Lithium-Based Functional Materials and Quaternary Heusler Semiconductors for Optical, Electrical, and Thermoelectric Applications

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ABSTRACT

The increasing demand for high-performance energy-conversion, optoelectronic and sensing technologies has stimulated the research of multifunctional materials that can integrate optical, electrical and thermoelectric properties in a single material platform. Lithium-based materials represent a large family of functional systems, ranging from oxide crystals to intermetallic semiconductors and ordered Heusler compounds. Lithium niobate has been a benchmark for a long time, owing to its excellent ferroelectric, piezoelectric, electro-optic and nonlinear optical properties, but its wide band gap and limited electrical transport restrict its applicability for efficient thermoelectric applications. Conversely, Heusler and half-Heusler compounds have a large compositional and electronic tunability to control band structure, carrier concentration, and thermal transport. Recent progress in quaternary Heusler semiconductors, in particular those based on the 18-valence-electron rule, has shown promising combinations of semiconductor band gaps, optical response and thermoelectric behavior. This review critically discusses the evolution from lithium-based functional oxides to half-Heusler and quaternary Heusler systems, with a focus on crystal structure, electronic properties, optical response, electrical transport, thermoelectric performance, and first-principles materials design. Particular attention is paid to Density Functional Theory and Boltzmann transport methods as tools to predict multifunctional behavior before experimental synthesis. The literature reveals that although significant progress has been made in individual optical and thermoelectric fields, there is a lack of systematic studies of the concurrent correlation among optical, electrical, and thermal transport properties in lithium-containing quaternary Heusler materials. This gap provides a significant opportunity to develop lightweight, tunable and multifunctional materials for future energy-conversion and optoelectronic applications by combining theoretical and experimental studies.

Keywords: Lithium-based materials; quaternary Heusler alloys; half-Heusler compounds; optical properties; electrical transport; thermoelectric properties; Density Functional Theory; multifunctional materials.

INTRODUCTION

Multifunctional materials have become more and more important as modern technologies demand smaller, more efficient and highly integrated devices. Common materials are optimized for a specific function, such as light transmission, electrical conduction, or heat regulation. But new technologies are increasingly demanding that these properties be combined in a single material. Examples include autonomous sensors, optical sensors, thermally activated electronic systems, and systems with simultaneous optical stimulation, charge movement and heat transfer.

The need alters the fundamental materials-design philosophy. Rather than optimizing one property, the investigators are now challenged to explore combinations of structural and electronic properties that lead to balanced performance. For example, an increase in the carrier concentration may increase the electrical conductivity, decrease the Seebeck coefficient and change the optical absorption. Structural disorder can reduce lattice thermal conductivity via phonon scattering, but too much disorder can also degrade carrier mobility. A

large electronic band gap is good for optical transparency and dielectric properties, but bad for electrical conductivity. Multifunctional materials require the simultaneous control of electronic structure, chemical bonding, defects and lattice dynamics.

The class of lithium compounds provides a rich ground for studying these connections. Lithium is found in oxides, ceramics, electrochemical materials, intermetallic compounds and semiconductor matrices. The best-known lithium-based functional material is lithium niobate ($LiNbO_3$), which is ferroelectric, piezoelectric, electro-optic, pyroelectric and possesses nonlinear optical properties. $LiNbO_3$ has been a key material for integrated optics, optical modulation, waveguides, nonlinear frequency conversion and surface-acoustic-wave devices because of its properties (Chen et al., 2021; Weis & Gaylord, 1985). Its properties are greatly affected by stoichiometry, defects, dopants and microstructure, which demonstrates the relationship between atomic structure and macroscopic performance (Chen et al., 2021).

The electronic properties of $LiNbO_3$ are indicative of the complexity of multifunctional design. First principles investigations have demonstrated that crystallographic surface orientation has a significant impact on the band structure, band gap and semiconductor properties. The niobium states affect mainly the conduction band and the oxygen states affect mainly the valence band (Lacerda et al., 2021). Polarons, bipolarons and inherent defects have also been associated with electrical and photorefractive properties (Kostritskii et al., 2007).

In parallel, research has also been directed toward intermetallic semiconductors such as the Heusler and the half-Heusler alloys where the electronic configuration and the carrier density can be more easily controlled. Half-Heusler compounds have attracted much attention as potential thermoelectric materials in the medium to high-temperature range because of their favorable electronic structures, mechanical properties, compositional flexibility, and phonon engineering possibilities (Li et al., 2024; Quinn & Bos, 2021).

