Rare-Earth Engineering of $CaAlSiN_3$: Coupled Spin, Optical, Magnetic, and Piezoelectric Responses from DFT+U+SOC

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Abstract. Rare-earth-substituted nitride materials have attracted increasing attention for multifunctional optoelectronic, magnetic, and electromechanical applications owing to their wide bandgaps, thermal robustness, and strong coupling between localized 4f states and host electronic structures. In this work, first-principles calculations based on spin-polarized density functional theory within the GGA+U framework, including spin–orbit coupling, are employed to investigate the effects of Er and Tb substitution on the structural, electronic, magnetic, optical, mechanical, and piezoelectric properties of $CaAlSiN_3$. The results reveal that rare-earth incorporation preserves the structural stability of the host lattice while inducing localized 4f-derived electronic states near the Fermi level. These impurity states reduce the bandgap, introduce spin asymmetry, and act as intermediate energy levels that modify interband transitions and shift the optical absorption edge toward lower photon energies. Density of states analysis confirms strong hybridization between rare-earth 4f states and host N-p/Al-Si-derived orbitals, while simulated X-ray absorption spectra show characteristic pre-edge and white-line features associated with unoccupied rare-earth states and dopant-induced electronic reconstruction. Optical calculations demonstrate enhanced dielectric response, refractive index, absorption intensity, and spectral coverage in the near-UV and visible regions, indicating improved optoelectronic activity. Spin-polarized results further show that Tb substitution produces pronounced local magnetic moments on Tb sites, suggesting magnetic semiconducting behavior relevant for spintronic applications. Mechanical and elastic analyses confirm that the doped systems remain mechanically stable, with rare-earth substitution producing composition-dependent lattice softening or stiffness enhancement depending on dopant concentration and local bonding environment. Notably, dopant-induced lattice distortion and asymmetric charge redistribution enhance the piezoelectric response, with improved longitudinal piezoelectric coefficients compared with pristine $CaAlSiN_3$. Overall, the findings demonstrate that rare-earth substitution provides an effective route for tuning the electronic structure, optical transitions, magnetism, mechanical stability, and electromechanical response of $CaAlSiN_3$, highlighting its potential for high-efficiency photonic devices, spintronic systems, piezoelectric energy conversion, and radiation-tolerant multifunctional applications.