Electronic Supplementary Material (ESI) for Materials Advances.

Supplementary information

Computational understanding role of vacancies and distortions in wurtzite ferroelectric memory materials: Implications for device miniaturization

Qiang Wang,[a] Shao–Xiang Go,[a] Chen Liu,[b] Minghua Li,[b] Yao Zhu,[b] Lunna Li,[a] Tae Hoon Lee,[c,d]

Desmond K. Loke [a,*]

[a] *Department of Science, Mathematics and Technology, Singapore University of Technology and Design, Singapore 487372, Singapore*
[b] *Institute for Microelectronics, Agency for Science, Technology and Research, Singapore 138634, Singapore*
[c] *Department of Engineering, University of Cambridge, Cambridge CB2 1PZ, UK*
[d] *School of Materials Science and Engineering, Kyungpook National University, Daegu 41566, Republic of Korea*
**Correspondence and requests for material should be addressed to D.K.L (e-mail: desmond_loke@sutd.edu.sg).*

Supplementary Figures

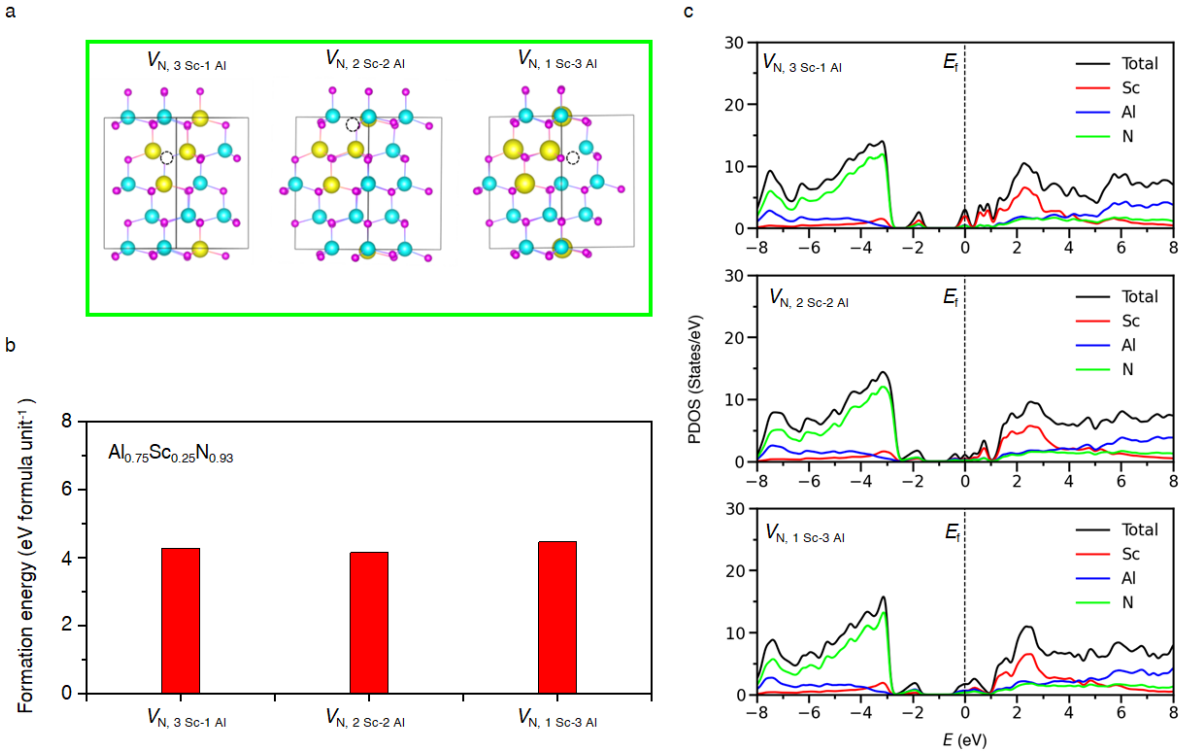


Fig. S1 Wurtzite structure and defect formation energies of three different AlScN models with one N vacancy. **a)** Snapshots of the AlScN–based systems. Sublattice A comprises N atoms (magenta), and sublattice B comprises Sc atoms (yellow) and Al atoms (cyan). **b)** Formation energies of different models with a N vacancy for the relaxed structures. **c)** Partial density of states (PDOS) of different AlScN models with a nitrogen vacancy in the relaxed state. The Fermi levels E_f were to set to zero energy.