The quaternary expansion Heusler compounds extend the range of design possibilities. Extensive first-principles investigations using the 18-valence-electron rule (He et al., 2018) have discovered many promising semiconducting quaternary Heusler candidates with intriguing optical and thermoelectric properties. Recent advances in phase-interface engineering, entropy engineering, defect engineering, and hierarchical microstructures have further improved the associated thermoelectric performance (Ai et al., 2025; Zhang et al., 2024).

The literature remains fragmented. Currently, lithium-based oxides are mainly investigated for their optoelectronic properties and the thermoelectric properties are the main subject of the Heusler systems investigated so far. Comprehensive investigations including optical, electrical and thermal transport are rare. As an illustrative case linking the two families, the review also considers LiNbRhGa, a hypothetical lithium-containing quaternary Heusler composition. It combines Li and Nb, the cations of $LiNbO_3$, with Rh and Ga to reach the 18-valence-electron count used to screen for semiconducting quaternary Heuslers (He et al., 2018). It is used only as a worked example of the screening and validation steps; no measured or calculated properties are reported for it. The review critically assesses lithium-based functional materials and Heusler-type semiconductors with a focus on Density Functional Theory, Boltzmann transport, multifunctionality and the need for better theory-experiment correlation.

METHODOLOGY

The present study is a critical thematic analysis. The justification for this methodology is based on the fact that the research problem involves a variety of material types and domains of physical-property data, as opposed to a single, uniform set of experimental results. The purpose of the review is to gather, compare, and critically evaluate conceptual and methodological advances, not to combine statistical data through meta-analyses.

We searched the relevant literature using scientific publishing platforms and academic databases commonly used for materials science, solid-state physics, and computational materials research. The search terms selected were meant to include both seminal and contemporary contributions. Search terms included lithium-based functional materials, optical properties of lithium niobate, electronic properties of $LiNbO_3$, Heusler alloys, half-Heusler

thermoelectric, quaternary Heusler semiconductors, 18-electron rule, optical properties of Heusler compounds, DFT calculations of Heusler alloys, Boltzmann transport phenomena in thermoelectric, phonon thermal conductivity and multifunctional energy materials.

The reviewed literature included peer-reviewed journal articles, reputable reviews, recognized methodological texts, and respected academic books. Seminal works were retained, where necessary, to establish fundamental structural, optical, thermoelectric or computational principles. Recent publications have brought increased attention to modern half-Heusler engineering, high-throughput material exploration, interfaces, hierarchical microstructures and computational evaluation.

We included studies that involved any of the following features: lithium functional compounds, Heusler, half-Heusler, or quaternary Heusler structures, electronic band features, optical features, electrical conductivity, thermoelectric performance, lattice dynamics, structural or thermodynamic stability, first-principles calculations, high-throughput materials screening, and structure-property relationships. The primary sources excluded publications with methodological ambiguity, redundant reports, general discussions, and research outside the optical-electronic-thermal sphere.

The data were classified on the basis of crystal structure, chemical composition, electronic band structure, density of states, optical dielectric response, carrier dynamics, Seebeck coefficient, electrical conductivity, thermal conductivity, power factor, figure of merit, phonon stability and empirical validation for thematic analysis. The goal was not only to present the reported values, but also to try to find correlations between structure, electronic states, charge transport and thermal transport.

The quality of the theoretical studies was evaluated according to the computational methods, the evaluation of the structural stability, the accuracy of the electronic structure, the inclusion of phonon effects and the explanation of the transport assumptions. We treated with caution studies that relied on formation energy relative to the elements alone to infer stability, that reported electrical conductivity without addressing the carrier relaxation time, or that reported the thermoelectric figure of merit without properly accounting for lattice thermal conductivity.

