



First-Principles Study of Lead-Free $\text{Rb}_2\text{LiTiCl}_6$ Double Perovskite: Structural, Electronic, Optical, and Mechanical Properties

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Abstract

Lead-free double halide perovskites are eco-friendly alternatives to toxic Pb-based perovskites. Using DFT (PBE functional, CASTEP), we studied $\text{Rb}_2\text{LiTiCl}_6$'s structural, electronic, optical, and mechanical properties. Results show it is a stable indirect-bandgap semiconductor with strong optical absorption and favorable dielectric properties, making it a promising candidate for solar light-harvesting applications.

Results and Discussion

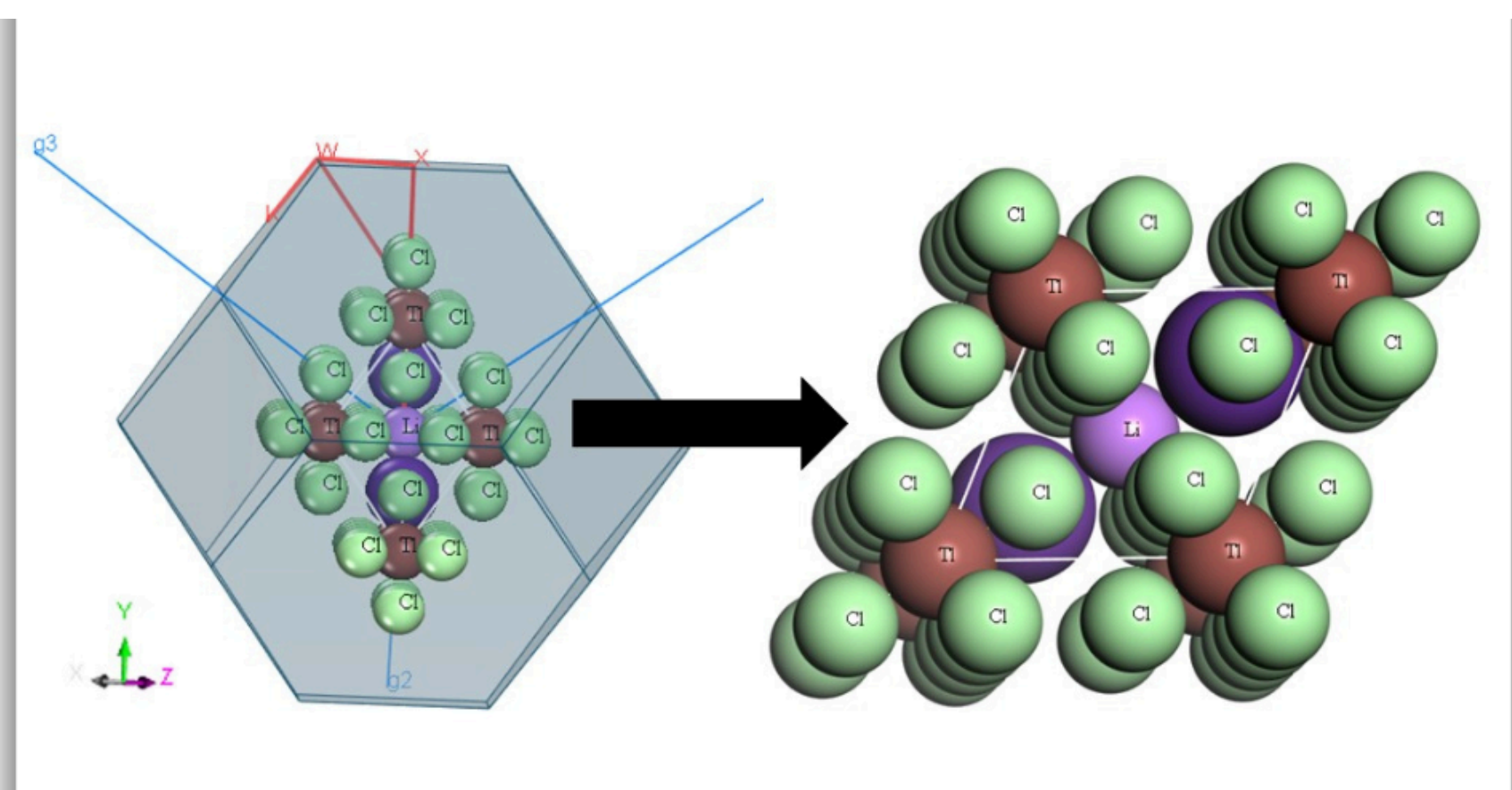


Fig. 1: Geometrically optimized cubic crystal of $\text{Rb}_2\text{LiTiCl}_6$ double perovskite