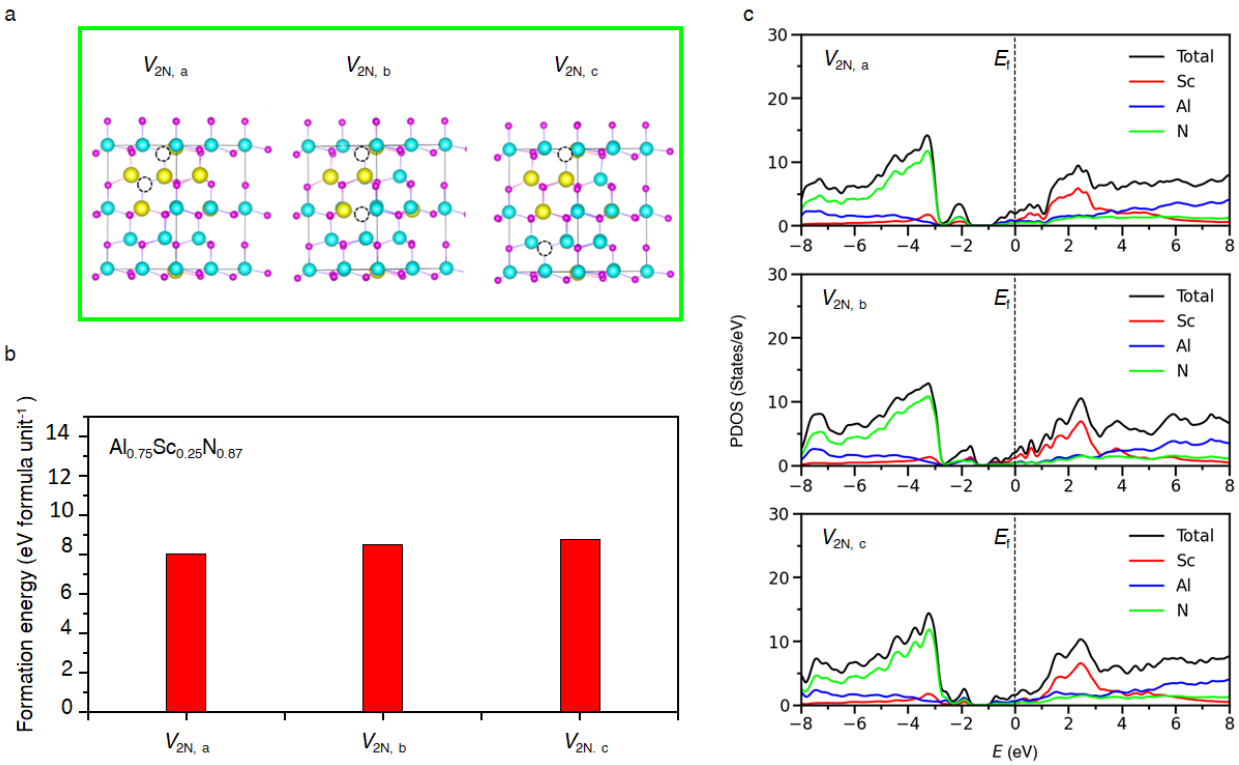


Fig. S2 Wurtzite structure and defect formation energies of three different AlScN models with two N vacancies. **a)** Snapshots of the AlScN–based system. Sublattice A comprises N atoms (magenta), and sublattice B comprises Sc atoms (yellow) and Al atoms (cyan). **b)** Formation energies of different models with two N vacancies for the relaxed structures. **c)** Partial density of states (PDOS) of different AlScN models with two N vacancies in the relaxed state. The Fermi levels E_f were to set to zero energy.