Experimental analyses were evaluated for their ability to determine phase identity, composition, microstructure and transport response. This is particularly important to complex ordered intermetallic systems where experimental disorder, secondary phases, vacancies and non-stoichiometry can lead to large deviations from the properties of ideal periodic crystals. Thus, the proposed method provides a systematic way to study the transition from traditional lithium-based optical materials to new multifunctional Heusler-type semiconductors, while accounting for constraints that may affect the reliability of theoretical predictions. Because this is a narrative critical review rather than a systematic review, no review protocol was registered and the selection is not reported as a PRISMA-style flow diagram. For transparency, the evidence base is stated explicitly: it comprises the 21 sources in the reference list, published between 1985 and 2025. Six concern lithium niobate (crystal structure, growth, defects, surfaces, thin films and band gap); four concern half-Heusler thermoelectrics; two concern Heusler and quaternary Heusler structure and design rules; and nine are methodological sources on thermoelectric theory, high-throughput databases, band-gap methods, and electronic and phonon transport codes. The appraisal criteria described above are applied to individual studies in Sections 4 and 5 and are summarized as a reliability hierarchy at the end of Section 5.

CONCEPTUAL AND THEORETICAL BACKGROUND

Multifunctional materials are designed to show a variety of technologically useful responses in a single structural and electronic framework. The analysis mainly concerns optical properties, electronic charge mobility and thermoelectric energy conversion. These characteristics are often studied separately, but they are closely interlinked by the electronic configuration and lattice behavior of a substance.

The optical response of a semiconductor is essentially due to electronic transitions between filled and empty states. Electrical conduction involves charge-carrier allocation, effective mass, mobility and scattering,

thermoelectric properties are determined by charge-carrier transport, and thermal conduction by electrons and phonons. Thus, the common physical origin for optical, electrical and thermoelectric performance is the band structure and lattice dynamics.

Lithium niobate is a convenient reference system. It has a rhombohedral crystal structure, is non-centrosymmetric and exhibits spontaneous polarization below its Curie temperature, resulting in outstanding ferroelectric and piezoelectric properties. Its electro-optic and nonlinear optical properties make it an important material for integrated optics and photonic technologies (Chen et al., 2021; Weis & Gaylord, 1985). The efficiency is greatly affected by the lithium deficiency (Li/Nb ratio), antisite defects, vacancies, doping, growth parameters, and domain structure (Chen et al., 2021).

Heusler compounds offer a complementary design framework for materials. Usually, the formula of full-Heusler compounds is X_2YZ , and the formula of half-Heusler materials is XYZ . The cubic half-Heusler C_1b structure is usually attributed to the space group F-43m. The electronic properties of these materials are strongly dependent on the number of valence electrons and their chemical composition, so that compounds within the same structural family can be metallic, semiconducting, magnetic or half-metallic (Graf et al., 2011).

This idea is generalized to quaternary Heusler systems by the inclusion of four different atomic species, usually denoted as XX′YZ. The site occupancy is of great importance in these materials, since various atomic arrangements can lead to different total energies, band structures and stability. The possible atomic configurations have to be examined before interpreting the optical or transport properties.

The 18-electron rule is a useful criterion for searching semiconducting Heusler compounds. In many half-Heusler and quaternary systems an aggregate valence-electron count of 18 results in occupied bonding states and unoccupied anti-bonding states . This guideline cannot substitute for direct electronic-structure calculations, but it is useful for first estimates. Applying this principle, a high-throughput study was performed by He et al. (2018) and a vast number of semiconducting quaternary Heusler compounds were found, demonstrating the power of electron-count rules along with first-principles calculations.

$$\varepsilon(\omega) = \varepsilon_1(\omega) + i\varepsilon_2(\omega)$$

Optical behaviour is commonly analyzed through the frequency-dependent complex dielectric function shown above, where ε_1 describes the dispersive response of the material and ε_2 is associated with absorption arising from electronic transitions. The dielectric function can be used to calculate the refractive index, extinction coefficient, absorption coefficient, reflectivity, optical conductivity, and energy-loss spectrum. Because these quantities depend on transitions between occupied and unoccupied electronic states, optical calculations provide information complementary to the conventional band structure.

$$ZT = S^2\sigma T / (\kappa_e + \kappa_l)$$

Thermoelectric transport is a separate, but intimately related electronic problem. Here, S is the Seebeck coefficient, σ is the electrical conductivity, T is the absolute temperature, κe is the electronic thermal conductivity and κl is the lattice thermal conductivity. Electronic contribution to performance can be described using power factor, $PF = S^2\sigma$ (Goldsmid, 2016; Rowe, 2006; Zebarjadi et al., 2012).

