ( $X=\text{Cl}^-, \text{Br}^-$ ) surfaces used in this work.

**Table S1:** Predicted transport properties of  $\text{NaMgX}_3$  bulk structures.

Structure	$E_a^D$ (eV)	$D_0$ ( $\text{cm}^2/\text{s}$ )	$E_a^\sigma$ (eV)	$\sigma_0$ (S/cm)
$\text{NaMgCl}_3$	0.78	$1.64 \times 10^{-16}$	0.75	$7.55 \times 10^{-12}$
$\text{NaMgBr}_3$	0.44	$5.47 \times 10^{-11}$	0.41	$2.05 \times 10^{-6}$



**Figure S3:** Energy versus reaction coordinate showing the Na<sup>+</sup> migration profile of the most stable and unstable NaMgX<sub>3</sub> surfaces, highlighting conduction channels and migration barriers.

The following lines present the augmented force field employed in this study, incorporating both the Buckingham potential and the Shell model as described in the main manuscript. During the geometry optimization there are no negative value of phonon calculation, which confirm the validation of the force field. The reader can copy-paste and save a \*.lib file for reproducibility.

---

species

Li core 1.0

Na core 1.0

K core 1.0

O core 0.183

O shel -2.183

Cl core 1.485

Cl shel -2.485

Br core 1.094

Br shel -2.094

Mg core 2.0

Ga core 3.0

Al core 3.0

Ca core 2.0

Sr core 2.0

Ba core 2.0

Zn core 2.0

buckingham

Li core Li core 360.53 0.161 0.0 0.0 10.0

Li core O shel 292.30 0.347 0.0 0.0 10.0

Li core Cl shel 421.04 0.334 0.0 0.0 10.0

Na core Na core 1788.19 0.159 0.0 0.0 10.0

Na core O shel 1226.84 0.307 0.0 0.0 10.0

Na core Cl shel 2314.70 0.290 0.0 0.0 10.0

O shel O shel 22764.3 0.149 13.19 0.0 10.0

O shel Cl shel 8286.91 0.259 62.20 0.0 10.0

Cl shel Cl shel 1227.20 0.321 14.53 0.0 10.0

Li core Br shel 1662.80 0.288 0.01 0.0 10.0

Na core Br shel 2593.10 0.301 0.0 0.0 10.0

Br shel Br shel 4259.60 0.375 196.30 0.0 10.0

Br shel O shel 2438.00 0.327 139.60 0.0 10.0

Br shel Cl shel 2743.40 0.348 105.42 0.0 10.0

Ga core Cl shel 924.20 0.3428 0.0 0.0 10.0

Ga core O shel 2901.12 0.2742 0.0 0.0 10.0  
Al core Cl shel 1736.12 0.2917 0.0 0.0 10.0  
Al core O shel 1725.0 0.2897 0.0 0.0 10.0  
Mg core O shel 1428.50 0.2945 0.0 0.0 10.0  
Mg core Cl shel 4914.54 0.2570 0.0 0.0 10.0  
Ca core O shel 1090.40 0.3437 0.0 0.0 10.0  
Ca core Cl shel 2302.00 0.3402 0.0 0.0 10.0  
Sr core O shel 959.10 0.3721 0.0 0.0 10.0  
Sr core Cl shel 2191.09 0.3457 0.0 0.0 10.0  
Ba core O shel 905.07 0.3976 0.0 0.0 10.0  
Ba core Cl shel 2704.55 0.3528 0.0 0.0 10.0  
Zn core Cl shel 9704.89 0.2320 0.0 0.0 10.0  
buck  
Al core Br shel 1636.12 0.3 0.0 0.0 10.0  
Ga core Br shel 847.20 0.34 0.0 0.0 10.0  
Br shel Mg core 1967.77 0.334 0.0 0.0 10.0  
Br shel Zn core 3399.11 0.264751 0.0 0.0 10.0  
Br shel Sr core 1271.43 0.44 0.0 0.0 10  
Br shel Ca core 1852.87 0.362 0.0 0.0 10.0  
Ba core Br shel 2604.37 0.343 0.0 0.0 10.0

spring  
Cl core 29.38  
O core 593.716  
Br core 18.30

---

## References

- 1 K. Robinson, G. V. Gibbs and P. H. Ribbe, *Science*, 1971, **172**, 567–570.
- 2 K. Momma and F. Izumi, *J. Appl. Crystallogr.*, 2011, **44**, 1272–1276.
- 3 R. Gaillac, P. Pullumbi and F. X. Coudert, *J. Phys. Condens. Matter*, 2016, **28**, 275201.