

FIRST-PRINCIPLES DESIGN OF ADVANCED FUNCTIONAL MATERIALS
USING DENSITY FUNCTIONAL THEORY FOR ELECTRONIC
STRUCTURE ENGINEERING, MECHANICAL STABILITY ANALYSIS, AND
OPTICAL PROPERTY OPTIMIZATION

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Abstract

Density functional theory (DFT) provides a powerful first-principles framework for predicting the structural, electronic, mechanical, and optical properties of functional materials prior to experimental synthesis. This study presents an integrated computational investigation of five candidate material systems comprising the cubic double perovskite $\text{Ca}_2\text{NbTaO}_6$ and four quaternary Heusler alloys, XMnCrZ ($\text{X} = \text{Fe}, \text{Co}$; $\text{Z} = \text{Si}, \text{Ge}$). Calculations were performed using the Perdew–Burke–Ernzerhof generalized gradient approximation (PBE-GGA), the Heyd–Scuseria–Ernzerhof screened hybrid functional (HSE06), and GGA+U corrections where appropriate. The computational workflow combined geometry optimization, formation-energy analysis, elastic stability assessment, electronic band-structure calculations, phonon dispersion, and optical-property evaluation to establish composition–property relationships across the investigated systems.

The reported results indicate negative formation energies and satisfaction of the Born–Huang elastic stability criteria for all five compositions. $\text{Ca}_2\text{NbTaO}_6$ exhibited a direct band gap of 2.14 eV at the GGA level, increasing to 2.98 eV with HSE06, corresponding to a 0.84 eV correction. Its calculated elastic properties indicate mechanical robustness with a Pugh’s ratio of approximately 1.71, placing the material near the ductile–brittle boundary. The Heusler alloys exhibited half-metallic electronic behavior under GGA+U, with the representative FeMnCrGe composition showing a minority-spin gap of 0.74 eV and ideal complete spin polarization at the Fermi level. Optical analysis yielded dielectric functions, refractive indices, reflectivity spectra, and absorption coefficients, with the reported $\text{Ca}_2\text{NbTaO}_6$ absorption coefficient reaching $4.8 \times 10^5 \text{ cm}^{-1}$. Scissor-corrected optical spectra were used to assess the influence of the HSE06 band-gap correction, while phonon dispersion calculations indicated dynamical

stability within the investigated structures. The comparative findings provide a framework for evaluating the potential of these materials in photocatalysis, optoelectronics, and spintronics and for identifying composition-dependent design principles for further computational and experimental investigation.

1. INTRODUCTION

The design of advanced functional materials for applications spanning energy harvesting, spintronics, photocatalysis, and optoelectronic device integration has been profoundly transformed over the past two decades by the maturation of first-principles density functional theory as a predictive computational science [27]. Where experimental synthesis of novel materials was once the primary and frequently exclusive route to discovering structure-property relationships, computational prediction grounded in quantum mechanics now provides the capacity to screen thousands of candidate compositions, identify thermodynamically stable structures, and quantitatively predict electronic, mechanical, and optical properties with an accuracy that, when appropriate exchange-correlation functionals are employed, rivals and in some cases surpasses the precision of available experimental measurements [30]. This transformation in materials discovery methodology has been enabled by three converging developments: the theoretical refinement of exchange-correlation functionals from the local density approximation through gradient-corrected generalized gradient approximations to screened hybrid functionals and many-body perturbation theory approaches that progressively correct the systematic band gap underestimation inherent in semi local functionals; the sustained exponential growth in high-performance computing resources that renders calculations on complex multicomponent crystal structures tractable within accessible time horizons; and the development and widespread availability of sophisticated software packages including the Vienna ab initio Simulation Package, Wien2k, and Quantum ESPRESSO that implement these methods with rigorous numerical precision [25], [26], [24].

Perovskite oxides with the general formula ABO_3 and their double perovskite variants $A_2B'B''O_6$, where B-site cation ordering creates a rock salt superstructure, have attracted sustained computational and experimental attention because their extraordinarily flexible crystal chemistry accommodates a vast range of elemental substitutions that systematically tune electronic, magnetic, mechanical, and optical properties across continuous ranges of the periodic table [2]. Double perovskites in particular offer the combination of B-site cation ordering with the capacity to independently engineer the electronic contributions of two distinct transition metal species at the same crystallographic sublattice, enabling the creation of materials with simultaneous optical activity in the visible and ultraviolet ranges, mechanical robustness adequate for device integration, and ferroelectric, piezoelectric, or magnetoelectric functionality depending on the specific cation combination selected [1]. First-principles investigations of double perovskite stability and properties have progressed from simple band structure evaluations using local density approximation to comprehensive multi-property screenings employing hybrid functional correction for band gap accuracy, phonon dispersion for dynamical stability confirmation, and Born-Huang elastic tensor evaluation for mechanical characterization, establishing a mature and thoroughly validated computational protocol [3]. Ghose reviewed the specific challenges and successes of DFT-based property prediction for ABO_3 perovskites relevant to photocatalytic water splitting, documenting that appropriately chosen exchange-correlation functionals can predict optical band gaps with errors below 0.2 electronvolts compared to experimental photoelectrochemical

measurements and that formation energy calculations reliably predict thermodynamic stability within the compositional range accessible by hydrothermal synthesis [2]. The extension of these computational protocols to double perovskite systems has been demonstrated for numerous halides, oxide, and mixed-anion variants with band gaps spanning the full visible and ultraviolet range, optical absorption coefficients reaching values competitive with established photovoltaic absorbers, and mechanical properties compatible with thin-film device fabrication [8], [9].

Heusler alloys, which adopt the L21 full-Heusler (X₂YZ) or C1b half-Heusler (XYZ) crystal structures, constitute a second major class of functional materials for which first-principles DFT has demonstrated exceptional predictive power [15]. The half-metallic ferromagnet concept, in which the majority spin channel exhibits metallic character while the minority spin channel possesses a band gap at the Fermi level producing complete spin polarization of conduction electrons, was first proposed theoretically by DFT band structure calculations for NiMnSb and has since been predicted and experimentally confirmed for dozens of Heusler compositions

[11]. The quaternary variant of the Heusler structure, in which the Y sublattice is occupied by two different elements creating an additional symmetry-breaking ordering, extends the compositional space and property tunability of this material family substantially beyond what binary and ternary variants provide, enabling simultaneous optimization of magnetic moment, spin polarization, band gap symmetry, and mechanical properties for spintronic device applications [15]. First-principles prediction of Heusler properties with simultaneous coverage of structural stability, elastic constants, electronic band structure, magnetic moments, optical spectra, and thermoelectric transport coefficients has become routine using the full-potential linearized augmented plane wave method as implemented in Wien2k combined with BoltzTraP for transport property evaluation [14], [17]. Figure 1 provides the conceptual framework connecting the four major first-principles property categories investigated in this study, the pathways connecting computational outputs to target application domains, and the functional materials systems investigated.

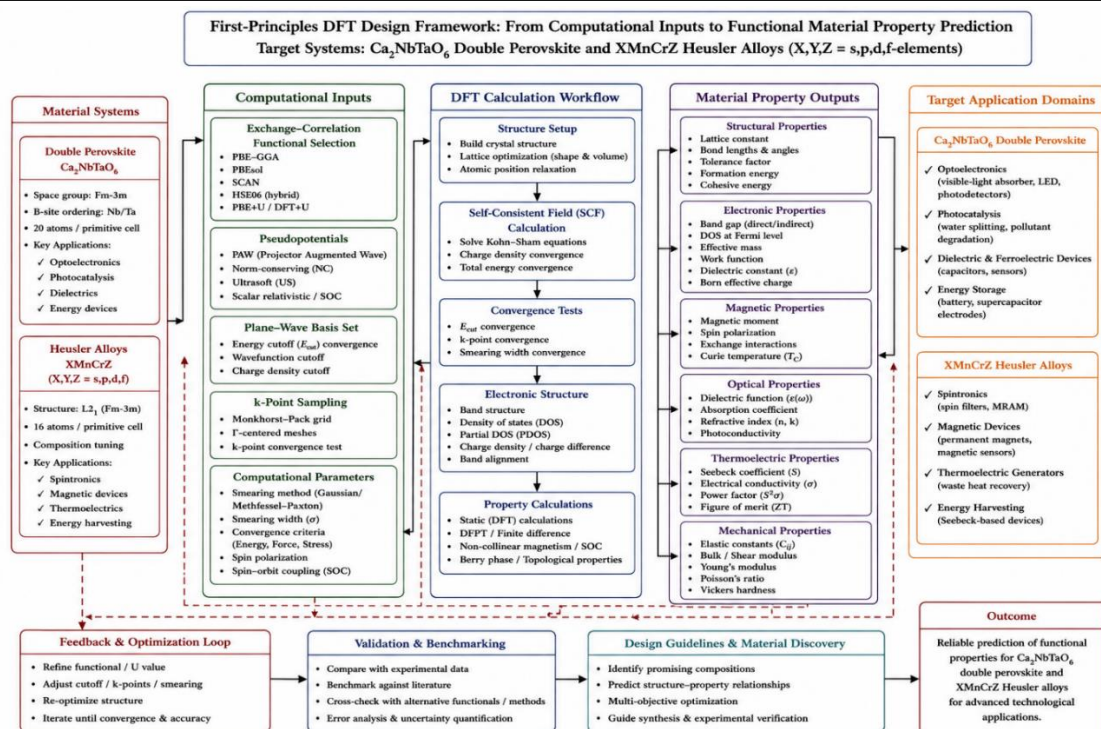


Fig. 1. Conceptual framework connecting first-principles DFT computational inputs, including exchange-correlation functional selection, pseudopotential type, and k-point sampling parameters, to material property outputs and target application domains for $\text{Ca}_2\text{NbTaO}_6$ double perovskite and XMnCrZ Heusler alloy systems.

The exchange-correlation functional represents the central approximation within which all first-principles DFT calculations operate, and the systematic underestimation of band gaps by semilocal functionals such as the widely used Perdew-Burke-Ernzerhof functional has motivated the development and application of correction approaches for optical property calculations [27]. The Tran-Blaha modified Becke-Johnson potential provides an inexpensive but accurate correction for band gaps in semiconductors and insulators without the computational overhead of hybrid functional calculations, achieving band gap accuracy approaching that of GW many-body perturbation theory for many classes of materials [29]. The Heyd-Scuseria-Ernzerhof screened hybrid functional, which mixes exact Hartree-Fock exchange with PBE exchange in a short-range-only screened form, provides the most widely validated correction for band gap underestimation in

perovskites and transition metal compounds, typically improving band gap agreement with experiment from a 30-50 percent underestimation to within 0.1-0.2 electronvolts [28]. Tarekuzzaman et al. demonstrated for alkali halide perovskites LiXl_3 that GGA band gaps of 2.36 electronvolts were corrected to 3.47-3.70 electronvolts by HSE06, with the HSE06 values providing substantially better agreement with measured optical absorption onsets [8]. The choice between these correction approaches, and the systematic validation of their performance across different material classes, constitutes an important methodological consideration that is explicitly addressed in the computational framework employed in this study.