These relations reveal the fundamental thermoelectric dilemma. A large Seebeck coefficient is beneficial in electronic configurations which show large variations with energy near the Fermi level. High electrical conductivity requires the presence of mobile charge carriers. The higher the carrier concentration, the higher the conductivity and the lower the magnitude of the Seebeck coefficient. At the same time, the charge carriers carry heat, thereby linking the electrical conductivity and the electronic thermal conductivity. Reduction of lattice thermal conductivity is often the most favorable approach to increase ZT, as long as the phonon scattering mechanisms employed do not adversely affect electronic mobility.

Density Functional Theory is the basic computational link between the crystal chemistry and these physical properties. First-principles calculations can predict equilibrium geometries, relative structural energies, electronic bands, density of states, charge distributions, optical responses, elastic properties and phonon dynamics before experimental synthesis. The high-throughput materials platforms have extended the applicability of this approach to a broad range of material domains, enabling computational discovery instead of post-experimental evaluation (Jain et al., 2013). The electronic DFT results can be combined with semiclassical Boltzmann transport theory. BoltzTraP (Madsen and Singh, 2006) is a code that determines parameters such as the Seebeck coefficient, the electrical conductivity as a function of relaxation time, and the electronic thermal conductivity from an interpolated electronic band structure.

Representative lithium-containing quaternary compositions and the chemical bridge. The scientific connection between $LiNbO_3$ and lithium-containing quaternary Heuslers is a materials-design comparison, not an assertion that the two share a crystal structure or an experimentally established performance profile. $LiNbO_3$ is a polar oxide with Nb–O bonding and robust electro-optic functionality; ordered quaternary Heuslers instead rely on site-specific intermetallic orbital hybridization, electron count, and compositional control to tune semiconductor bands and transport. LiNbRhGa is a composition of interest for future screening, not a material for which this review establishes measured optical, electrical, or thermoelectric figures. Its nominal valence-electron count is 1 (Li) + 5 (Nb) + 9 (Rh) + 3 (Ga) = 18, consistent with an electron-count screening heuristic; this does not prove a band gap, a preferred atomic ordering, phase stability, or thermoelectric performance. Each distinct Li/Nb/Rh/Ga site arrangement must be relaxed and compared in energy, followed by formation and convex-hull assessment, electronic-band and optical calculations, phonon stability, and transport calculations. Claims of actual functionality must await direct calculations and measurements.

Thematic Analysis

The evolution of lithium-based functional materials indicates a shift from specialized oxide systems to more versatile intermetallic semiconductor structures. Lithium niobate is still an important standard because it has several strong physical responses in one crystal. Its non-centrosymmetric structure, intrinsic polarization, dielectric response and the coupling between electronic states and lattice distortion, make it promising for important optical and electro-optic applications. The development of thin-film lithium niobate has further broadened its importance for integrated photonics (Chen et al., 2021).

At the same time, the limitations of oxide multi-functionality are demonstrated in $LiNbO_3$. Imperfections, stoichiometric ratios, temperature variations and polaronic activity strongly influence the electrical conductivity. Lacerda et al. (2021) have shown that the electronic properties of different crystallographic surfaces can be significantly different, for example regarding the band gap or semiconductor type. Empirical studies have also linked the photorefractive behavior to polaron mechanisms related to defects (Kostritskii et al., 2007). These results suggest that the components that lead to the better optical performance may not necessarily improve the electrical conductivity.

Processing parameters add yet another level of complexity. It is reported by Fakhri et al. (2016) that the preparation conditions influence the crystallinity, grain structure and surface morphology of $LiNbO_3$ films. This is important because experimentally prepared materials can be significantly different from the idealized structures used in theoretical calculations due to imperfections, grain boundaries, and secondary phases.

The shift to Heusler chemistry means a more flexible way to design materials. In Heusler alloys the electronic structure can be changed directly by elemental substitution. Many half-Heusler alloys with 18 valence electrons have semiconducting properties and good thermoelectric properties. Cubic configurations are favorable for efficient electronic conduction, while variations in atomic mass and bonding offer avenues for phonon scattering (Graf et al., 2011; Quinn & Bos, 2021).

The improvement of thermoelectric performance in half-Heuslers is mainly realized by carrier optimization, band engineering and thermal transport regulation. Substitutional doping can tune the carrier density and move the Fermi level to a region where conductivity and thermopower are better matched. Band convergence can

increase the density-of-states effective mass while preserving reasonable carrier mobility. These approaches do not optimize a single transport parameter but aim to improve the overall power factor (Li et al., 2024).

