Electronic Supplementary Information (ESI)

Density Functional Theory Calculations for Band Gap and formation energy of $Pr_{4-x}Ca_xSi_{12}O_{3+x}N_{18-x}$; a Highly Disordered Compound with Low Symmetry and a Large Cell Size

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Table S1. Calculated VASP energy of all the reactants in the chemical reaction scheme adopted for the formation of $Pr_{4-x}Ca_xSi_{12}O_{3+x}N_{18-x}$.

	Space Group	KJ/mol
Ca3N2	R-3c	-2541.95
	Ia-3	-2548.2
	C2/m	-2523.48
	P-3m1	-2480.54
PrN	Fm-3m	-1506.82
	P4/nmm	-1448.37
Si3N4	P31c	-5525.45
	P6_3	-5525.52
	Fd-3m	-5426.31
	I-43d	-5458.38
	P6_3/m	-5525.51
	Pnma	-5332.01
SiO2	P63/mmc	-2236.43
	P42/mnm	-2233.89
	P_3221	-2287.38
	Cmcm	-2287.14
	Immm	-2286.46
	P6222	
	P3_121	-2282.05

We adopted the most frequent entry in the ICSD for each binary reactant compound and used their VASP energy for the formation energy calculation. The adopted entries are marked in yellow.

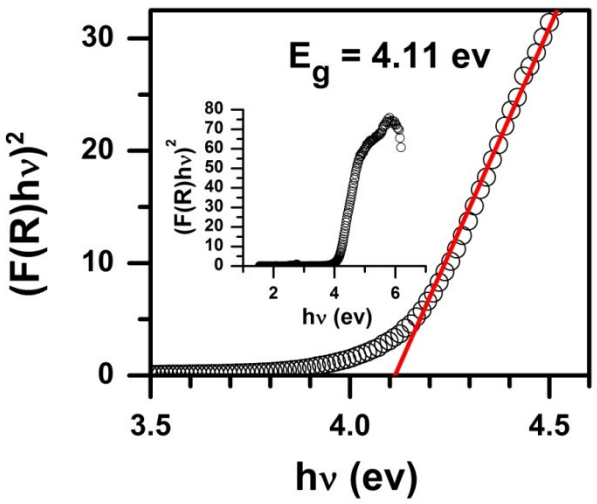

Fig. S1 The $\{F(R)\ h\nu\}^2$ vs. energy ($h\nu$) plot, the straight line in the plot intersects the energy axis at **4.11** eV.

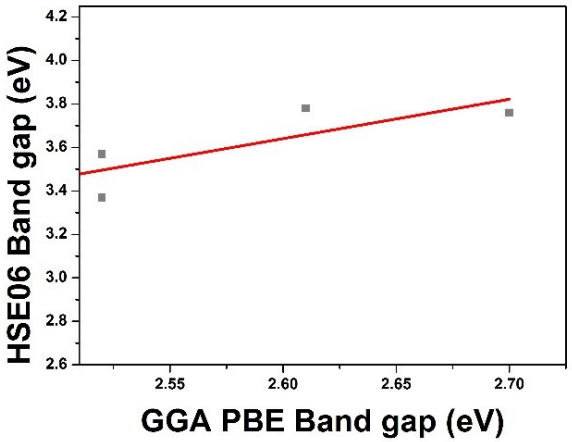

Fig. S2 The HSE06-calculated band gap vs. the GGA-PBE-calculated band gap for several representative configurations, showing a certain correlation.

