Electronic Supplementary Information (ESI) File

From Atomic Structure to Functional Properties: Orthorhombic Disphenoidal $NaAlBr_4$ as a Solid-State Electrolyte

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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

Example of geometry optimization of $NaAlBr_4$ in Pnma space group

The user can copy and paste the following lines into a .gin file (e.g., NaAlBr4_Pnma.gin) and execute the run using:
gulp.exe < NaAlBr4_Pnma.gin > NaAlBr4_Pnma.txt
The output file NaAlBr4_Pnma.txt will contain the calculated lattice energy with other relevant properties. No negative frequencies are observed, implying stability and transferability of the force field.

##

```
opti conp conse qok nomod pres prop phon nodens inten nofreq pot efg
pressure 0 GPa
ftol 1e-005
gtol 0.0001
xtol 1e-005
maxcyc 1000
omega 1000 50 180
title
GULP calculation from Gulp for NaAlBr4_Pnma
end
cell
14.330153 7.696717 7.662034 90.000000 90.000000 90.000000 1 1 1 1 1 1
fractional
Br1 core 0.304551 0.507261 -0.736225 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.304551 0.507261 -0.736225 -2.094000 1.000000 0.0 1 1 1
Na1 core 0.150853 0.750000 -0.551466 1.000000 1.000000 0.0 1 1 1
Al1 core 0.398612 0.750000 -0.796980 3.000000 1.000000 0.0 1 1 1
Br1 core 0.442932 0.750000 -0.088516 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.442932 0.750000 -0.088516 -2.094000 1.000000 0.0 1 1 1
Br1 core 0.031151 0.750000 -0.873262 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.031151 0.750000 -0.873262 -2.094000 1.000000 0.0 1 1 1

Species
Al1 core Al
Br1 core Br
Br1 shel Br
Na1 core Na
spacegroup
P N M A
library library.lib # The library
dispersion 7
0 0 0 to 0 0 0.5
0 0 0.5 to -0.5 0 0.5
-0.5 0 0.5 to -0.5 0 0
-0.5 0 0 to -0.5 0.5 0
-0.5 0.5 0 to 0 0.5 0
0 0.5 0 to 0 0.5 0.5
```

0 0.5 0.5 to -0.5 0.5 0.5
dump NaAlBr4_Pnma.grs
output movie arc NaAlBr4_Pnma
output phonon NaAlBr4_Pnma
output frc NaAlBr4_Pnma
output osc NaAlBr4_Pnma

##

Table S1. Lattice parameters (in) and energy gap (Eg) of optimized $NaAlBr_4$ in $P2_12_12_1$ space group derived from DFT (using different functional) and FF computations. The Δ-values represent the deviations of lattice parameters with respect to those reported for $NaAlCl_4$ in Ref. 24.

	a (Å)	*b* (Å)	*c* (Å)	Eg (eV)
Pnma	13.8157	7.4231	7.5094	4.52
Ref[a]	13.8099	7.5219	7.5243	4.15[b]
Δ	-0.0058	0.0989	0.0149	-0.3660

[a]reference values are taken from Material Project database: https://next-gen.materialsproject.org/materials/mp-1210155?chemsys=Al-Br-Na
[b]The reported Eg value is approximate and using a loose *k*-point mesh

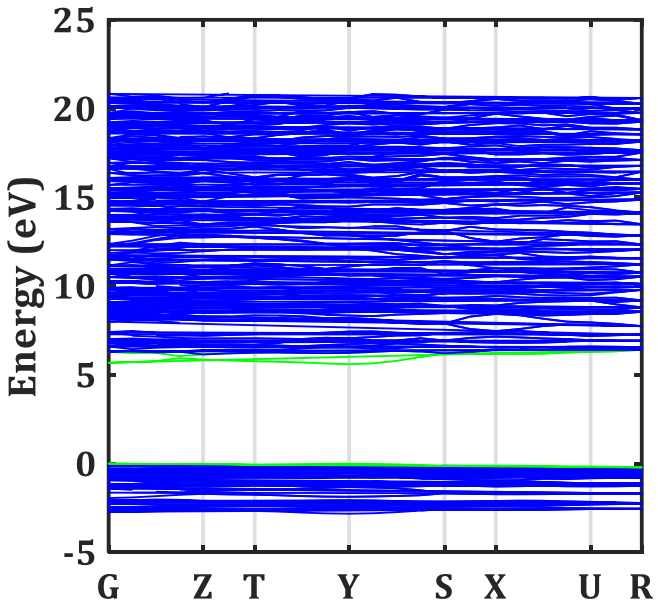

Fig S1: a) Band structure of $NaAlBr_4$ (space group Pnma) computed using the PBESOL functional.