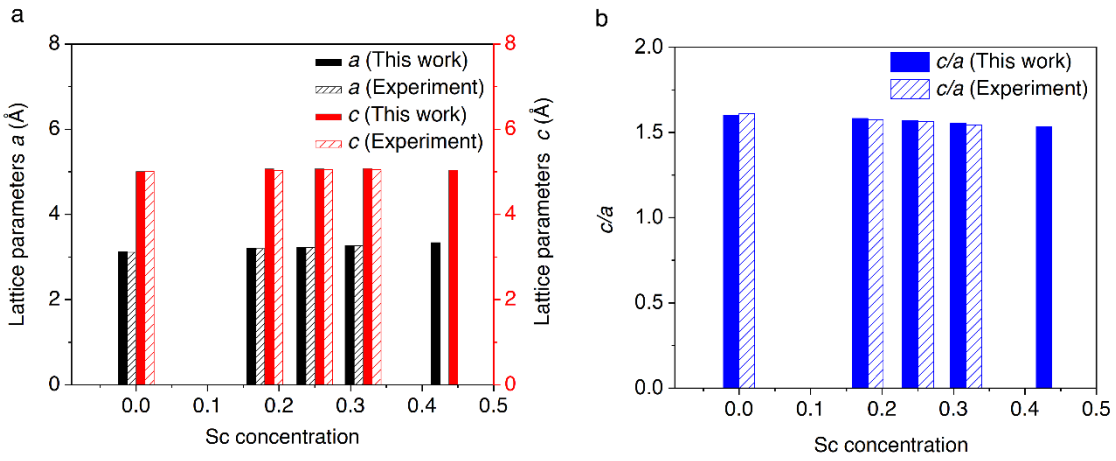


Fig. S3 a, b) Sc concentration dependent lattice parameters a) *a*, *c* and b) ratio *c/a* of $Al_{1-x}Sc_xN$. Results of this work (solid bars) agree well with the experimental results (texture bars). [1]

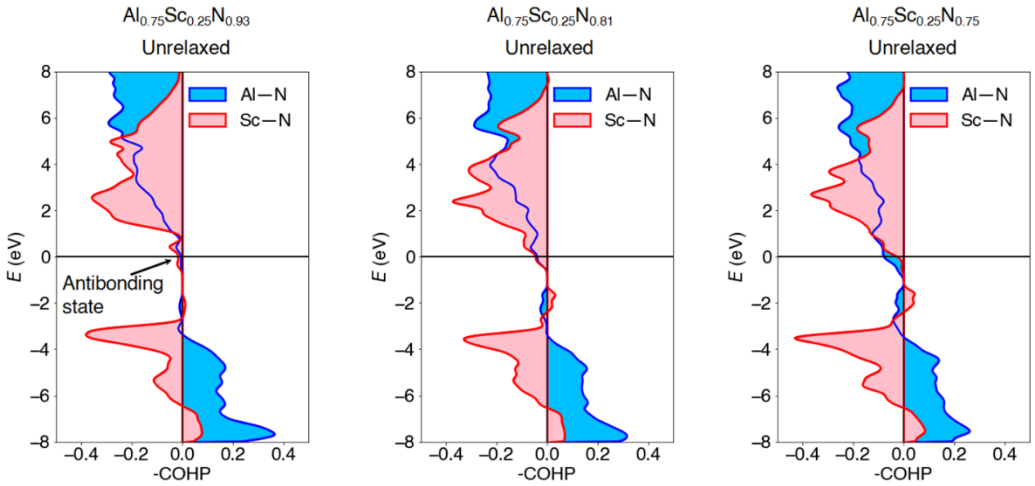


Fig. S4 COHP analysis of AlScN models with N vacancies for the unrelaxed structures**.** The COHP of average values of Al–N (blue regions) and Sc–N (red regions) interactions in the $Al_{0.75}Sc_{0.25}N_{0.93}$, $Al_{0.75}Sc_{0.25}N_{0.81}$ and $Al_{0.75}Sc_{0.25}N_{0.75}$ for the unrelaxed structures. The Fermi levels E_f were to set to zero energy. The right and left sides of the plot show bonding and anti–bonding interactions, respectively.