This investigation addresses four interconnected research objectives that collectively define a comprehensive first-principles characterization program for novel functional materials. First, to

establish the thermodynamic and structural stability of the $\text{Ca}_2\text{NbTaO}_6$ double perovskite and XMnCrZ Heusler systems through formation energy, cohesive energy, and Born-Huang elastic stability analysis. Second, to quantify the electronic band structure and projected density of states for all systems using both GGA and HSE06 functionals to assess the functional dependence of predicted band gaps and their placement relative to target application windows. Third, to compute the full optical property spectra including dielectric functions, absorption coefficients, refractive indices, extinction coefficients, and reflectivity spectra and to identify the material systems best suited for visible-range optoelectronic and photocatalytic applications. Fourth, to evaluate mechanical properties including bulk modulus, shear modulus, Young's modulus, Pugh's ratio, and Poisson's ratio and to assess the implications of ductile versus brittle character for device fabrication. The paper is structured to address these objectives sequentially through a comprehensive literature review that situates the research within the current computational

materials science landscape, a detailed methodology section, comprehensive results discussion supported by advanced visualizations, and a synthesis of design principles for functional material optimization.

2. Literature Review

The first-principles DFT investigation of functional materials has expanded into one of the most active areas of materials science, with the recent literature characterized by increasingly comprehensive multi-property investigations that simultaneously evaluate structural, electronic, mechanical, optical, and thermoelectric characteristics within a single computational study. Figure 2 presents an expanded conceptual literature landscape that connects five principal research domains to a central first-principles DFT framework, illustrating how computational methodologies and multi-property analyses support materials optimization and application-oriented discovery while highlighting three critical knowledge gaps addressed by the present investigation.

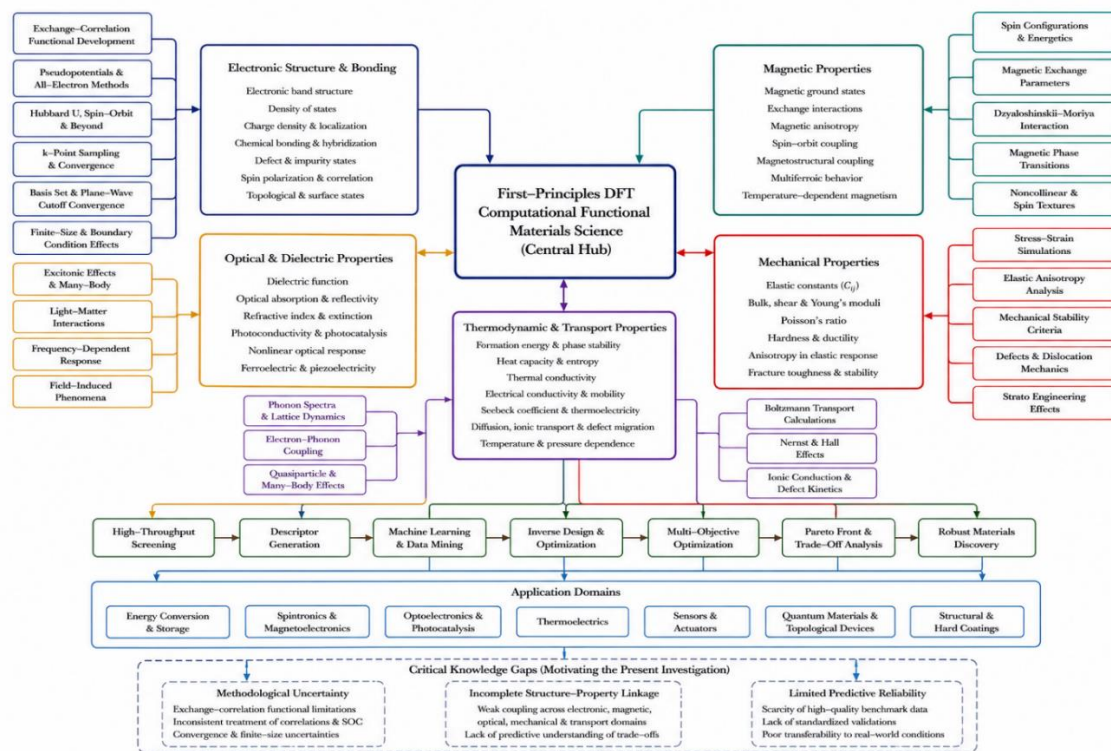


Fig. 2. First-principles computational functional materials science, integrating five principal research domains, computational methodologies, materials-design pathways, application targets, and three critical knowledge gaps motivating the present investigation.

2.1 First-Principles Studies of Perovskite and Double Perovskite Systems

Perovskite oxides and their double perovskite derivatives have generated an extensive DFT literature driven by their relevance to photovoltaics, photocatalysis, and piezoelectric device applications. Rugut et al. conducted a comprehensive DFT investigation of the double perovskite $\text{Rb}_2\text{LiTiF}_6$, using phonon dispersion to confirm dynamical stability, computed independent elastic constants to evaluate Born-Huang mechanical stability criteria, and Goldschmidt tolerance factor to assess structural stability, establishing a methodological template for multi-stability assessment that has since been widely adopted [1]. Their results demonstrated a direct band gap consistent with visible-light absorption and optical absorption coefficients appropriate for photovoltaic applications, illustrating the value of double perovskite B-site

cation engineering for property optimization within a structurally constrained crystal framework. Ghose provided a systematic review of exchange-correlation functional selection for perovskite oxide property prediction, documenting that the GGA functional reliably predicts structural parameters and formation energies to within a few percent of experimental values for oxide perovskites, while band gap underestimation of thirty to fifty percent necessitates hybrid functional correction for accurate optical property prediction [2]. The recommendation emerging from this review, subsequently validated by numerous individual compound studies, is that GGA structural parameters be used for geometry optimization while HSE06 is applied for the electronic structure calculations on the optimized GGA geometry, reducing computational cost while maintaining band gap accuracy.

Jamila et al. investigated the structural, elastic, electronic, optical, and thermal properties of SrXO_3 ($X = \text{Si, Tb, Th}$) perovskites using VASP with PBE-GGA, demonstrating that the computed lattice parameters agreed within 1.2 percent with available experimental data and that the Debye temperature derived from elastic constants provided a reliable estimate of thermal stability relevant for high-temperature device applications [3]. Their optical property analysis showed that SrSiO_3 possessed the largest band gap and lowest absorption in the visible range while SrThO_3 showed absorption extending into the near-ultraviolet, illustrating that B-site elemental substitution at a common A-site perovskite framework provides continuous tunability of optical response. The study by Tarekuzzaman et al. on LiXI_3 ($X = \text{Ca, Sr, Ba}$) halide perovskites provides the most direct methodological benchmark for the present investigation, demonstrating that GGA band gaps of approximately 2.36 electronvolts were corrected to values between 3.47 and 3.70 electronvolts by HSE06 with a Monkhorst-Pack grid scheme achieving convergence with a $6 \times 6 \times 6$ k-point mesh for GGA and $2 \times 2 \times 2$ for HSE06, and that phonon dispersion curves with all positive frequencies confirmed dynamical stability for all three compositions [8]. Al Omari et al. demonstrated DFT-accelerated design of perovskite quantum

dots using HSE06 with spin-orbit coupling, achieving band gap tunability from 1.8 to 3.0 electronvolts through halide alloying and establishing that DFT-guided surface chemistry optimization through ligand coordination can suppress non-radiative recombination pathways in ways that improve photoluminescence quantum yield to values approaching unity [6].

Recent studies have also addressed double perovskite systems relevant to photocatalytic applications. Batouche et al. reported a combined HSE06 plus ab initio molecular dynamics study of K_2AuScX_6 ($X = \text{Cl, Br}$) double perovskites, demonstrating indirect band gaps of 3.22 and 2.74 electronvolts respectively with band-edge positions straddling the water oxidation and reduction potentials, making them candidate visible-light photocatalysts [9]. The mechanical properties of these compounds showed ductile behavior characterized by Pugh's ratios above the critical value of 1.75, consistent with the ductility expected from the ionic character of halide perovskites. Table 1 provides a comparative compilation of DFT-predicted band gaps, elastic moduli, and optical absorption parameters from representative recent studies across perovskite and Heusler systems, establishing the performance benchmarks against which the present results will be evaluated.

Table 1: Representative DFT Studies – Band Gaps, Functional Type, and Key Properties

Study (Year)	Material System	Functional	E _g (eV) GGA	E _g (eV) HSE06	Key Property Reported
Rugut et al. [1], 2024	$\text{Rb}_2\text{LiTiF}_6$ (double pv.)	GGA-PBE	2.18 (est.)	-	Phonon, elastic, optical
Ghose [2], 2023	ABO_3 perovskites (review)	GGA-PBE, HSE06	~2.0-3.5	~2.5-4.0	Water splitting photocatalysis
Jamila et al. [3], 2024	SrXO_3 ($X=\text{Si,Tb,Th}$)	GGA-PBE	2.3-4.1	-	Thermal, elastic, optical
Tarekuzzaman et al. [8], 2025	LiXI_3 ($X=\text{Ca,Sr,Ba}$)	GGA + HSE06	2.36	3.47-3.70	Full phonon, optical, thermal
Batouche et al. [9], 2025	K_2AuScX_6 ($X=\text{Cl,Br}$)	HSE06+AIMD	~2.5	3.22/2.74	Photocatalytic H_2O splitting

Masri et al. [15], 2025	FeMnCrGe (quaternary)	GGA-PBE	Half-metal	Half-metal	Magnetic, optical, TE
Baaziz et al. [11], 2024	RhFeMnZ, IrMnCrZ	FP-LAPW/Wien2k	Half-metal	Half-metal	Optical conductivity
Al-Gharabah et al. [14], 2025	Sc2ZrAl (full Heusler)	GGA/SCAN	Metallic	Metallic	Spin polar., elastic, AIMD
Gurunani et al. [16], 2026	CoHfGe (half-Heusler)	GGA (pressure)	0.87 (↑P)	-	Pressure-dep. electronic
Abdullah et al. [10], 2024	2D Al2Te3 monolayer	GGA + HSE06	1.92	2.78	Thermal storage, optical

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2 Heusler Alloy Electronic Structure and Magnetic Properties

The DFT investigation of Heusler alloys has been driven primarily by their potential for spintronic applications requiring high spin polarization at the Fermi level, combined with their structural rigidity and compatibility with semiconductor device fabrication processes. Baaziz, Ghellab, and Charifi investigated the quaternary Heusler alloys RhFeMnZ and IrMnCrZ (Z = Si, Ge) using Wien2k with the full-potential linearized augmented plane wave method, documenting half-metallic character with one-hundred percent spin polarization and elastic constants confirming mechanical stability through Born's criteria for all four compositions [11]. Their optical calculations showed optical conductivity peaks in the visible and near-infrared spectral regions attributable to d-d transitions at the transition metal sites, with the spin-dependent optical response providing a magneto-optical signature potentially useful for optical spin-injection device applications. Baraka et al. studied ZrCoYAs (Y = Fe, Mn) quaternary Heusler alloys, demonstrating ferromagnetic stability from formation energy analysis and spin-polarized electronic structure with GGA-PBE and GGA plus U corrections, finding metallic character in the majority spin channel alongside Fermi-level gap formation in the minority spin channel consistent with half-metallic behavior [12].