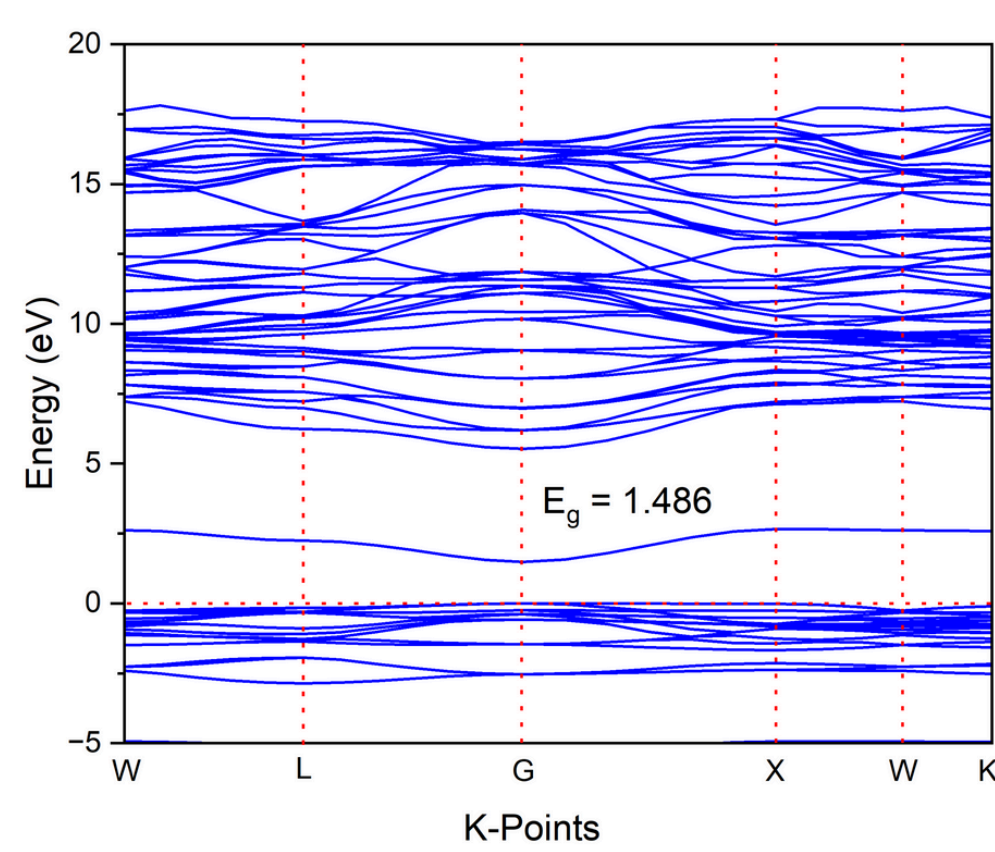


Fig. 2: Band structure of double perovskite $\text{Rb}_2\text{LiTiCl}_6$.

Structural and Electronic Properties

$\text{Rb}_2\text{LiTiCl}_6$ crystallizes in a cubic structure (**Fig. 1**) (Fm-3m) with Rb, Li, Ti, and Cl occupying the 8c, 4b, 4a, and 24e Wyckoff sites, respectively. The optimized lattice constant is 7.39 Å, giving a unit cell volume of 285.58 Å³, and the Goldschmidt tolerance factor ($t = 0.823$) confirms its structural stability. Electronic band structure calculations (**Fig. 2**) reveal an indirect band gap of ~1.49 eV, with the valence band maximum at Γ and the conduction band minimum between X and W. While indirect, this band gap can reduce carrier recombination, and tuning via cation/anion substitution or strain engineering could enhance its optoelectronic performance, making $\text{Rb}_2\text{LiTiCl}_6$ a promising material for solar energy applications.