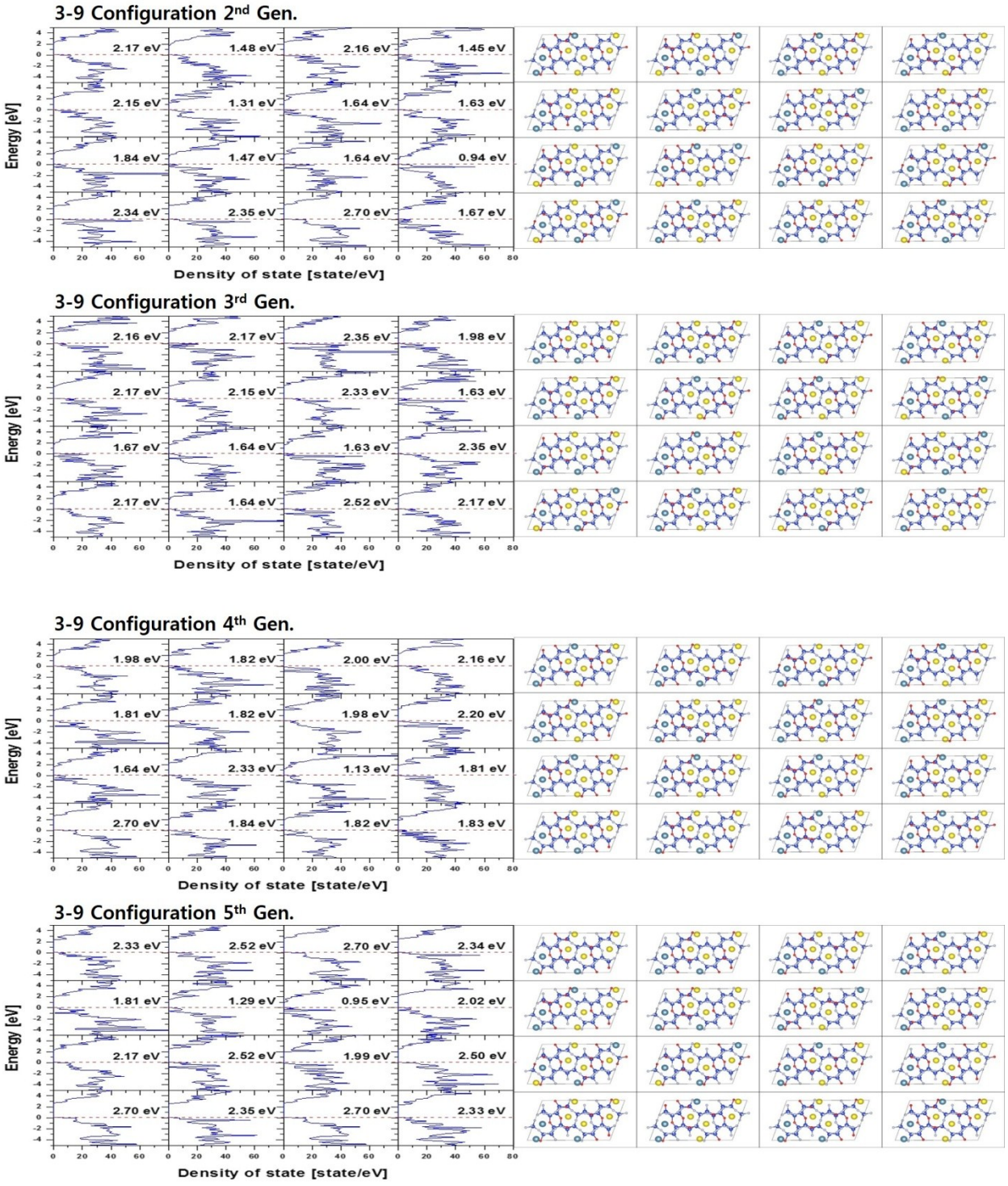

Fig. S3 Configurations from 2nd to 5th generation viewed in the b direction, along with total DOS and calculated band gap energies for 3-9 configuration.