##

Example of Al vacancy formation energy in GULP code

The user can copy and paste the following lines into a .gin file (e.g., Al-vac.gin) and execute the run using:
gulp.exe < Al-vac.gin > Al-vac.txt

The output file Al-vac.txt will contain the calculated Al vacancy formation energy along with other relevant properties.

```
############################################################
opti conp defect
title
GULP calculation of Al vacancy formation energy
end

cell
6.835600 13.526800 10.467700 90.000000 90.000000 90.000000 1 1 1 1 1 1

fractional
Na1 core 1.498060 0.627310 0.692790 1.000000 1.000000 0.0 1 1 1
Al1 core 1.481830 0.122870 1.248270 3.000000 1.000000 0.0 1 1 1
Br1 core 0.692200 0.043160 1.387450 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.692200 0.043160 1.387450 -2.094000 1.000000 0.0 1 1 1
Br1 core 0.667910 0.212620 1.095320 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.667910 0.212620 1.095320 -2.094000 1.000000 0.0 1 1 1
Br1 core 0.707110 0.507830 1.366700 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.707110 0.507830 1.366700 -2.094000 1.000000 0.0 1 1 1
Br1 core 0.781350 0.268810 0.640680 1.094000 1.000000 0.0 1 1 1
Br1 shel 0.781350 0.268810 0.640680 -2.094000 1.000000 0.0 1 1 1

Species
Br1 core Br
Br1 shel Br
Al1 core Al
Na1 core Na
spacegroup
P 21 21 21
library library.lib
#supercel 1 1 1
centre    0.411823   0.102928   0.229780 # at Al-site
vacancy  0.411823   0.102928   0.229780 #Al vacancy creation
size 13 27
############################################################
```

Band structure chart derived from GGA and different approximations.