Mechanical Properties

The elastic constants of $\text{Rb}_2\text{LiTiCl}_6$ ($C_{11} = 31.73$ GPa, $C_{12} = 13.87$ GPa, $C_{44} = 11.03$ GPa) satisfy the Born criteria, confirming mechanical stability. Bulk ($B = 19.82$ GPa), shear ($G = 10.19$ GPa), and Young's ($E = 23.29$ GPa) moduli indicate moderate stiffness with ductile behavior (Poisson's ratio $\nu = 0.28$). A low anisotropy factor ($A_u = 0.053$) reflects near-isotropic mechanical properties, while the Debye temperature ($\theta_D = 185.74$ K) and sound velocity ($V_m = 1909.83$ m/s) highlight thermal stability. Phonon dispersion (**Fig. 6**) shows no imaginary frequencies, confirming dynamical stability. Compared to related perovskites, $\text{Rb}_2\text{LiTiCl}_6$ exhibits enhanced ductility and vibrational stability, making it a mechanically robust material suitable for durable optoelectronic applications.

Introduction

Perovskite solar cells (PSCs) offer high efficiency, low-cost fabrication, and flexibility, but Pb toxicity limits their commercialization. Pb-free double perovskites ($\text{A}_2\text{BB}'\text{X}_6$) provide an eco-friendly alternative with tunable bandgaps and excellent optoelectronic properties. Rubidium-based DPs are underexplored despite their potential. Here, we use DFT to study $\text{Rb}_2\text{LiTiCl}_6$'s structural, electronic, and optical properties as a sustainable perovskite candidate.

Density of States and PDOS

The total and partial density of states (**Fig. 3-4**) analyses confirm the semiconducting nature of $\text{Rb}_2\text{LiTiCl}_6$ with an indirect band gap. The valence band is mainly dominated by Cl p-orbitals, strongly hybridized with Ti d-states, while the conduction band is primarily shaped by Ti and Li s-orbitals. This orbital contribution highlights the role of Cl in bonding and Ti/Li in charge transport. The strong p-d hybridization in the VB and s-state dominance in the CB suggest favorable electronic transitions, reinforcing the material's potential for optoelectronic applications.

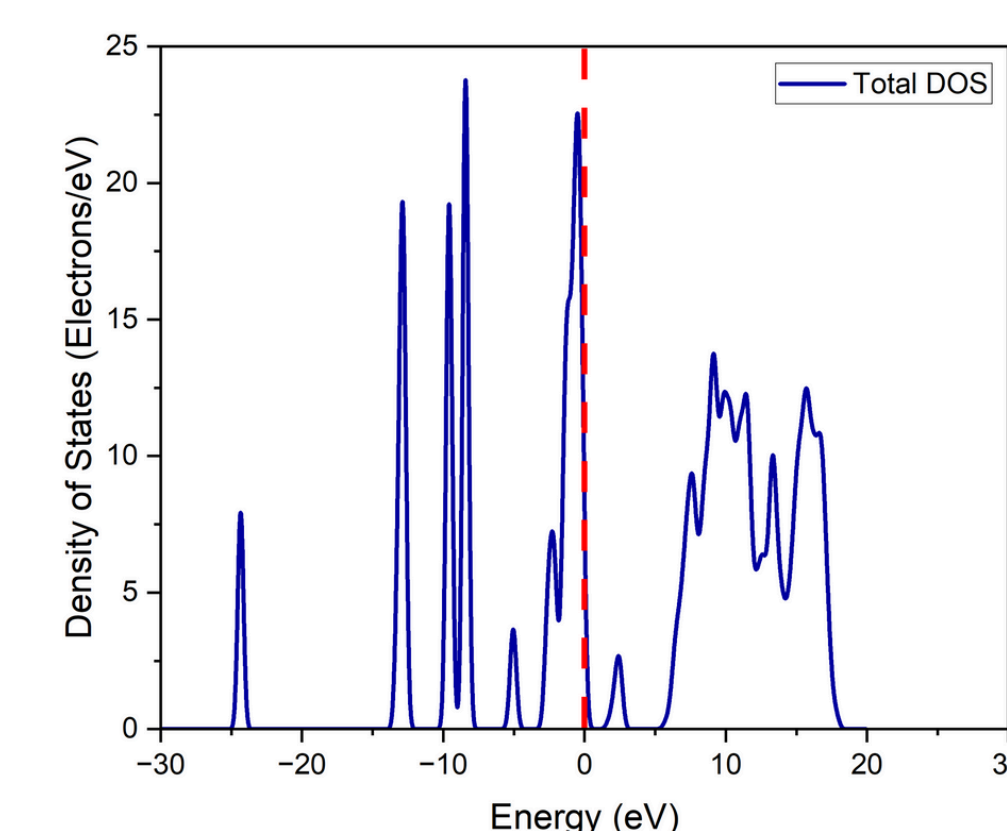


Fig. 3: TDOS of double perovskite $\text{Rb}_2\text{LiTiCl}_6$.