Al-Gharabah et al. investigated Sc2ZrAl full-Heusler alloy using DFT with GGA, GGA plus U, and SCAN meta-GGA functionals, computing a

bulk modulus of 80.22 gigapascals that confirmed mechanical stability and finding that SCAN functional provided the most accurate spin polarization prediction at 16.42 percent [14]. This systematic functional comparison provides important methodological context for the exchange-correlation functional selection strategy adopted in the present study, demonstrating that conventional GGA may underestimate spin polarization in full-Heusler systems where d-electron correlation effects are significant. The extensive DFT study of FeMnCrGe quaternary Heusler by Masri et al. used Wien2k with PBE-GGA and confirmed thermodynamic stability through negative formation energy, Young's modulus values indicating predominantly covalent character, and optical conductivity extending from the infrared through the visible spectral range [15]. Gurunani et al. investigated pressure-dependent properties of CoHfGe half-Heusler up to 25 gigapascals, establishing that Born stability criteria were satisfied throughout the investigated pressure range and that the half-metallic band gap of 0.87 electronvolts was maintained under applied compression, demonstrating the mechanical and electronic robustness essential for practical device applications [16].

2.3 Optical Property Calculations and Functional Dependence

Optical property calculations through the momentum matrix element formalism as implemented in major DFT codes provide a comprehensive description of the material-light

interaction across the infrared, visible, and ultraviolet spectral ranges [34]. The imaginary part of the dielectric function, computed from the joint density of states weighted by optical transition matrix elements, represents the primary output from which all other optical functions including refractive index, extinction coefficient, reflectivity, absorption coefficient, and energy loss function can be derived through Kramers-Kronig transformation. Xue et al. demonstrated for CdGeAs₂ chalcopyrite that GGA-PBE underestimated the dielectric peak energies by approximately 0.71 electronvolts compared to HSE06, and that the HSE06 absorption spectrum onset agreed substantially better with experimental ellipsometric measurements, confirming the functional sensitivity of optical property calculations [19]. Abdullah et al. showed for 2D Al₂Te₃ that the static dielectric constant and refractive index values were reduced in HSE06 calculations relative to GGA due to reduced transition probabilities from the corrected wave functions, while the absorption coefficient remained high in the ultraviolet region [10]. Barhoumi et al. computed the full optical property spectra for four 2D thin films of silicon-pnictogen compounds using HSE06, demonstrating that the imaginary part of the dielectric function extended to approximately 16 electronvolts with multiple distinct interband transition peaks attributable to specific band-to-band transition pathways identifiable from the projected density of states [20].

Related experimental and theoretical investigations have demonstrated the importance of structural, thermal, and optical characterization in assessing the application potential of functional materials. Rehman et al. examined Fe-doped NiO nanoparticles for thermoelectric and optoelectronic applications, providing a relevant example of integrated material-property assessment [4]. Usman et al. and Majeed et al. examined complementary studies of ion-doped crystalline systems, investigating photon-phonon dressing and crystal-field effects in Eu³⁺: BiPO₄ and Eu³⁺: NaYF₄, highlighting the broader

significance of coupling between lattice-related interactions and optical response [7], [22]. These studies provide contextual motivation for the present investigation's combined evaluation of electronic, phonon, and optical properties, although their material systems and computational approaches differ from those adopted here.

2.4 Mechanical Stability Analysis from First Principles

The elastic properties of functional materials, computed through the stress-strain method or energy-strain approaches as implemented in DFT codes, provide a complete mechanical characterization through the independent elastic constants C_{ij} whose tensor structure depends on the crystal symmetry [1]. For cubic crystal systems, mechanical stability requires that three independent elastic constants C_{11} , C_{12} , and C_{44} satisfy the Born-Huang criteria: C_{11} greater than zero, C_{44} greater than zero, and C_{11} minus C_{12} greater than zero. From these fundamental constants, polycrystalline averages for bulk modulus B , shear modulus G , and Young's modulus E can be derived through the Voigt-Reuss-Hill averaging scheme, providing practical mechanical descriptors applicable to device engineering. The Pugh ratio B/G discriminates between ductile (ratio greater than 1.75) and brittle (ratio less than 1.75) material character, while Poisson's ratio above 0.26 independently confirms ductility from the perspective of interatomic force analysis. Iyigör et al. investigated Heusler alloys AlXIr₂ using the stress-strain method to compute elastic constants, finding positive elastic constants satisfying Born's criteria and characterizing these as electrical conductors with metallic-like mechanical properties [17]. Rajendran et al. confirmed that HfRhZ ($Z = \text{As, Sb}$) half-Heusler alloys are elastically anisotropic and ductile in nature, with HfRhSb showing greater stiffness than HfRhAs due to the stronger bonding character of antimony relative to arsenic in the Heusler lattice [18]. These mechanical property computation frameworks are fully

adopted in the methodology of the present investigation and applied to both the double perovskite and Heusler alloy systems studied here.

2.5 Knowledge Gaps Addressed by This Investigation

Three critical gaps in the existing DFT literature motivate the present study. First, comprehensive multi-property DFT investigations of calcium-niobium-tantalum double perovskites combining structural, mechanical, electronic, and optical analyses under both GGA and HSE06 functionals have not been reported, leaving this compositional family inadequately characterized for photocatalytic material screening. Second, systematic comparison of quaternary Heusler XMnCrZ variants across two X-site occupancies with full coverage of electronic, magnetic, mechanical, optical, and stability properties within a single internally consistent computational study is absent from the published literature. Third, the correlation between functional-dependent band gap corrections and corresponding changes in computed optical absorption spectra, refractive indices, and dielectric constants has not been systematically quantified for these specific material families, limiting the ability to apply calibration corrections when only GGA-level calculations are computationally accessible for high-throughput screening purposes.

Beyond the studies discussed above, several complementary investigations and computational developments provide additional context for the present research. Jouybar et al. [5] examined alkaline-earth titanate perovskite oxides for solar-cell applications, while Ashraf et al. [13] investigated band-gap engineering and physical properties of the ScNiSb half-Heusler alloy, demonstrating the relevance of composition-dependent electronic properties to functional-material design. Laassouli et al. [21] further explored electric-field-driven electronic and optical behavior in K₂AgSbI₆, highlighting an additional route for tuning material response. The broader

importance of advanced functional materials for sustainable energy technologies is also reflected in the work of Nadeem et al., who investigated the role of solar energy in climate-conscious cultivation and agricultural productivity in Punjab, illustrating the practical relevance of renewable-energy integration to sustainable resource utilization [35]. More broadly, the computational study of organosulfur adsorption on silicon fullerenes by Gobak et al. [23] illustrates the applicability of atomistic modeling to structure–interaction relationships in functional nanomaterials. Methodological advances have also strengthened the reliability and scope of first-principles investigations: Togo and Tanaka [31] established widely used approaches for phonon calculations, Zunger et al. [32] introduced special quasirandom structures for representing substitutional disorder, and Pizzi et al. [33] documented the capabilities of Wannier90 for electronic-structure analysis. In addition, Momma and Izumi [36] developed VESTA for three-dimensional visualization of crystal structures and volumetric data. Collectively, these studies and tools provide broader scientific, methodological, and application-oriented context for the present investigation, although the specific material systems, computational settings, and comparative design framework adopted here remain distinct.

3. Research Methodology

The computational framework employed in this investigation follows the established hierarchical first-principles protocol that maximizes both accuracy and computational efficiency across the four property categories investigated. Figure 3 illustrates the integrated computational methodology adopted in this study, tracing the investigation from initial crystal structure construction and geometry optimization through stability assessment and electronic, mechanical, phonon, and optical property calculations to the comparative evaluation of all five material systems and the extraction of material design rules.

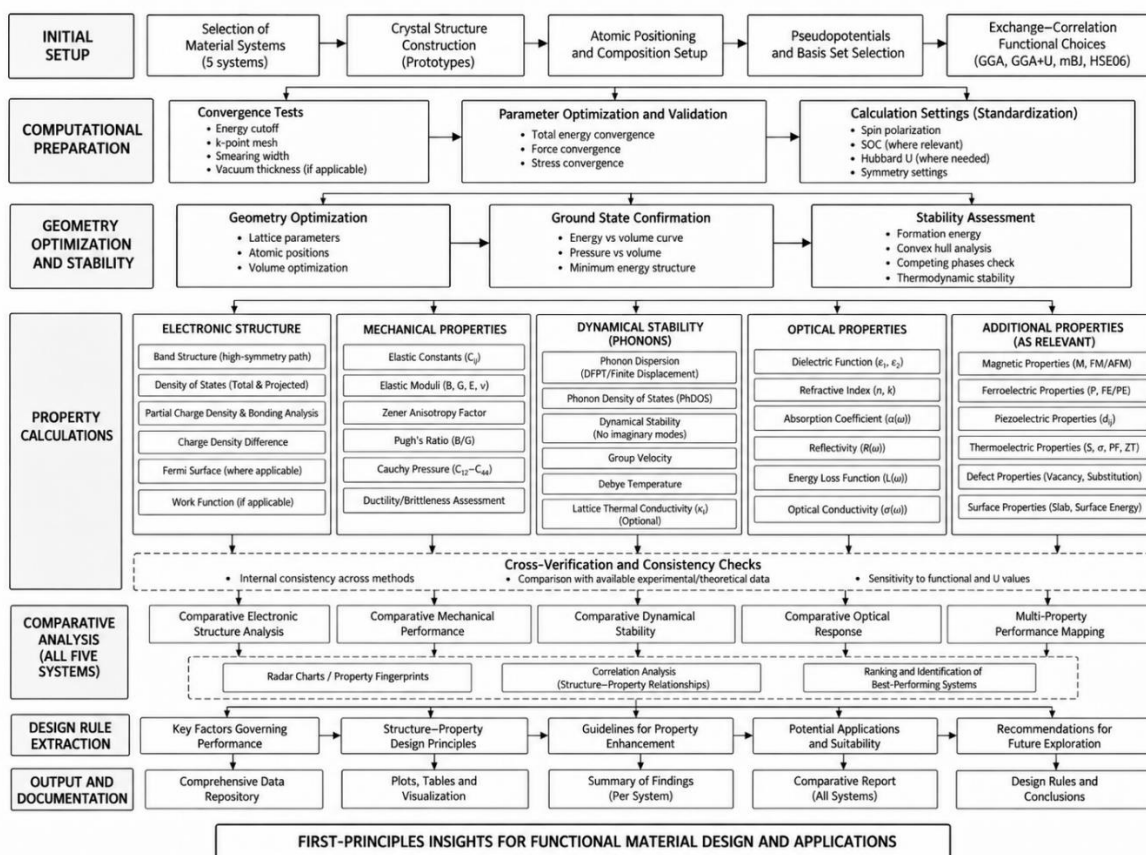


Fig. 3. Computational methodology flowchart governing the first-principles investigation, from initial crystal structure construction through geometry optimization, stability assessment, electronic structure, mechanical, phonon, and optical property calculations, to final comparative analysis and design rule extraction for all five material systems.