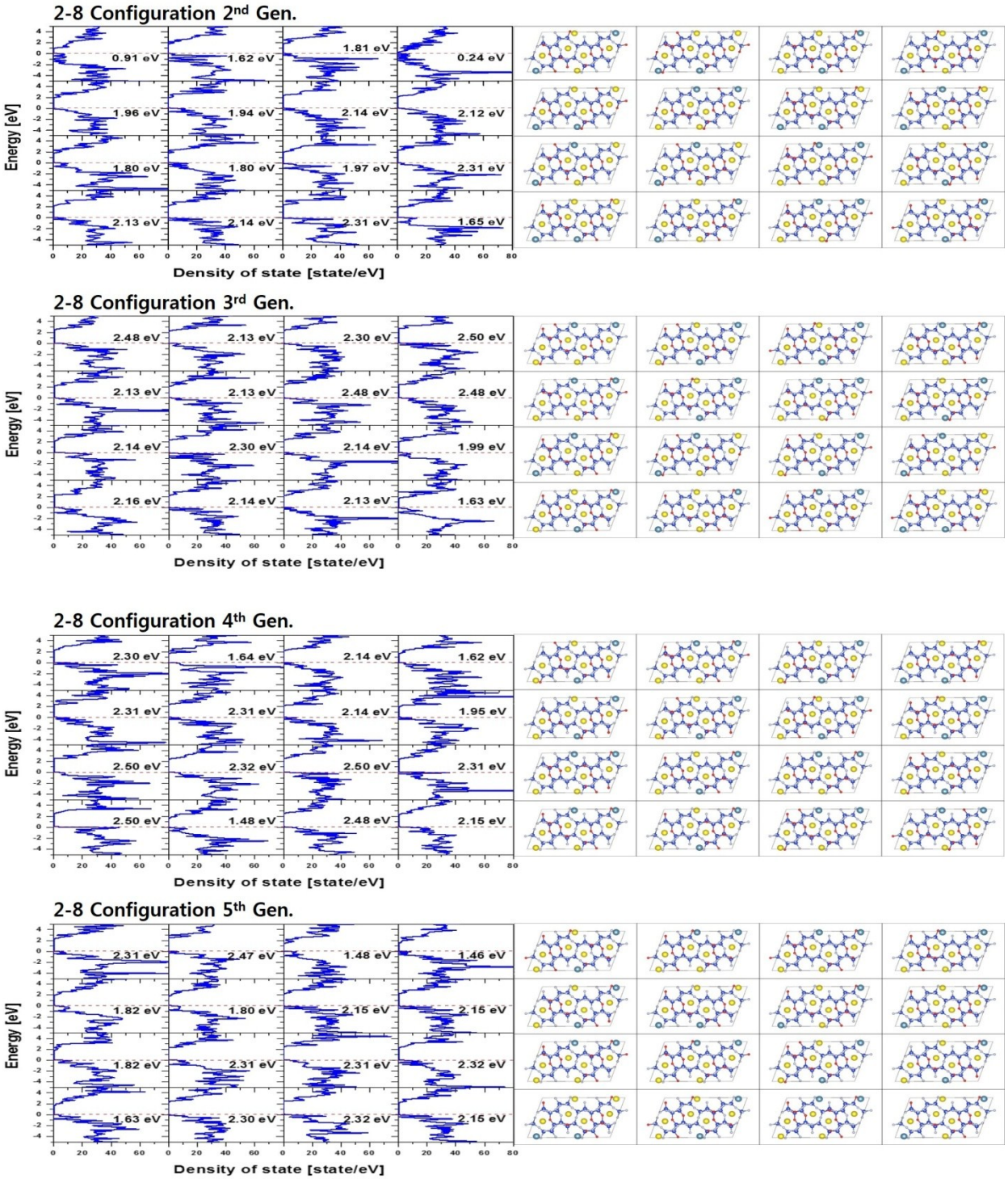

Fig. S4 Configurations from 2nd to 5th generation viewed in the b direction, along with total DOS and calculated band gap energies for 2-8 configuration.

Details of the agreement factors obtained in the Rietveld Refinement using Fullprof program

The indicator in the refinements is generally the various R-factors which are defined as follows[1]:

(i) R-pattern : $R_P = 100 \dfrac{\sum |y_i(obs) - y_i(calc)|}{\sum (y_i(obs))}$

(ii) R-weighted profile : $R_{WP} = 100 \left\{ \dfrac{\sum wi(y_i(obs) - y_i(calc))^2}{\sum w_i (y_i(obs))^2} \right\}^{1/2}$

(iii) R-expected : $R_e = 100 \left[\dfrac{(N-P)}{\sum w_i y_{oi}^2} \right]^{1/2}$

In the above expressions 'y_i' is the intensity at any arbitrarily chosen point '*i*', $w_i = 1/\sigma_i^2$, σ_i^2 being the variance of the observation, N and P are number of observations and variables respectively.

The goodness of fit of the system is also represented by an indicator called χ- squared and expressed as

$$\chi^2 = \left[\frac{R_{WP}}{R_e} \right]^2$$

References

1 R. A. Young, *The Rietveld Method* , International Union of Crystallography Oxford University Press, New York (1996).