Comparison of the compositions $Al_{0.75}Sc_{0.25}N_{0.93}$ and $Al_{0.75}Sc_{0.25}N_{0.81}$ in the unrelaxed state also show that these antibonding interactions increase with an increased N vacancy concentration.

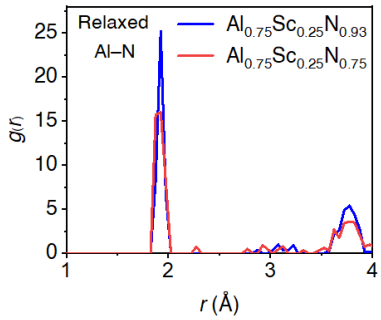


Fig. S5 PCF analysis of Al–N bonds of the relaxed AlScN models with N vacancies.

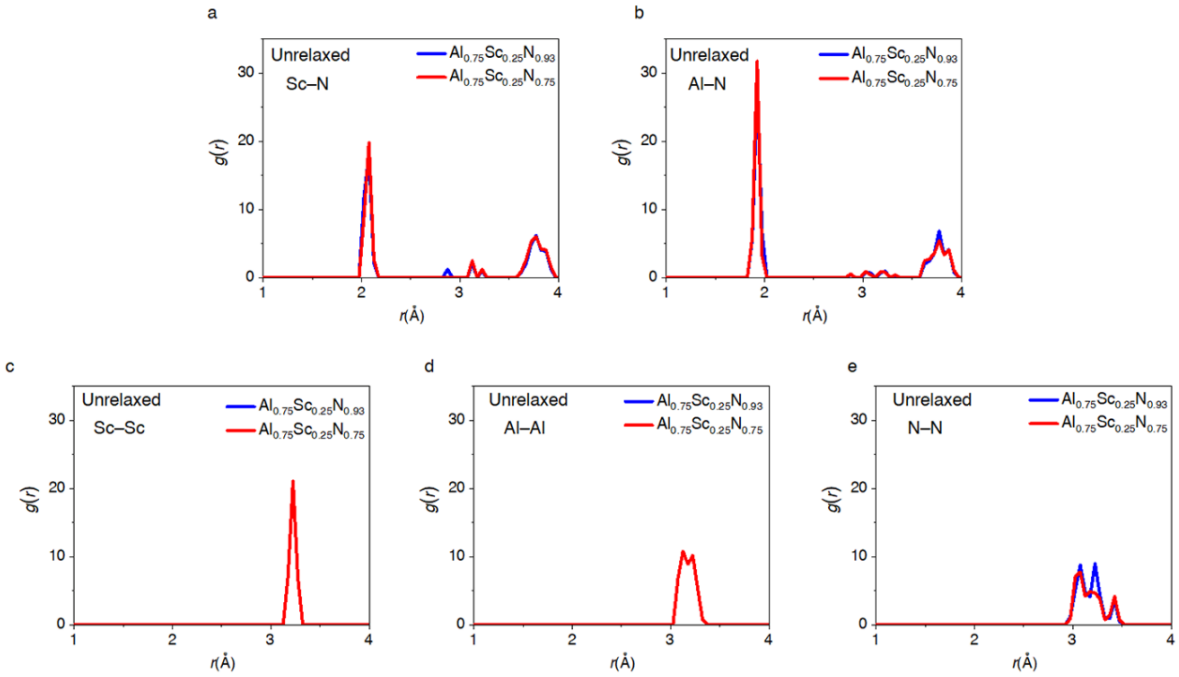


Fig. S6 PCF analysis of structural features of AlScN models with N vacancies in the unrelaxed state. **a–e)** PCF analyses for the a) N–N, b) Al–Al, c) Sc–Sc, d) Sc–N and e) Al–N bonds for the systems with different N vacancy concentrations.