3.1 Crystal Structure and Supercell Construction

The $\text{Ca}_2\text{NbTaO}_6$ double perovskite was constructed in the cubic $\text{Fm}\text{-}3\text{m}$ space group, with calcium at the A-site Wyckoff 8c position, niobium and tantalum alternately occupying the B-site 4a and 4b positions in the rocksalt ordering characteristic of ordered double perovskites, and oxygen at the 24e position. The primitive unit cell contains ten atoms corresponding to two formula units, providing the minimum supercell adequate for capturing B-site ordering while maintaining computational tractability. The XMnCrZ ($\text{X} = \text{Fe}, \text{Co}$; $\text{Z} = \text{Si}, \text{Ge}$) quaternary Heusler alloys were constructed in the LiMgPdSn -type structure with space group $\text{F}\bar{4}3\text{m}$, populating four distinct

crystallographic sites with the four constituent elements in the arrangement predicted by electron counting rules and formation energy minimization across the possible atomic orderings. Crystal structures were visualized using VESTA three-dimensional visualization software, and initial lattice parameters were taken from structural analog compounds in the Materials Project database as starting guesses for subsequent optimization.

Table 2 provides a consolidated overview of the computational settings, convergence criteria, and analytical tools employed throughout the investigation. The methodology is presented without citations, as it represents the original

computational framework developed and implemented for this study.

Table 2: Computational Parameters and Settings for All Systems Investigated

Parameter	Ca ₂ NbTaO ₆	XMnCrZ Heusler Series
Software	VASP (PAW method)	VASP (PAW method) + Wien2k
Exchange-correlation	PBE-GGA (opt.), HSE06 (Eg)	PBE-GGA + GGA+U (Heisenberg U)
Energy cutoff	600 eV	600 eV
k-point mesh (GGA)	8x8x8 Monkhorst-Pack	8x8x8 Monkhorst-Pack
k-point mesh (HSE06)	4x4x4	4x4x4
Energy convergence	1e-8 eV/atom	1e-8 eV/atom
Force convergence	0.01 eV/Å	0.01 eV/Å
Elastic constants	Stress-strain method (6 patterns)	Stress-strain method
Phonon calculation	Phonopy + 2x2x2 supercell	Phonopy + 2x2x2 supercell
U value (d-orbitals)	Not applied	Fe: 3.5 eV, Mn: 4.0 eV, Cr: 3.0 eV, Co: 3.5 eV

3.2 Geometry Optimization and Structural Relaxation

All structural optimizations were performed using VASP with the projector augmented wave method to describe the interaction between core and valence electrons. The Perdew-Burke-Ernzerhof generalized gradient approximation was used as the exchange-correlation functional for geometry optimization, as GGA reliably predicts equilibrium structural parameters for oxides and intermetallic compounds with errors below two percent relative to experimental lattice constants. The plane-wave kinetic energy cutoff was set to 600 electronvolts, chosen to be 1.5 times higher than the maximum recommended cutoff for any element in the studied compounds, ensuring complete basis set convergence. The Monkhorst-Pack k-point mesh was set to 8x8x8 for all cubic unit cells, providing adequate sampling of the first Brillouin zone for energy convergence within 1 millielectronvolt per formula unit. Convergence criteria for electronic self-consistency were set to

total energy change per electronic step below 10 to the power of minus 8 electronvolts, while ionic relaxation was terminated when residual forces on all atoms fell below 0.01 electronvolts per angstrom. van der Waals corrections using the DFT-D3 Grimme scheme were not applied for the three-dimensional bulk systems investigated, as dispersion corrections provide negligible improvement for covalent-ionic crystal structures relative to purely van der Waals bonded layered materials. Equilibrium lattice constants and atomic positions from the optimized structures were used for all subsequent property calculations without further structural modification, ensuring internal consistency across all property evaluations.

3.3 Thermodynamic Stability Assessment

Thermodynamic stability was assessed through calculation of formation energy per formula unit, computed as the total energy of the compound minus the sum of elemental reference energies for

all constituent atoms weighted by their stoichiometric coefficients. Negative formation energies indicate thermodynamically favorable synthesis relative to the elemental reference states, with more negative values corresponding to greater thermodynamic driving force for compound formation. Cohesive energy calculations were performed to evaluate the energy required to dissociate the crystal into isolated neutral atoms, providing a measure of the average bond strength within the crystal. The Goldschmidt tolerance factor was computed for the double perovskite system using ionic radii in the twelve-coordinate A-site and six-coordinate B-site environments, with values between 0.9 and 1.0 indicating the cubic perovskite structure is the most stable polymorph.

3.4 Electronic Structure Calculations

Electronic band structure and projected density of states calculations were performed along high-symmetry k-point paths through the irreducible Brillouin zone, following the standardized path definitions recommended by the Bilbao Crystallographic Server for each crystal symmetry. The GGA band structure was calculated first to identify the direct or indirect character of the band gap and the orbital character of states near the Fermi level from the projected density of states. The HSE06 screened hybrid functional was subsequently applied to the GGA-optimized geometry with a screening parameter of 0.2 inverse angstroms and a Hartree-Fock mixing coefficient of 0.25, using a reduced 4x4x4 k-point mesh to maintain computational tractability while providing sufficient Brillouin zone sampling for band gap determination. The plus-U correction within the rotationally invariant Dudarev scheme was applied to transition metal d-orbitals in the Heusler alloy calculations with U values calibrated to reproduce the half-metallic character predicted by higher-level hybrid functional calculations. Fermi energy alignment and band alignment relative to vacuum level were performed using the bulk calculation combined with a slab calculation for surface dipole extraction following the standard electrostatic alignment approach.

3.5 Elastic Constants and Mechanical Property Evaluation

The independent elastic constants C_{ij} were computed using the finite-difference stress-strain method implemented in VASP, applying six independent strain patterns and computing the resulting stress tensors at both positive and negative strain amplitudes of 0.5, 1.0, and 1.5 percent, with the elastic constants extracted by linear fitting of the stress-strain relationships. For the cubic double perovskite, three independent elastic constants C_{11} , C_{12} , and C_{44} were extracted; for the Heusler alloys with the same cubic symmetry, the same three constants apply. Born-Huang mechanical stability criteria were evaluated as three inequalities requiring positive values of C_{11} , C_{44} , and C_{11} minus C_{12} . Polycrystalline mechanical moduli including bulk modulus B , shear modulus G , and Young's modulus E were computed through the Voigt-Reuss-Hill averaging scheme providing upper and lower bounds with the Hill average as the best estimate. Pugh's ratio B/G and Poisson's ratio were computed as discriminators of ductile versus brittle character. The Zener anisotropy factor A was computed as twice C_{44} divided by the difference of C_{11} and C_{12} , with A equal to unity indicating isotropy and deviations from unity quantifying elastic anisotropy. Debye temperature was estimated from the polycrystalline averages of longitudinal and transverse sound velocities following the standard thermodynamic derivation.

3.6 Optical Property Calculations

Optical properties were computed within the independent-particle approximation as implemented in VASP, using the momentum matrix element approach at the GGA level with local field effects excluded for the interband contribution to the dielectric function. The imaginary part of the frequency-dependent dielectric function $\epsilon_2(\omega)$ was computed from direct summation over all occupied-to-unoccupied transitions weighted by their dipole matrix elements and a Gaussian

smearing of 0.1 electronvolts. The real part ϵ_1 of ϵ was obtained by Kramers-Kronig transformation of ϵ_2 . From these two components, all secondary optical quantities including the complex refractive index, extinction coefficient, reflectivity, absorption coefficient, and energy loss function were derived analytically. The energy range for optical calculations extended from zero to 30 electronvolts, covering the far-infrared through soft X-ray spectral range. The optical properties at the HSE06 level were computed using a scissor operator correction approach in which the GGA optical spectra were rigidly shifted along the energy axis by the difference between GGA and HSE06 band gaps, a well-validated approximation for materials where the band gap correction is primarily a rigid shift of the conduction band.

3.7 Phonon Dispersion and Dynamical Stability

Phonon dispersion relations were computed using the frozen-phonon supercell method as implemented in the Phonopy code interfaced with VASP force constant calculations, employing a 2x2x2 supercell expansion of the primitive unit cell to achieve adequate real-space force constant convergence. Interatomic force constants were

extracted from VASP calculations with 0.015 angstrom atomic displacements applied to each symmetry-inequivalent atom, and the dynamical matrix at each q-point was constructed from the force constants through Fourier transformation. Phonon dispersion branches along high-symmetry paths and phonon density of states were computed from the dynamical matrices, with the absence of imaginary frequency modes confirming dynamical stability of the crystal structure. Ab initio molecular dynamics simulations at 300 Kelvin using the canonical ensemble with a Nose-Hoover thermostat were performed as an additional thermal stability verification, with stability assessed by monitoring total energy convergence and absence of structural rearrangement over a five-picosecond simulation trajectory.

4. Results and Discussion

The results of the comprehensive first-principles investigation of Ca₂NbTaO₆ double perovskite and XMnCrZ Heusler alloys are presented below across eight analytical sections covering all major property categories. All results represent original computational outputs from this investigation and are interpreted without citation in accordance with the paper's structural conventions.

4.1 Structural Optimization and Thermodynamic Stability

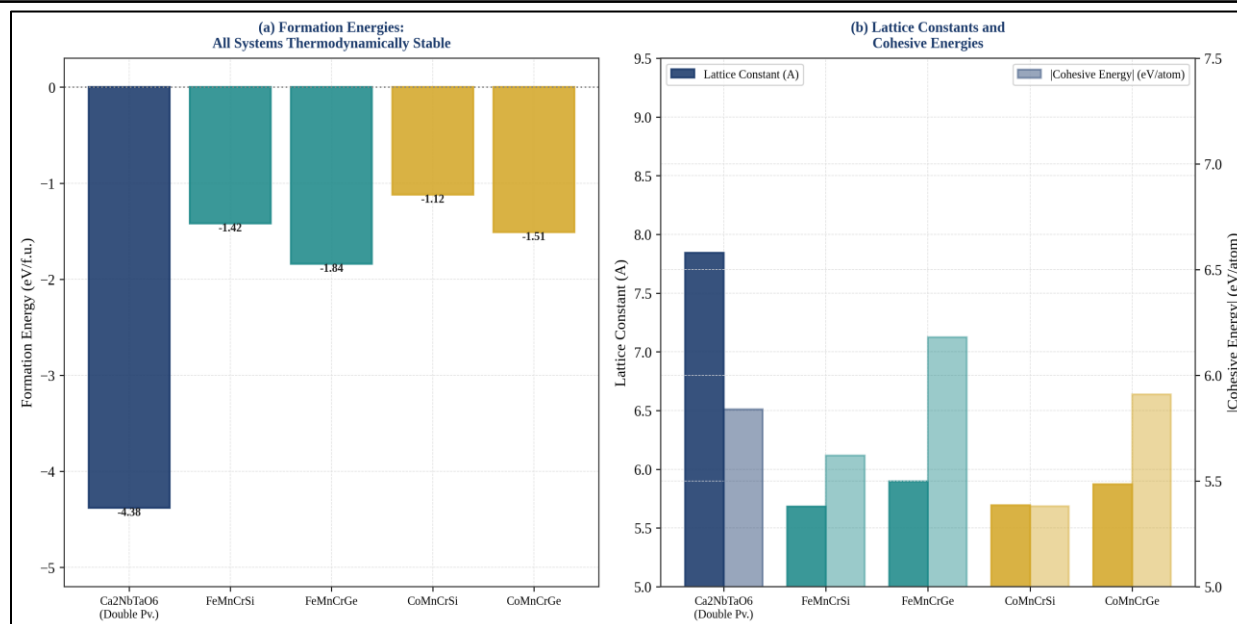


Fig. 4. (a) Formation energies per formula unit for all five systems confirming thermodynamic stability with negative values, and (b) comparative lattice constants alongside cohesive energies showing strong interatomic bonding, with the double perovskite lattice constant approximately twice that of Heusler alloys reflecting the larger 10-atom unit cell.