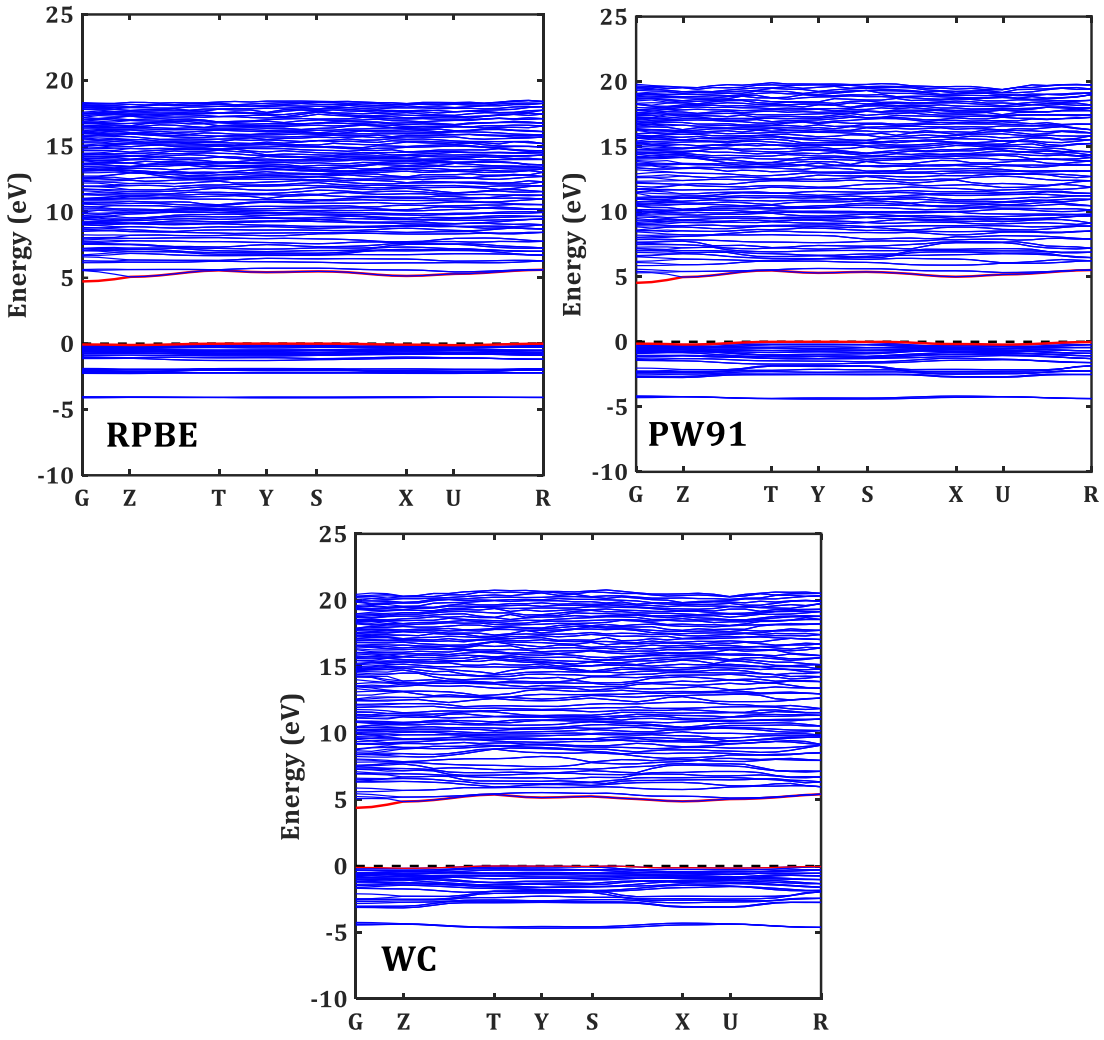

Figure S2: **a)** Band structure of $NaAlBr_4$ computed using the revised Perdew-Burke-Ernzerhof (RPBE), Perdew-Wang (PW91) and Wu-Cohen (WC) functionals. Dash lines represent the Fermi level.

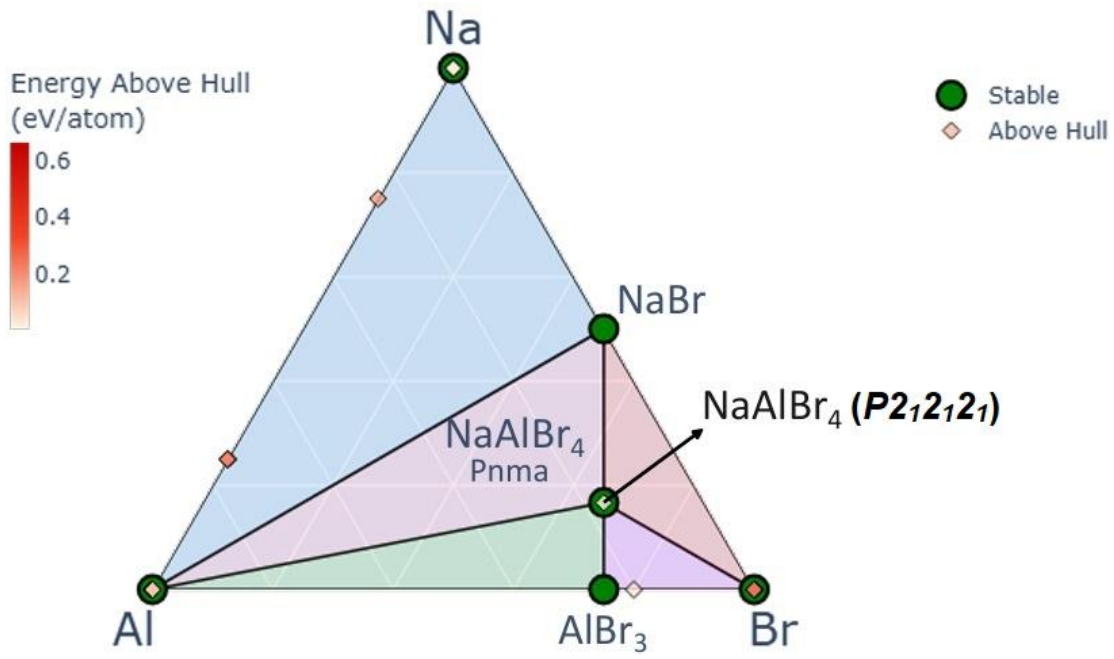

Figure S3. Ternary phase diagram of the Na-Al-Br system showing the energy above the convex hull (eV/atom) of $NaAlBr_4$. Green circles indicate stable compounds; diamond markers denote metastable phases.