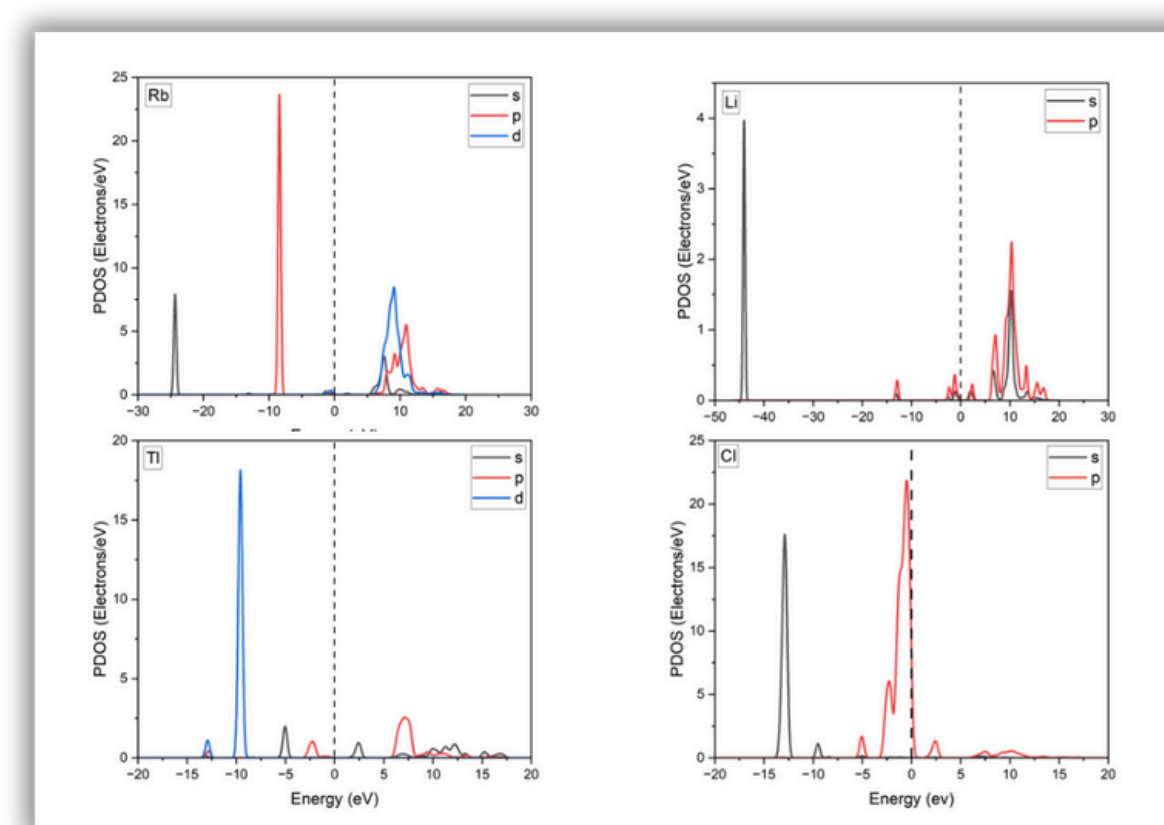


Fig. 4: PDOS of double perovskite $\text{Rb}_2\text{LiTiCl}_6$.