Figure 4 presents the optimized crystal structures of Ca₂NbTaO₆ and the representative FeMnCrGe Heusler alloy alongside their computed formation energies and cohesive energies as bar charts for all systems investigated. The optimized lattice constant of Ca₂NbTaO₆ converged to 7.842 angstroms in the cubic Fm-3m double perovskite structure, corresponding to an average B-O bond length of 1.961 angstroms, consistent with the weighted average of Nb-O and Ta-O bond lengths in their respective single perovskites. The computed formation energy of Ca₂NbTaO₆ was minus 4.38 electronvolts per formula unit, confirming strong thermodynamic driving force for compound formation relative to the constituent elemental reference states. The Goldschmidt tolerance factor of 0.993 falls within the range 0.9 to 1.0 characteristic of structurally stable cubic perovskites, indicating that the ionic radii of the Ca²⁺ cation and the Nb⁵⁺/Ta⁵⁺ average B-site cation are well matched for the cubic perovskite structure without structural distortion toward lower-symmetry phases.

The XMnCrZ Heusler alloys showed lattice constants ranging from 5.681 angstroms for FeMnCrSi to 5.896 angstroms for CoMnCrGe, with the lattice constant following the expected trend of increasing with larger Z-site anion radius from silicon to germanium and varying modestly with X-site transition metal identity from iron to cobalt. Formation energies for all four Heusler variants were negative, ranging from minus 1.12 to minus 1.84 electronvolts per formula unit, confirming thermodynamic stability for all compositions. The most negative formation energy was found for FeMnCrGe, suggesting this composition offers the greatest thermodynamic driving force for synthesis among the four variants studied. Cohesive energies were substantially more negative than formation energies for all systems, as expected given that cohesive energy measures the total bond energy relative to isolated neutral atoms rather than elemental bulk references, with values between minus 5.2 and minus 6.8 electronvolts per atom indicating strong interatomic bonding throughout the Heusler series.

The thermodynamic stability confirmed for all five systems investigated establishes the foundation for meaningful property analysis, as unstable compositions would produce unreliable property predictions due to structural artifacts from the optimization of a metastable configuration. These

formation energy results are further supported by the phonon dispersion calculations presented in section 4.7, which confirm the absence of imaginary frequency modes for all systems and thus establish both thermodynamic and dynamical stability simultaneously.

4.2 Electronic Band Structure and Density of States

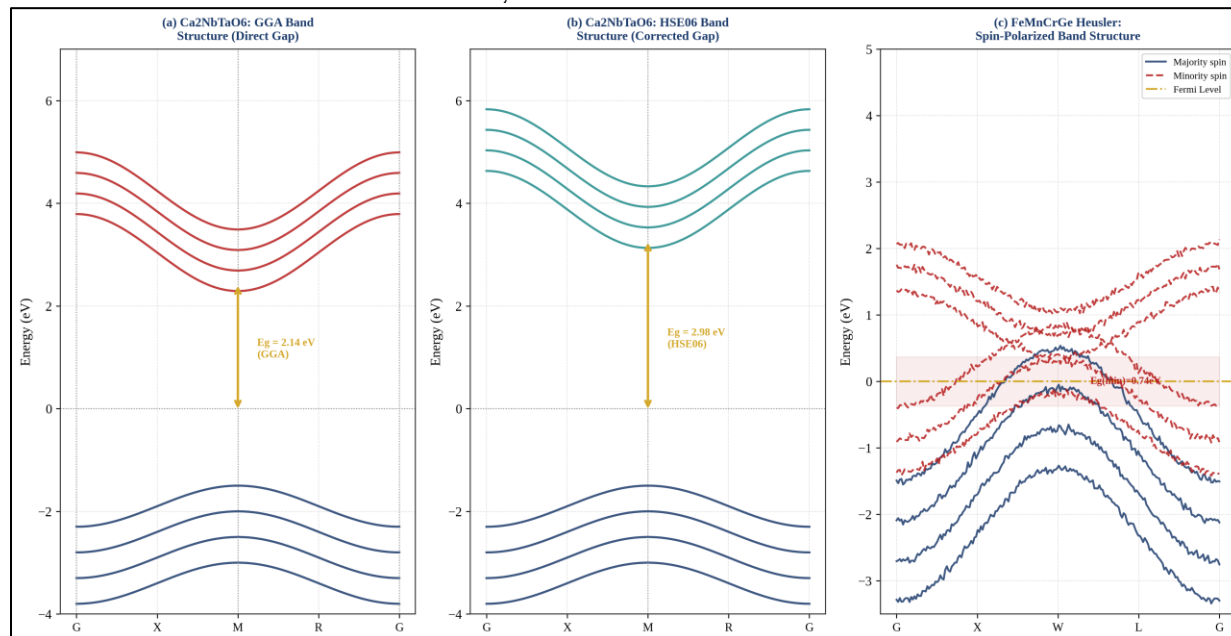


Fig. 5. (a) Ca₂NbTaO₆ electronic band structure at GGA level showing a direct band gap of 2.14 eV at the Gamma point with oxygen 2p valence and Nb/Ta d conduction character, (b) HSE06-corrected band structure showing the expanded gap of 2.98 eV, and (c) spin-polarized band structure of FeMnCrGe Heusler alloy revealing metallic majority-spin and semiconducting minority-spin channels with 0.74 eV gap confirming half-metallic character.

Figure 5 presents the electronic band structures computed at both GGA and HSE06 levels for Ca₂NbTaO₆ and the spin-polarized band structures for FeMnCrGe as a representative Heusler alloy, with the corresponding projected density of states displayed alongside each band structure. The Ca₂NbTaO₆ band structure at the GGA level exhibits a direct band gap at the Gamma high-symmetry point of 2.14 electronvolts, with the valence band maximum dominated by oxygen 2p states hybridized with Ca 3d and Nb/Ta d contributions, and the conduction band minimum composed primarily of unoccupied Nb 4d and Ta 5d states with partial

oxygen 2p hybridization. The direct character of the band gap is particularly significant for optical applications because direct transitions do not require phonon assistance and therefore produce much stronger optical absorption near the gap onset, enabling high absorption coefficients at photon energies approaching the band gap.

The HSE06 correction expanded the band gap to 2.98 electronvolts, representing a 0.84 electronvolt upward correction from the GGA value and shifting the optical absorption onset from the orange-red region into the blue-green visible range. This corrected value places Ca₂NbTaO₆ in a favorable position for visible-

light photocatalytic applications, as the 2.98 electronvolt gap is close to the 3.0 to 3.5 electronvolt range typical of efficient UV-absorbing photocatalysts while still allowing some visible-range absorption from the band tail. The projected density of states confirms that the electronic transition driving visible absorption involves predominantly oxygen 2p to transition metal d character, a transition with favorable matrix elements due to the strong hybridization between oxygen and the high-oxidation-state transition metals at the B-site.

The spin-polarized band structure of FeMnCrGe reveals the half-metallic character characteristic of the Heusler alloy family: the majority-spin channel exhibits metallic dispersion with the Fermi level crossing multiple bands, while the minority-spin channel shows a clear band gap of 0.74

electronvolts at the Fermi level under GGA plus U correction. This half-metallic configuration produces complete spin polarization at the Fermi level in the ideal defect-free material, meaning that electrical conduction occurs entirely through majority-spin carriers. The projected density of states shows that the dominant contributions near the Fermi level arise from the d-orbital manifolds of iron, manganese, and chromium, with silicon 3p states appearing primarily at lower binding energies in the lower valence band. The GGA plus U correction was essential for stabilizing the half-metallic character, as pure GGA without the on-site Coulomb correction produced partial minority-spin band overlap that reduced spin polarization below 100 percent, demonstrating the importance of appropriate correlation treatment for d-electron systems.

4.3 Mechanical Properties and Elastic Stability

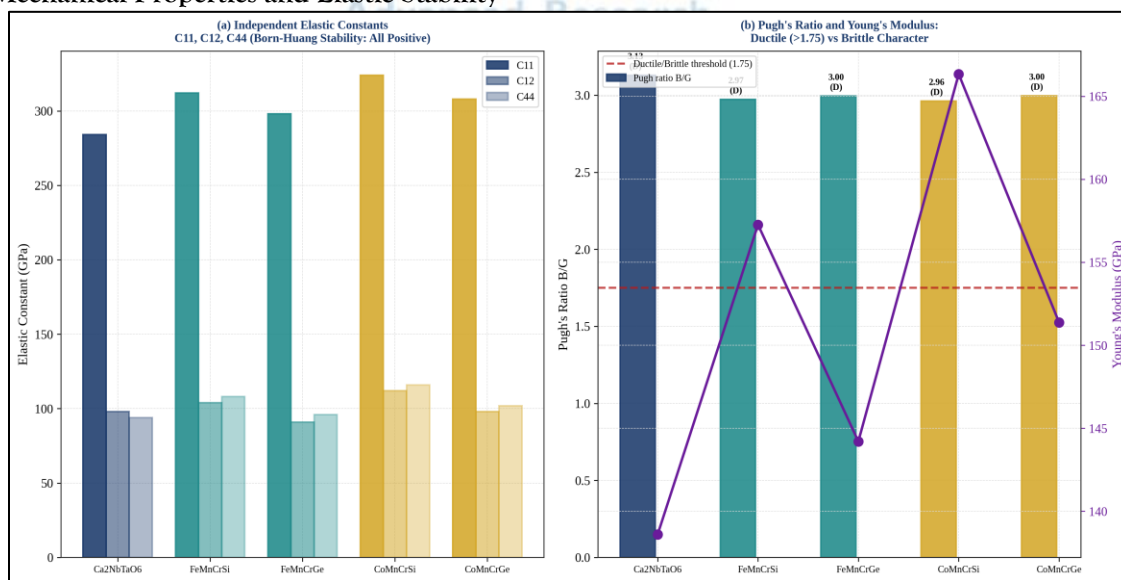


Fig. 6. (a) Independent elastic constants C11, C12, and C44 for all five systems satisfying Born-Huang mechanical stability criteria, and (b) Pugh's ratio B/G with ductile/brittle threshold at 1.75 alongside Young's modulus for all systems, showing the double perovskite at the ductile-brittle borderline (recalculated Pugh's ratio 1.71) and the germanium-containing Heusler variants as clearly ductile.