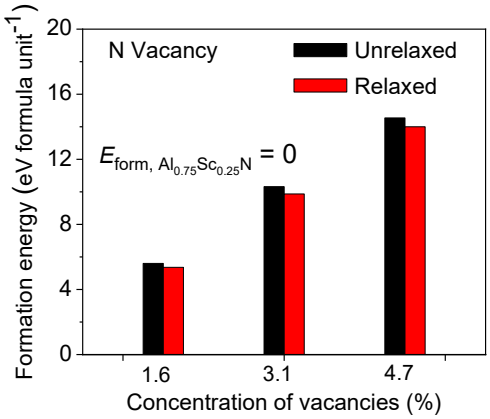


Fig. S7 Formation energies of the 128–atom AlScN model in the relaxed state for different concentrations of N vacancies.

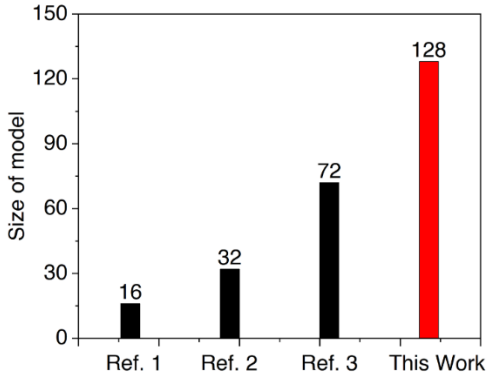
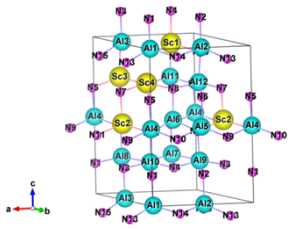


Fig. S8 Comparison of the size of model utilized in this work with that of-state-of-the-art simulations of AlScN materials [2-4].

Table S1. –ICOHPs values of Al–N and Sc–N bonds in $Al_{0.75}Sc_{0.25}N_{0.93}$ under relaxed state.

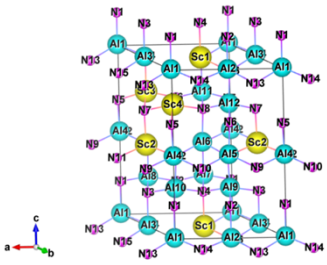
Bond type	–ICOHP (eV/bond)	Bond type	–ICOHP (eV/bond)
Al–N bond			
Al1–N1	1.40795	Al7–N1	1.88992
Al1–N13	1.63191	Al7–N2	1.8233
Al1–N14	1.84841	Al7–N4	2.11666
Al2–N2	1.85005	Al7–N9	2.06656
Al2–N13	2.12609	Al8–N1	1.90135
Al2–N14	1.99527	Al8–N2	1.89362
Al2–N15	2.10547	Al8–N3	1.85411
Al3–N3	1.47627	Al8–N10	2.16604
Al3–N14	1.80509	Al9–N2	1.83396
Al3–N15	1.69261	Al9–N3	1.74845
Al4–N5	1.81439	Al9–N4	2.05922
Al4–N9	1.50806	Al9–N11	2.14637
Al4–N10	1.69574	Al10–N1	1.67368
Al4–N12	1.73719	Al10–N3	1.65255
Al5–N5	1.99918	Al10–N4	2.05361
Al5–N9	1.67822	Al10–N12	2.16566
Al5–N10	1.84993	Al11–N5	1.86395
Al5–N11	1.73973	Al11–N6	1.68895
Al6–N8	1.93497	Al11–N8	1.67071
Al6–N9	1.70093	Al11–N13	1.65237
Al6–N11	1.83753	Al12–N6	1.67161
Al6–N12	1.92462	Al12–N7	1.94118
		Al12–N8	1.6209
		Al12–N15	1.78105
Sc–N bond			
Sc1–N4	1.23219	Sc3–N5	1.34061
Sc1–N13	1.12398	Sc3–N6	1.18650
Sc1–N15	1.18627	Sc3–N7	1.70133
Sc2–N7	1.65469	Sc3–N14	1.06077
Sc2–N10	1.25421	Sc4–N5	1.46588
Sc2–N11	1.29225	Sc4–N7	1.80352
Sc2–N12	1.29802	Sc4–N8	1.09161



Numbering of atoms for the composition $Al_{0.75}Sc_{0.25}N_{0.93}$.