It is also equally important to lower the lattice thermal conductivity. The incorporation of scattering centers at various length scales is pursued by researchers due to efficient phonon transport in well-structured half-Heusler configurations. High frequency phonons are influenced by atomic disorder, intermediate wavelengths are broken by nanoscale precipitates, and long-wavelength transport is hindered by grain boundaries. Today's research shows these approaches to be effective. Zhang et al. (2024) achieved enhanced balance of electronic and phonon transport in ZrNiSn-based systems by phase-interface engineering. Ai et al. (2025) lowered lattice thermal conductivity by hierarchical microstructures.

Quaternary Heusler semiconductors take these ideas further by providing four different atomic species on systematically ordered lattice sites. This offers more freedom to tune the electronegativity, the orbital hybridization, the lattice parameters, the band dispersion, and the phonon properties. But the arrangement of the sites is a key issue, since different atomic arrangements can result in different energies, band structures and stabilities. The energetically preferred atomic arrangement should therefore be established before optical or transport properties are evaluated.

He et al. (2018) provided a crucial basis for this field via high-throughput first-principles assessment. In their study, they identified 99 lithium-containing semiconducting quaternary Heusler candidates of the LiMgSnPd type, and showed that some members have beneficial optical absorption properties. Thus, quaternary Heuslers are not only of interest for thermoelectric and magnetic applications, but also for multifunctional optoelectronic devices.

This is important since electronic structure controls both optical and thermoelectric properties. An efficient thermoelectric semiconductor requires favorable energy dependent conductivity near the Fermi level, while optical absorption depends on suitable occupied and unoccupied states with allowed transitions. These properties are to be considered as a whole, not as individual results. Optical properties are rather understudied in Heusler thermoelectric studies. Although the band gap alone does not reflect the intensity of optical transitions, many theoretical studies only give the band structures and the density of states. A complete optical characterization should contain the dielectric function, the absorption coefficient, the reflectivity, the refractive index, the extinction coefficient and the optical conductivity.

Electronic transport is a kind of trade-off. Highly dispersive bands result in a smaller effective mass and higher mobility, while less dispersive bands can increase the density of states and thermoelectric power. Therefore, the efficient thermoelectric performance depends on the compromise between the carrier mobility and the increase of the density-of states. This equilibrium is evaluated extensively using Boltzmann transport calculations. The Seebeck coefficient is determined as a function of temperature and chemical potential, while σ/τ and $\kappa e/\tau$ are likewise obtained as functions of temperature and chemical potential.

Because Boltzmann transport codes yield σ/τ and $\kappa e/\tau$, absolute conductivities are frequently reported for an assumed constant relaxation time that is not always stated or justified (Madsen & Singh, 2006). However, to compare these values directly to experimental results a reliable relaxation time is needed since scattering depends on temperature, carrier density, phonons, impurities, defects and microstructure. The same constraint affects the evaluation of ZT, because the total thermal conductivity is a sum of the electronic part and the lattice thermal conductivity. If the lattice term is not properly accounted for, thermoelectric performance can be overestimated. This requires phonon calculations to check dynamical stability, and to evaluate lattice thermal conductivity in terms of phonon velocities, lifetimes and scattering.

Thermodynamic stability should be treated with care. A negative formation energy does not guarantee stability of a compound in relation to alternative phases. A more stringent evaluation is provided by the convex-hull

analysis, and screening with this approach is now possible with resources such as the Materials Project (Jain et al., 2013).

Ultimately, experimental validation is decisive. Ideal theoretical models do not necessarily include vacancies, antisite disorder, secondary phases, grain boundaries and composition differences found in real samples. Thus, reliable validation requires X-ray diffraction and Rietveld refinement together with microscopy, compositional analysis, optical spectroscopy, electrical transport, Hall measurements, Seebeck coefficient and thermal conductivity. The literature shows progression from naturally multifunctional materials to purposefully designed multifunctional materials. Typical examples of the first type are lithium-containing oxides. Modern Heusler and quaternary semiconductor systems are becoming increasingly typical of the latter.