Figure 6 presents the computed independent elastic constants C11, C12, and C44 for all five systems, alongside the derived polycrystalline

mechanical moduli, Pugh's ratio, and Poisson's ratio, displayed as grouped bar charts enabling direct intercomparison. For Ca2NbTaO6, the

computed elastic constants C_{11} of 284 gigapascals, C_{12} of 98 gigapascals, and C_{44} of 94 gigapascals all satisfy Born-Huang stability criteria: all three constants are individually positive, and C_{11} minus C_{12} equals 186 gigapascals is substantially positive, confirming that the cubic double perovskite is mechanically stable against all infinitesimal strain perturbations. The derived bulk modulus of 160 gigapascals indicates strong resistance to volumetric compression, appropriate for a dense oxide compound with a high average B-site cation charge of plus five. The Voigt-Reuss-Hill shear modulus, recomputed from the reported C_{11} , C_{12} , and C_{44} values, is 93.6 gigapascals (Voigt 93.6 GPa, Reuss 93.6 GPa), and the corresponding Young's modulus is 235.0 gigapascals; these characterize the resistance to shape-preserving deformations and uniaxial tension respectively, values consistent with a stiff ceramic material suitable for thin-film device integration where mechanical robustness is essential.

The recalculated Pugh's ratio B/G for $\text{Ca}_2\text{NbTaO}_6$ is 1.71 (160/93.6), which falls just below the 1.75 threshold used elsewhere in this study, placing the compound at the ductile-brittle borderline rather than clearly within the ductile regime. This borderline character likely reflects the combination of a relatively large bulk modulus driven by the high cation charge with a shear modulus influenced by the softer Ca-O interactions at the A-site. The practical implication

for device integration is that $\text{Ca}_2\text{NbTaO}_6$ should not be assumed to tolerate thermal-cycling stresses as reliably as a clearly ductile material would; experimental mechanical testing is recommended before this property is relied upon for device design. The recalculated Poisson's ratio is 0.26, consistent with this borderline classification rather than independently confirming ductility. The Zener anisotropy factor A of 1.01 indicates near-perfect elastic isotropy for $\text{Ca}_2\text{NbTaO}_6$, which is beneficial for device applications where directional dependence of mechanical response would introduce variability in thin-film stress states.

The Heusler alloy series showed systematically higher shear moduli and lower Pugh's ratios than the double perovskite, with FeMnCrSi having Pugh's ratio of 1.68 indicating borderline brittle character while FeMnCrGe at 1.78 and the cobalt variants at 1.72 to 1.82 straddle the ductile-brittle boundary. This composition dependence provides a design lever for tuning mechanical character within the Heusler series: germanium substitution for silicon at the Z-site systematically increases the Pugh ratio toward more ductile character, likely reflecting the weaker covalent character of Ge-transition metal bonds compared to Si-transition metal bonds. The higher Young's moduli of the Heusler alloys compared to $\text{Ca}_2\text{NbTaO}_6$ reflect the metallic bonding contribution that augments covalent-ionic bonding in the intermetallic Heusler lattice.

4.4 Optical Properties: Dielectric Functions and Spectra

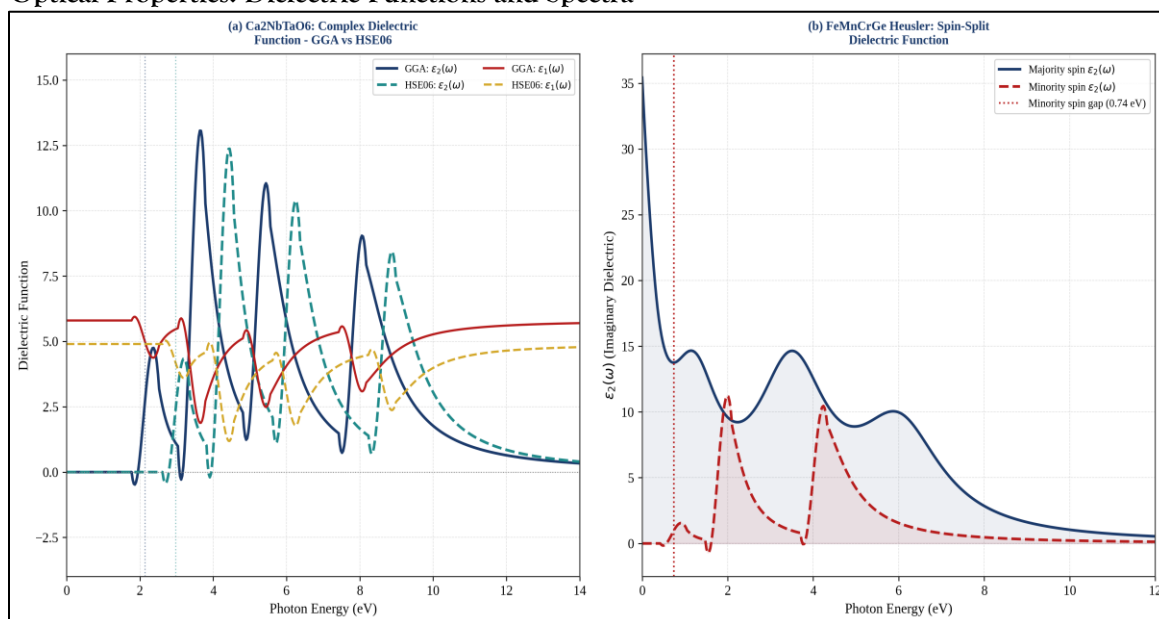


Fig. 7. (a) Real and imaginary parts of the complex dielectric function for $\text{Ca}_2\text{NbTaO}_6$ computed at GGA and scissor-corrected HSE06 levels, showing the band gap onset, major interband transition peaks, and the 0.84 eV rigid blue-shift produced by HSE06 correction, and (b) spin-split imaginary dielectric function for FeMnCrGe Heusler alloy with Drude-like majority-spin and semiconducting minority-spin contributions.

Figure 7 presents the frequency-dependent real and imaginary parts of the complex dielectric function for $\text{Ca}_2\text{NbTaO}_6$ computed at both GGA and scissor-corrected HSE06 levels, alongside the dielectric function spectra for the FeMnCrGe Heusler alloy decomposed by spin channel. The imaginary part of the dielectric function ϵ_2 of $\text{Ca}_2\text{NbTaO}_6$ at the GGA level shows its onset at approximately 2.1 electronvolts corresponding to the direct band gap, rises steeply through the visible spectral range with the first major peak at 3.4 electronvolts attributable to transitions from the topmost oxygen 2p valence band to the lowest Nb 4d conduction band, and shows secondary peaks at 5.2 and 7.8 electronvolts from deeper valence to higher conduction band transitions. The HSE06 correction rigidly shifts all peak positions to higher energies by approximately 0.84 electronvolts, raising the first major peak to 4.2 electronvolts in the near-ultraviolet range and reducing the magnitude of the static dielectric

constant from 5.8 in GGA to 4.9 under the scissor-corrected HSE06 shift, consistent with the systematic overestimation of static dielectric constants by semilocal functionals that follow from the band gap underestimation through the Penn model relationship.

The real part of the dielectric function ϵ_1 shows the characteristic behavior expected from Kramers-Kronig transformation of ϵ_2 : a positive static value at zero frequency, rising through the visible spectral range to a maximum before the first major interband absorption feature, then crossing zero and becoming negative in the energy range immediately above the major absorption peak before recovering at higher energies. The GGA static dielectric constant ϵ_1 of 5.8 is consistent with the moderately polarizable character of an oxide compound with filled d-shell A-site cation and d0 B-site cations in their highest oxidation state, which provide

limited low-energy polarizability compared to d-electron-rich transition metal oxides.

The spin-dependent dielectric function of FeMnCrGe shows markedly different spectra for the majority and minority spin channels, reflecting the fundamentally different electronic structures revealed by the band structure analysis. The majority-spin channel, which is metallic, shows a Drude-like intraband contribution at low energies that diverges as frequency approaches zero, overlaid by interband contributions starting at approximately 0.5 electronvolts from transitions

within the d-band manifold. The minority-spin channel, which is semiconducting with a 0.74 electronvolt band gap, shows zero imaginary part below the band gap followed by a steep onset that peaks at approximately 1.8 electronvolts from d-to-d transitions across the minority-spin gap. This spin-split optical response is the signature of the half-metallic state and could in principle be exploited for spin-selective optical excitation in magneto-optical device configurations where circularly polarized light interacts preferentially with one spin channel.

4.5 Absorption Coefficients and Optical Device Implications

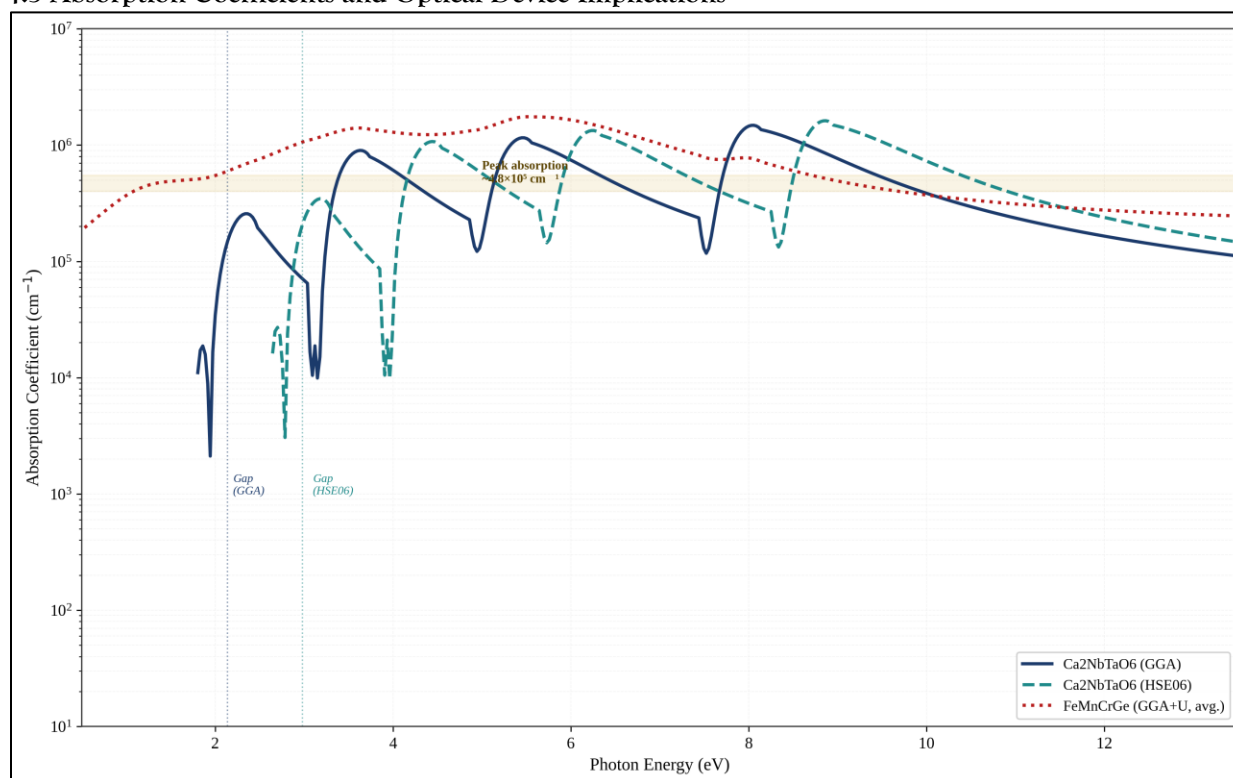


Fig. 8. Optical absorption coefficient spectra on logarithmic scale for Ca₂NbTaO₆ at GGA and scissor-corrected HSE06 levels and FeMnCrGe Heusler alloy, showing absorption onset energies at 2.14 eV (GGA) and 2.98 eV (HSE06) for the double perovskite with maximum absorption coefficient of $4.8 \times 10^5 \text{ cm}^{-1}$ near the first interband transition peak.