Table S2. –ICOHPs values of Al–N and Sc–N bonds in $Al_{0.75}Sc_{0.25}N_{0.93}$ under unrelaxed state.

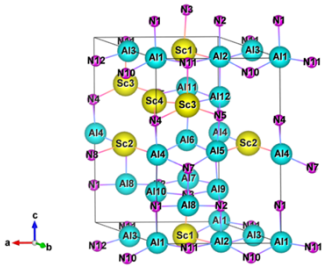
Bond type	–ICOHP (eV/bond)	Bond type	–ICOHP (eV/bond)
Al–N bond			
Al1–N1	1.43404	Al7–N1	1.86084
Al1–N13	1.77315	Al7–N2	1.80716
Al1–N14	1.78874	Al7–N4	2.15347
Al2–N2	1.81861	Al7–N9	2.07026
Al2–N13	2.10463	Al8–N1	1.90565
Al2–N14	1.98765	Al8–N2	1.94196
Al2–N15	2.09442	Al8–N3	1.87866
Al3–N3	1.48353	Al8–N10	2.15759
Al3–N14	1.7806	Al9–N2	1.81969
Al3–N15	1.81121	Al9–N3	1.72337
Al4–N5	1.86061	Al9–N4	2.05279
Al4–N9	1.49147	Al9–N11	2.10538
Al4–N10	1.68096	Al10–N1	1.68247
Al4–N12	1.69045	Al10–N3	1.64395
Al5–N5	2.00428	Al10–N4	2.05021
Al5–N9	1.66854	Al10–N12	2.15304
Al5–N10	1.81347	Al11–N5	1.82617
Al5–N11	1.68617	Al11–N6	1.66089
Al6–N8	1.99424	Al11–N8	1.66933
Al6–N9	1.68614	Al11–N13	1.67801
Al6–N11	1.79807	Al12–N6	1.65042
Al6–N12	1.8729	Al12–N7	1.91451
		Al12–N8	1.60108
		Al12–N15	1.73716
Sc–N bond			
Sc1–N4	1.25411	Sc3–N5	1.383
Sc1–N13	1.16354	Sc3–N6	1.13783
Sc1–N15	1.20295	Sc3–N7	1.76057
Sc2–N7	1.65424	Sc3–N14	0.98434
Sc2–N10	1.22761	Sc4–N5	1.41252
Sc2–N11	1.33788	Sc4–N7	1.77724
Sc2–N12	1.28295	Sc4–N8	1.09199



Numbering of atoms for the composition $Al_{0.75}Sc_{0.25}N_{0.93}$.

Table S3. –ICOHPs values of Al–N and Sc–N bonds in $Al_{0.75}Sc_{0.25}N_{0.75}$ under relaxed state.

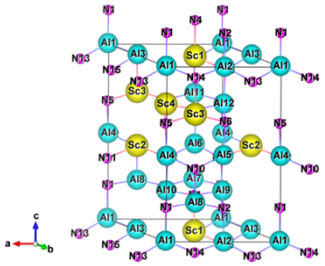
Bond type	–ICOHP (eV/bond)	Bond type	–ICOHP (eV/bond)
Al–N bond			
Al1–N1	0.99082	Al7–N1	1.96933
Al1–N10	1.36999	Al7–N2	1.89289
Al1–N11	1.31139	Al7–N3	2.06150
Al2–N2	1.53151	Al8–N1	1.59327
Al2–N10	2.01809	Al8–N2	1.61426
Al2–N11	1.70827	Al8–N7	1.35853
Al2–N12	1.99916	Al9–N2	1.56243
Al3–N11	1.45376	Al9–N3	1.89695
Al3–N12	1.11759	Al9–N8	1.92249
Al4–N4	1.6061	Al10–N1	1.52544
Al4–N7	1.66791	Al10–N3	1.84154
Al4–N9	1.44615	Al10–N9	1.82002
Al5–N5	2.00561	Al11–N4	1.77495
Al5–N7	1.5193	Al11–N5	1.75956
Al5–N8	1.54503	Al11–N6	1.62824
Al6–N6	2.03209	Al11–N10	1.77261
Al6–N8	1.71675	Al12–N5	1.39305
Al6–N9	1.77173	Al12–N6	1.28137
		Al12–N12	1.51700
Sc–N bond			
Sc1–N3	1.00753	Sc3–N4	1.23160
Sc1–N10	1.14678	Sc3–N5	1.10956
Sc1–N12	1.01977	Sc3–N11	1.05721
Sc2–N7	1.49311	Sc4–N4	1.33977
Sc2–N8	1.22692	Sc4–N6	1.17057
Sc2–N9	1.22735		