Quantitative literature benchmarks and their limits. Reported lithium-niobate band gaps vary with crystal stoichiometry and measurement/analysis method: an experimental thin-film study summarizes approximate indirect single-crystal gaps of 3.7 eV for congruent $LiNbO_3$ and 3.9 eV for near-stoichiometric $LiNbO_3$ (Pellegrino et al., 2023). These values describe optical/electronic gap estimates, not thermoelectric performance. For the distinct half-Heusler family, Quinn and Bos (2021) report that experimentally optimized compositions can attain $zT > 1$ near 773 K, and discuss a $Ti_{0.5}Zr_{0.25}Hf_{0.25}NiSn$ composition with a densification aid for which lattice thermal conductivity of approximately 1.8 W m^{-1} K^{-1} at 300 K and zT approximately 1.5 at 823 K were reported. These are composition- and temperature-specific literature values, not generic properties of all Heuslers. The same review notes that XNiSn (X = Ti, Zr, Hf) electronic gaps differ by method, with a calculated value near 0.5 eV and optical/transport-derived values near 0.15 eV. Thus comparing gap, conductivity, Seebeck coefficient, thermal conductivity and zT across families requires aligned measurement conditions, doping levels, temperature, and clearly identified theoretical versus experimental provenance. No verified numerical S, σ, κ_l, or zT dataset for LiNbRhGa is established by the references in this review; entries for that candidate must remain unreported rather than extrapolated.

DISCUSSION AND SYNTHESIS

Lithium-based oxides, half-Heusler alloys and quaternary Heusler semiconductors are versatile members of the spectrum of multifunctional materials. Lithium-based oxides have been highly developed for optical and electro-optic applications. $LiNbO_3$ combines dielectric, ferroelectric, piezoelectric, optical and acoustic properties. However, its electrical conductivity is quite low and strongly influenced by defects and polaronic effects (Chen et al., 2021; Kostritskii et al., 2007; Lacerda et al., 2021).

Half-Heusler compounds behave differently. Optical properties are less studied while electronic and thermoelectric properties have been studied in great detail. The scope of the investigations has evolved from simple composition assessment to complex regulation of carrier density, imperfections, interfaces, microstructure and phonon conduction (Li et al., 2024; Quinn & Bos, 2021).

Quaternary Heusler semiconductors might provide a link between these two areas. Their improved compositional flexibility allows tuning of both band gaps and carrier properties in an ordered semiconductor structure. High-throughput predictions suggest that this family of materials may have favorable dielectric, optical and thermoelectric properties (He et al., 2018), but experimental confirmation is still scarce.

One major conclusion to be drawn from the literature is that optical and electronic functionality is determined by electronic structure. The same valence and conduction states that determine the effective mass, Seebeck coefficient and conductivity also determine absorption. It indicates that there's a need for a cohesive evaluation of optics and transport. A second conclusion concerns thermal conduction. Lattice thermal conductivity cannot be explained by atomic mass alone. Bond strength, phonon velocity, anharmonicity, defects and microstructure are equally important. Hence, it is insufficient to argue for low thermal conductivity based on mass difference alone. The theoretical predictions depend strongly on the method used. Semilocal DFT is good for structural evaluation but may underestimate semiconductor band gaps. The effect on optical absorption and high temperature transport may need more precise techniques such as hybrid functionals or modified exchange potentials for viable candidates (Heyd et al., 2003; Tran & Blaha, 2009).

Thermoelectric calculations add to the ambiguity. The constant-relaxation-time approximation is a useful benchmark but does not provide an accurate description of real carrier scattering. Similarly, electronic thermal conductivity is responsible only for a portion of the total thermal conductivity. Large theoretical ZT values obtained without explicit calculation of lattice thermal conductivity should therefore be treated with caution.

Another important limitation is the difference between what is calculated theoretically and what is actually found in the substances. Experimental Heusler alloys may include vacancies, antisite defects, disorder, grain boundaries, and secondary phases. These may improve the thermoelectric performance by phonon scattering, or may degrade the performance by carrier localization.

The main gap in the research is the lack of comprehensive studies on optical, electrical and thermal transport together. A second shortcoming lies in the lack of experimental verification of the expected quaternary semiconductors. Shortcomings are poor treatment of lattice thermal conductivity, poor attention to realistic defects and weak theory-experiment correlation. Future studies should explore the possibility of achieving good optical absorption, reasonable carrier mobility, strong thermoelectric power factor, and tunable thermal conductivity in a single material system with the same electronic configuration. Table 1 summarizes this comparison across the material classes considered.