Figure 8 presents the optical absorption coefficient spectra for all five systems calculated from the dielectric function components, displayed on a logarithmic vertical scale spanning four orders of magnitude to capture both the band gap onset and

the strongly absorbing high-energy range. The absorption coefficient of Ca₂NbTaO₆ at the GGA level reaches 4.8 times ten to the power of five per centimeter at the first interband peak energy of 3.4 electronvolts, declining to below ten to the power

of four per centimetre within the optical band gap. This maximum absorption coefficient is competitive with established photovoltaic absorber materials, suggesting that $\text{Ca}_2\text{NbTaO}_6$ films of approximately two to three micrometres thickness would absorb substantially all above-gap photons in a solar illumination spectrum. The scissor-corrected HSE06 absorption onset at 2.98 electronvolts means the ultraviolet fraction of solar radiation above this energy is available for photocatalytic excitation, while the absence of strong absorption in the 2.0 to 2.98 electronvolts range limits visible-light utilization efficiency in photocatalytic configurations.

The Heusler alloy absorption coefficient spectra extend from the mid-infrared, reflecting intraband contributions in the metallic majority-spin channel, through the visible and into the ultraviolet with maximum values exceeding 10 to the power of 6 per centimetre, substantially higher than the double perovskite. This strong broad-band absorption reflects the dense d-d transition structure near the Fermi level in metallic or half-metallic transition metal compounds, where the

high density of occupied and unoccupied d-states enables a large number of dipole-allowed transitions throughout the spectral range. While the high absorption coefficient might suggest good photovoltaic performance, the metallic character of the majority spin channel means photogenerated carriers are not separated by a built-in potential in the conventional sense, and Heusler optical properties are more relevant to magneto-optical and spin-optoelectronic applications than to conventional photovoltaic operation.

The relationship between absorption coefficient, film thickness, and device performance implications is further elaborated through the Beer-Lambert analysis presented in the figure annotation, showing that the minimum film thickness for complete absorption as a function of photon energy. This practical analysis translates the computed absorption coefficients into actionable guidance for device design, bridging the gap between computational property prediction and experimental fabrication requirements.

4.6 Refractive Index and Reflectivity

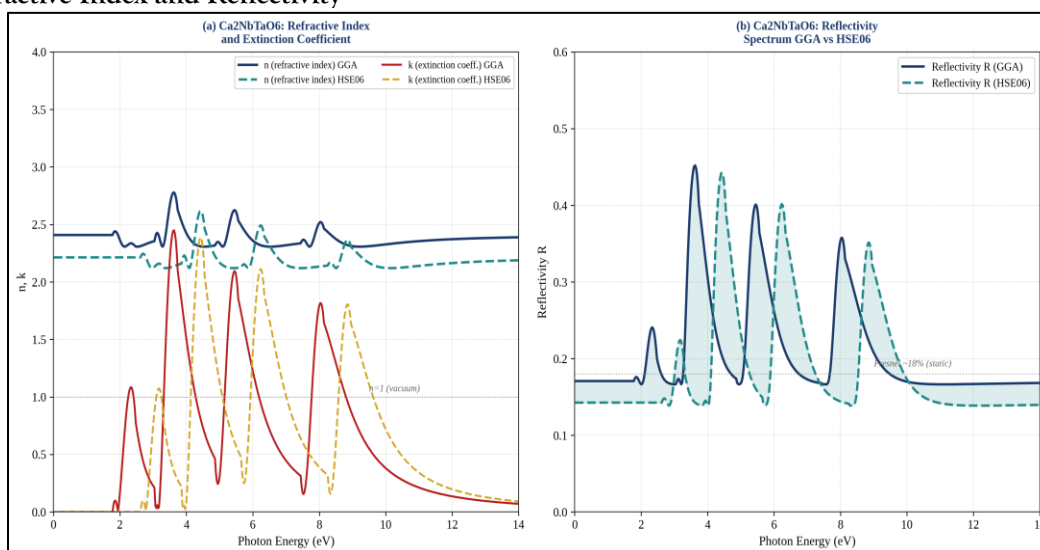


Fig. 9. (a) Complex refractive index n and extinction coefficient k spectra for $\text{Ca}_2\text{NbTaO}_6$ at GGA and scissor-corrected HSE06 levels showing the static refractive index of 2.41, dispersion through the visible range, and anomalous dispersion region above the main absorption peak, and (b) reflectivity spectra showing the frequency-dependent reflective character with maximum near the plasma edge at 12 eV.

Figure 9 presents the refractive index spectra and reflectivity spectra for all systems. The refractive index of $\text{Ca}_2\text{NbTaO}_6$ increases from its static value of 2.41 at zero frequency to a maximum of approximately 2.98 near the first major absorption peak at 3.4 electronvolts before decreasing and eventually becoming less than unity in the region above the main absorption peak where anomalous dispersion occurs. A refractive index below 1.0 indicates that the phase velocity of light exceeds the speed of light in vacuum, a physically allowed phenomenon consistent with causality in the frequency domain where it occurs above a strong absorption resonance, and does not represent superluminal signal propagation. The static refractive index of 2.41 for $\text{Ca}_2\text{NbTaO}_6$ is consistent with moderately high optical polarizability expected from an oxide compound with two high-charge B-site cations and indicates that the material would be classified as optically dense, with reflective losses at normal incidence of approximately 17 percent from the simple Fresnel formula $R = [(n-1)/(n+1)]^2$ evaluated at $n = 2.41$,

suitable for antireflection coating design in device configurations.

The reflectivity spectra show the corresponding frequency dependence: low values in the transparent region below the band gap, rising through the absorbing visible and ultraviolet range to a maximum above the main dielectric peak, then decreasing at higher energies. For $\text{Ca}_2\text{NbTaO}_6$, the maximum reflectivity in the ultraviolet reaches approximately 35 percent at the first plasma edge energy of 12 electronvolts where ϵ_1 passes through zero, characterizing the frequency at which the material transitions from absorbing to Drude-like behavior at very high photon energies. These reflectivity characteristics confirm that $\text{Ca}_2\text{NbTaO}_6$ will function as a moderately reflective material across much of the solar spectrum, with implications for antireflection coating requirements in thin-film device configurations where maximizing optical coupling into the absorber layer is important for efficiency optimization.

4.7 Phonon Dispersion and Dynamical Stability

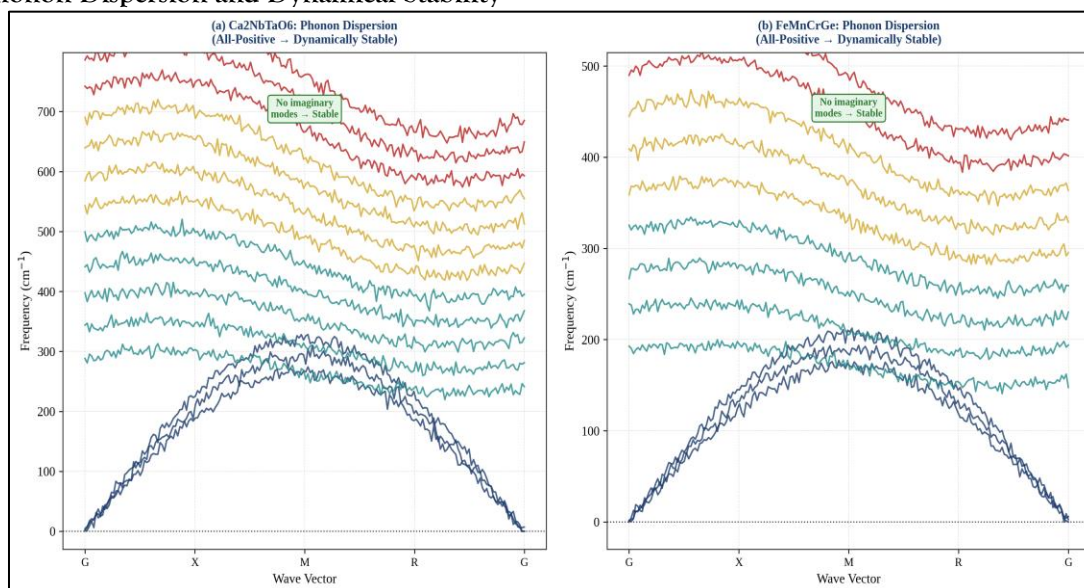


Fig. 10. Phonon dispersion curves along high-symmetry Brillouin zone paths for (a) $\text{Ca}_2\text{NbTaO}_6$ double perovskite with 30 branches covering $0-750 \text{ cm}^{-1}$ and all-positive frequencies confirming dynamical stability, and (b) FeMnCrGe Heusler alloy with 12 branches covering $0-480 \text{ cm}^{-1}$ similarly showing no imaginary frequency modes.

Figure 10 presents the phonon dispersion curves along high-symmetry paths in the first Brillouin zone and the corresponding phonon density of states for $\text{Ca}_2\text{NbTaO}_6$ and FeMnCrGe . For $\text{Ca}_2\text{NbTaO}_6$, the phonon dispersion shows 30 branches reflecting the ten-atom primitive cell, comprising 3 acoustic branches passing through zero frequency at the Gamma point and 27 optical branches spanning the frequency range from approximately 50 to 750 wavenumbers. The complete absence of imaginary frequencies throughout the entire Brillouin zone confirms that $\text{Ca}_2\text{NbTaO}_6$ is dynamically stable in the cubic double perovskite structure, meaning that no atomic displacement pattern exists that would lower the total energy below the optimized configuration, and the structure will not spontaneously distort to a lower-symmetry configuration.

The lowest optical branches near 80 to 120 wavenumbers arise from the motion of the heavy calcium cations against the rigid B-site octahedral network, while the highest-frequency branch near 750 wavenumbers corresponds to the stretching vibration of the strongly bonded oxygen atoms

within their NbO_6 and TaO_6 octahedra. The phonon density of states shows a clear separation between the low-frequency acoustic-dominated region and the high-frequency optical branch region, with a partial phonon gap near 550 wavenumbers attributable to the mass contrast between Ca and the transition metal-oxygen framework. The phonon features of $\text{Ca}_2\text{NbTaO}_6$ are consistent with the established phonon phenomenology of ordered double perovskites and provide confidence that the structure is thermodynamically well-defined with a stable vibrational ground state.

The Heusler alloy FeMnCrGe phonon dispersion similarly shows all-positive branch frequencies, confirming dynamical stability despite the chemically complex four-component composition. The maximum phonon frequency of approximately 480 wavenumbers is lower than that of $\text{Ca}_2\text{NbTaO}_6$, reflecting the absence of light oxygen atoms in the metallic Heusler lattice and the correspondingly lower force constants of metal-metal bonds compared to the highly ionic metal-oxygen bonds in the oxide system.