The numbering of atoms for the composition $Al_{0.75}Sc_{0.25}N_{0.75}$.

Table S4. –ICOHPs values of Al–N and Sc–N bonds in $Al_{0.75}Sc_{0.25}N_{0.75}$ under unrelaxed state.

Bond type	–ICOHP (eV/bond)	Bond type	–ICOHP (eV/bond)
Al–N bond			
Al1–N1	1.01866	Al7–N1	1.97084
Al1–N10	1.43072	Al7–N2	1.85532
Al1–N11	1.36213	Al7–N3	2.05874
Al2–N2	1.59093	Al8–N1	1.64838
Al2–N10	1.97142	Al8–N2	1.68682
Al2–N11	1.74751	Al8–N7	1.76536
Al2–N12	1.95204	Al9–N2	1.62205
Al3–N11	1.53663	Al9–N3	1.88131
Al3–N12	1.09528	Al9–N8	2.02815
Al4–N4	1.63872	Al10–N1	1.54279
Al4–N7	1.52927	Al10–N3	1.80578
Al4–N9	1.2974	Al10–N9	1.85396
Al5–N5	1.98063	Al11–N4	1.71755
Al5–N7	1.51183	Al11–N5	1.68762
Al5–N8	1.5133	Al11–N6	1.60101
Al6–N6	2.07103	Al11–N10	1.77056
Al6–N8	1.57122	Al12–N5	1.33914
Al6–N9	1.62891	Al12–N6	1.24934
		Al12–N12	1.42897
Sc–N bond			
Sc1–N3	1.01474	Sc3–N4	1.20300
Sc1–N10	1.11407	Sc3–N5	1.11131
Sc1–N12	1.04781	Sc3–N11	1.09734
Sc2–N7	1.37999	Sc4–N4	1.32966
Sc2–N8	1.15835	Sc4–N6	1.13443
Sc2–N9	1.22982		



The numbering of atoms for the composition $Al_{0.75}Sc_{0.25}N_{0.75}$.

Table S5. Comparison of average –ICOHPs values of Al–N and Sc–N bonds in compositions $Al_{0.75}Sc_{0.25}N_{0.93}$ and $Al_{0.75}Sc_{0.25}N_{0.75}$ in the relaxed state and unrelaxed state.

Composition	Sc–N bond		Al–N bond	
	Average –ICOHP (eV/bond)		Average –ICOHP (eV/bond)	
	Unrelaxed	Relaxed	Unrelaxed	Relaxed
$Al_{0.75}Sc_{0.25}N_{0.93}$	1.3336	1.3351	1.7804	1.8057
$Al_{0.75}Sc_{0.25}N_{0.75}$	1.1655	1.1846	1.6476	1.6487

References

1. M. Akiyama, T. Kamohara, K. Kano, A. Teshigahara, Y. Takeuchi and N. Kawahara, *Advanced Materials*, 2009, **21**, 593-596.
2. H. Momida, A. Teshigahara and T. Oguchi, *AIP Advances*, 2016, **6**, 065006.
3. D. F. Urban, O. Ambacher and C. Elsässer, *Physical Review B*, 2021, **103**, 115204.
4. K. Furuta, K. Hirata, S. A. Anggraini, M. Akiyama, M. Uehara and H. Yamada, *Journal of Applied Physics*, 2021, **130**, 024104.