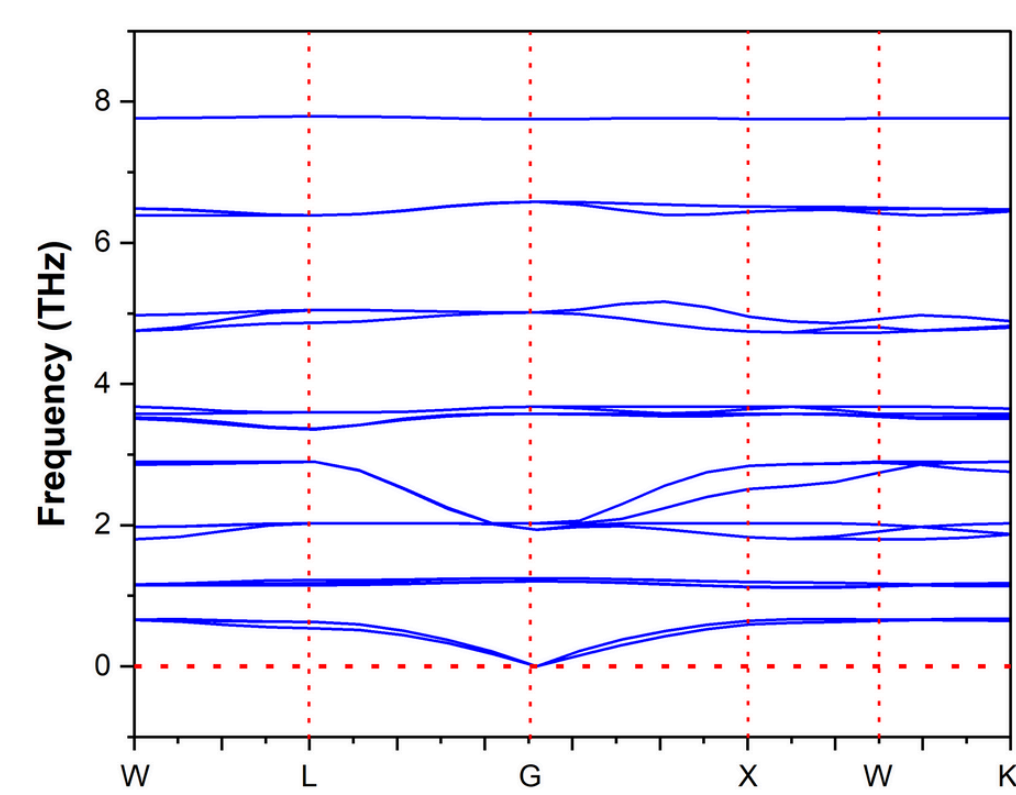


Fig. 6: Phonon calculation of double perovskite $\text{Rb}_2\text{LiTiCl}_6$.

Optical Properties

The optical response of $\text{Rb}_2\text{LiTiCl}_6$ was analyzed via its dielectric function, absorption, reflectivity, refractive index, conductivity, and energy loss spectra (**Fig. 5**). At low photon energies (0–2.5 eV), the real part of the dielectric function dominates, indicating strong polarizability, while the imaginary part increases above 2.5 eV, confirming enhanced photon absorption with a peak near 3 eV. The absorption spectrum shows strong activity in the UV range (5–10 eV), supported by high optical conductivity and energy loss peaks around 10–17 eV, reflecting robust charge carrier excitation and plasmon resonance. The refractive index (~2.0 at low energy) decreases with photon energy, while the extinction coefficient peaks between 5–15 eV. Moderate reflectivity in the UV and low reflectivity at higher energies indicate good transparency. Overall, $\text{Rb}_2\text{LiTiCl}_6$ exhibits strong UV absorption, stable dielectric behavior, and excellent optical activity, making it a promising candidate for UV optoelectronic and photovoltaic applications.

Computational Methodology

- Framework: DFT using CASTEP (Materials Studio)
- Functional: GGA-PBE; ultrasoft pseudopotentials
- Geometry Optimization: LBFGS algorithm; 0 GPa pressure/stress
- Convergence: Energy 1×10^{-5} eV/atom, Force 0.03 eV/Å, Cut-off 500 eV, k-points $10 \times 10 \times 10$
- Electronic Properties: Band structure, TDOS, PDOS
- Optical Properties: Dielectric function, absorption, reflectivity, refractive index, energy loss, optical conductivity
- Mechanical Properties: Elastic constants via stress-strain method
- Phonon Analysis: To confirm dynamical stability

Conclusion

DFT calculations show that $\text{Rb}_2\text{LiTiCl}_6$ is a lead-free, environmentally friendly double perovskite with promising optoelectronic potential. It has an indirect band gap of ~1.48 eV, strong UV absorption, a high refractive index, and efficient charge carrier dynamics. Mechanical and phonon analyses confirm dynamical and mechanical stability, with moderate bulk (19.82 GPa) and Young's (23.29 GPa) moduli, Poisson's ratio of 0.28, and thermal stability ($\theta_D = 185.74$ K). These combined optical, mechanical, and thermal properties make $\text{Rb}_2\text{LiTiCl}_6$ a robust, ductile, and thermally resilient candidate for next-generation UV optoelectronic and photovoltaic devices.

References

1. M. A. Hasan, I. M. M. Rahman, M. U. Khandaker, P. K. Singh, and F. I. Chowdhury, "First-principles study of lead-free $\text{Rb}_2\text{LiTiCl}_6$ double perovskite: Structural, electronic, optical, and mechanical properties," Next Research, vol. 2, no. 3, p. 100408, 2025, doi: 10.1016/j.nexres.2025.100408.