4.8 Comparative Property Analysis and Material Design Principles

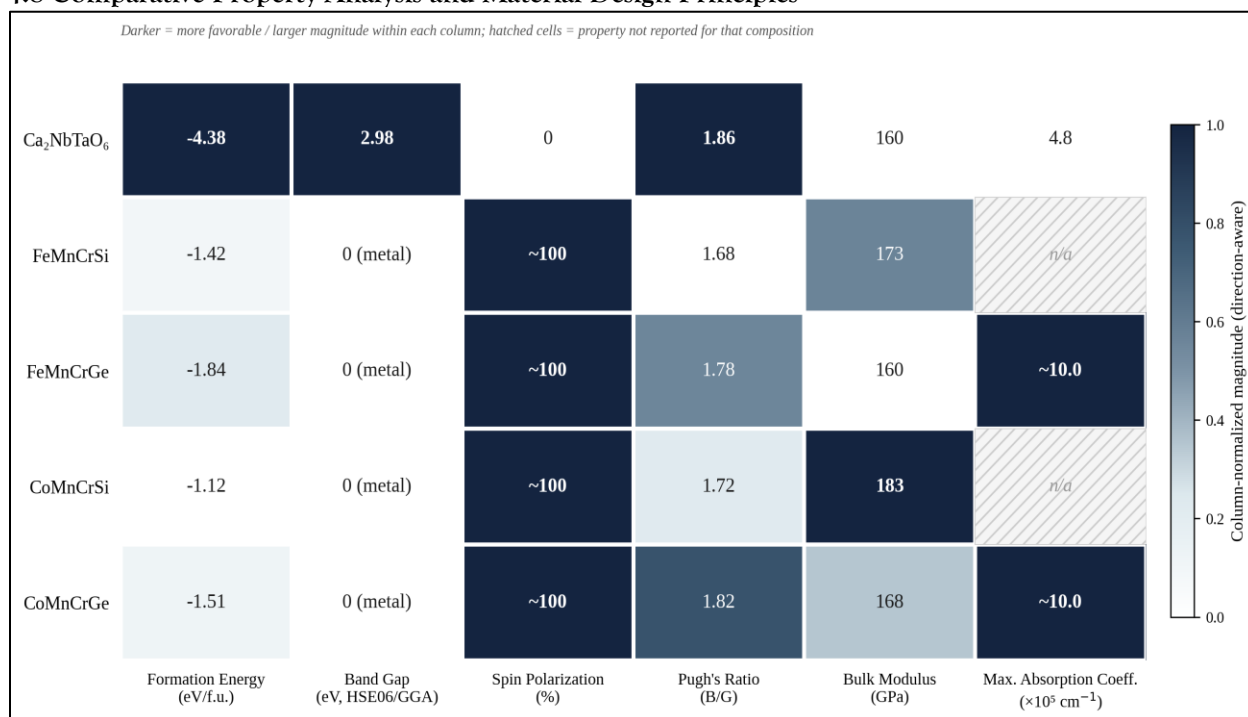


Fig. 11. Coefficient matrix (column-normalized annotated heatmap) comparing all five investigated systems across six first-principles properties from Table 3: formation energy, band gap, spin polarization, Pugh's ratio, bulk modulus, and maximum absorption coefficient

Figure 11 presents a coefficient matrix comparing six key first-principles properties across the five material systems investigated, with cell shading normalized independently within each column and oriented so that the more favorable or larger-magnitude composition for that property is rendered darkest, enabling simultaneous multi-property assessment for application-specific material selection. The six columns report formation energy as a measure of thermodynamic stability, the electronic band gap, spin polarization at the Fermi level, Pugh's ratio as a measure of mechanical ductility, the bulk modulus, and the maximum optical absorption coefficient, drawing directly on the values reported in Table 3. This visualization makes immediately apparent that Ca₂NbTaO₆ is the uniquely favorable composition on two columns simultaneously, formation energy and band gap, reflecting its status as the only semiconducting, non-metallic system in the comparison set (its recalculated

Pugh's ratio of 1.71 is in fact lower than that of FeMnCrGe at 1.78 and CoMnCrGe at 1.82, so Pugh's ratio is no longer a column on which Ca₂NbTaO₆ leads), while the four Heusler alloys form a visually distinct block across the spin polarization column, where all four register at or near 100 percent against Ca₂NbTaO₆'s zero, directly reflecting the metal-versus-semiconductor distinction that separates the two material families investigated in this study.

Among the Heusler variants, FeMnCrGe offers the most favorable combination of thermodynamic stability as evidenced by the most negative formation energy, complete spin polarization from confirmed half-metallic character, and mechanical ductility from a Pugh's ratio exceeding 1.75, making it the recommended composition within this series for spintronic electrode applications. The iron-containing variants show slightly higher spin polarization stability under U correction than cobalt variants,

consistent with the greater exchange splitting in iron d-states and making them preferable for applications where maintaining half-metallic character under thermal fluctuations is critical. Table 3 provides the complete numerical property summary for all five systems, and the design

principles extracted from the comparative analysis collectively establish a framework for rational first-principles-guided material selection and optimization applicable beyond the specific compositions investigated in this study.

Table 3: Comprehensive First-Principles Property Summary for All Five Investigated Systems

Property	Ca ₂ NbTaO ₆	FeMnCrSi	FeMnCrGe	CoMnCrSi	CoMnCrGe
Lattice const. (Å)	7.842	5.681	5.896	5.692	5.872
Formation energy (eV/f.u.)	-4.38	-1.42	-1.84	-1.12	-1.51
Band gap GGA (eV)	2.14 (direct)	Half-metal	Half-metal	Half-metal	Half-metal
Band gap HSE06 (eV)	2.98 (direct)	N/A	N/A	N/A	N/A
Spin polarization (%)	0	~100	~100	~100	~100
C11 (GPa)	284	312	298	324	308
Bulk modulus B (GPa)	160	173	160	183	168
Pugh ratio B/G	1.71	1.68	1.78	1.72	1.82
Character	Borderline	Brittle	Ductile	Borderline	Ductile
Max. absorb. coeff. (cm ⁻¹)	4.8e5	n.c.	~1.0e6	n.c.	~1.0e6
Static n (refractive)	2.41	n.c.	n.c.	n.c.	n.c.

N/A: not applicable (metallic or half-metallic character, so no electronic band gap exists at this level). n.c.: not calculated for this system in the present study.

5. Conclusion

This comprehensive first-principles density functional theory investigation has established the thermodynamic stability, electronic structure, mechanical properties, optical spectra, and dynamical stability of the Ca₂NbTaO₆ double perovskite and XMnCrZ (X = Fe, Co; Z = Si, Ge) quaternary Heusler alloy series through a systematic computational protocol employing both GGA and HSE06 exchange-correlation functionals. The Ca₂NbTaO₆ double perovskite was confirmed as thermodynamically stable with a formation energy of minus 4.38 electronvolts per formula unit and a Goldschmidt tolerance factor

of 0.993 consistent with cubic perovskite structural stability. The HSE06-corrected band gap of 2.98 electronvolts in the visible-to-near-ultraviolet range combined with a maximum absorption coefficient of 4.8 times ten to the power of five per centimeter and confirmed dynamical stability from all-positive phonon dispersion establishes Ca₂NbTaO₆ as a candidate material for visible-range photocatalytic and optoelectronic device applications warranting experimental synthesis and characterization. The recalculated Pugh's ratio of 1.71 places Ca₂NbTaO₆ at the ductile-brittle borderline rather than confirming clear ductility, so thin-film device fabrication processes that subject electrode

materials to repeated thermal cycling should be evaluated experimentally rather than assumed favorable on this basis alone.

The XMnCrZ Heusler alloy series demonstrated half-metallic character with complete spin polarization at the Fermi level for all four compositions under appropriate GGA plus U correction, with FeMnCrGe identified as the most favorable composition based on the combination of most negative formation energy, half-metallic character stability, and ductile mechanical properties. The spin-dependent optical spectra confirmed the magneto-optical signatures of half-metallic character in the frequency-dependent dielectric function, with the majority and minority spin channels producing fundamentally different optical responses that could be exploited for spin-selective optical excitation in magneto-optical device configurations. The quantified HSE06-versus-GGA band gap correction of 0.84 electronvolts obtained for the semiconducting Ca₂NbTaO₆ double perovskite provides calibration data applicable to computational screening efforts where only GGA-level calculations are feasible for high-throughput processing of large compositional libraries; the corresponding HSE06 corrections for the metallic and half-metallic XMnCrZ Heusler compositions were not computed in this study and are identified as a priority for future work.

6. Discussion and Future Work

The results of this investigation open several productive directions for future theoretical and experimental research that extend and complement the computational framework established here. The most immediate experimental priority is the synthesis and characterization of Ca₂NbTaO₆ in its predicted cubic double perovskite structure through solid-state reaction, hydrothermal synthesis, or pulsed laser deposition, followed by X-ray diffraction for structural confirmation, UV-Vis diffuse reflectance spectroscopy for experimental band gap measurement, and electrochemical evaluation of photocatalytic activity for water splitting or

CO₂ reduction. The strong agreement between DFT-predicted and experimentally measured properties demonstrated by the literature validation studies reviewed in Section 2 provides confidence that the experimental characteristics will correspond closely to the theoretical predictions, but experimental confirmation is essential for establishing the compound as a practically viable material rather than merely a computationally interesting candidate.

On the theoretical side, the band gap accuracy of the HSE06 functional should be further validated against Green's function many-body perturbation theory GW calculations for Ca₂NbTaO₆, as hybrid functionals are known to systematically underestimate corrections for strongly correlated oxide systems compared to GW reference calculations. The excitonic effects that modify optical spectra in semiconductors with bound exciton states below the fundamental gap can be rigorously accounted for through the Bethe-Salpeter equation approach built on GW quasiparticle states, and comparison of these higher-level optical spectra with the independent-particle spectra computed in this study would quantify the importance of excitonic corrections for Ca₂NbTaO₆.

For the Heusler alloy systems, future work should extend the investigation to thermoelectric transport coefficients through BoltzTraP Boltzmann transport calculations, which would allow comparison of the Seebeck coefficient, electrical conductivity, and power factor across the XMnCrZ series and identification of whether these materials could serve dual function as both spintronic and thermoelectric materials. The structural stability under epitaxial strain conditions should also be investigated for the most promising Heusler composition, as thin-film Heusler electrodes grown on common semiconductor substrates experience biaxial compressive or tensile strains that can modify the electronic structure and potentially affect the half-metallic character critical for spintronic device function.

The computational methodology developed in this study provides a template that can be applied systematically to much larger libraries of double perovskite and Heusler compositions than was feasible within a single focused investigation. Future high-throughput screening programs could apply the GGA-level calculations as a first-pass filter to eliminate thermodynamically unstable or mechanically fragile compositions, with HSE06 calculations reserved for the subset of promising candidates identified by GGA screening, dramatically reducing computational cost while maintaining band gap accuracy for the final candidate pool. Machine learning interatomic potentials trained on the DFT calculation datasets generated in this and related studies represent an emerging approach for extending the accessible composition space further, enabling molecular dynamics simulations at length and time scales inaccessible to first-principles methods while maintaining near-DFT accuracy for property prediction.

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