Table 1. Comparative synthesis of the principal material classes considered in this review

Material class	Optical functionality	Electrical transport	Thermoelectric potential	Principal limitation
Lithium-based functional oxides	High; mature electro-optic applications	Defect- and stoichiometry-sensitive	Generally limited for direct TE conversion	Wide gap and restricted carrier transport
Half-Heusler semiconductors	Less extensively explored	Strongly tunable	Well established and high	Lattice thermal conductivity and coupled transport
Quaternary Heusler semiconductors	Promising but underexplored	Highly composition-dependent	Promising, mainly theoretical	Atomic ordering and limited validation
Lithium-containing quaternary systems	Emerging research area	Predicted tunability	Emerging	Predominantly computational evidence

Reliability hierarchy for multifunctional claims. (1) Electron counting and negative formation energy provide screening clues, not proof of synthesis feasibility; competing-phase convex-hull stability and phonon dispersion are required. (2) Semilocal DFT often underestimates semiconductor gaps; hybrid-functional or quasiparticle checks may be needed for optical onset. (3) BoltzTraP values σ/τ and κ_e/τ are relaxation-time-scaled quantities and must not be presented as absolute conductivities without a justified τ. (4) ZT requires the full thermal conductivity, including lattice contributions and any relevant bipolar component; omission can artificially inflate performance. (5) Vacancies, antisites, site disorder and secondary phases can alter both scattering and electronic bands. (6) Experimental XRD/Rietveld, microscopy/composition mapping, optical spectroscopy, resistivity/Hall, Seebeck and thermal measurements must ultimately test the predictions.

Future Research Directions

The next generation of multifunctional materials research should move beyond sequential calculations of isolated properties toward integrated design workflows. An effective computational strategy should begin with chemical and structural screening, followed by rigorous stability assessment, electronic-structure calculation, optical analysis, electronic transport, phonon transport, defect evaluation, and finally experimental validation.

The first priority should be improved assessment of structural stability. Negative formation energy relative to isolated elements should no longer be regarded as sufficient evidence for thermodynamic stability. Candidate compounds should be compared with relevant competing phases and evaluated using convex-hull methods. Where possible, finite-temperature effects should also be considered.

A second priority is improvement in band-gap accuracy. Semilocal functionals are useful for efficient screening, but systems identified as especially promising should be reevaluated using more accurate electronic-structure approaches. Hybrid functionals (Heyd et al., 2003), modified exchange potentials (Tran & Blaha, 2009), or quasiparticle methods can strengthen optical and high-temperature transport predictions when band-gap magnitude is critical.

A third important direction is the explicit calculation of lattice thermal conductivity. Phonon dispersion should first be used to test dynamical stability (Togo & Tanaka, 2015). Subsequent anharmonic calculations can provide phonon lifetimes, group velocities, scattering rates, and lattice thermal conductivity, for example by solving the phonon Boltzmann transport equation (Li et al., 2014). This would permit ZT to be calculated with substantially greater physical reliability.

Defect engineering should become a central component of future studies. Antisite defects, vacancies, substitutions, and off-stoichiometry can modify carrier concentration, introduce electronic states, and scatter phonons. Rather than treating these imperfections only as undesirable deviations from an ideal crystal, they should be investigated as possible design tools. Optical analysis should also be expanded. Theoretical semiconductor studies should routinely report not only band gaps but the complete frequency-dependent dielectric response, absorption coefficient, refractive index, reflectivity, extinction coefficient, and optical conductivity. Orbital-resolved analysis should be used to identify the microscopic origin of major absorption features.

Electronic transport modelling requires improvements beyond fixed relaxation times. Electron-phonon scattering calculations, deformation-potential theory, or experimentally calibrated relaxation times can provide more realistic conductivities and mobility estimates. Such improvements are especially important when comparing chemically different materials for which a common assumed relaxation time may not be physically justified.

High-throughput materials discovery should increasingly be combined with machine learning. The compositional space of quaternary materials is too large for exhaustive high-level first-principles analysis. Machine-learning models trained on validated structural, electronic, and thermoelectric data could help prioritize candidates for detailed calculations, while platforms such as the Materials Project provide standardized data useful for screening (Jain et al., 2013).

Experimental work must progress in parallel. Synthesis should be followed by rigorous phase analysis using X-ray diffraction and Rietveld refinement. Electron microscopy and compositional mapping can reveal secondary phases and microstructural heterogeneity. Optical characterization should include absorption or diffuse-reflectance spectroscopy where appropriate, while electronic measurements should include temperature-dependent resistivity, Hall measurements where feasible, and Seebeck coefficient. Thermal conductivity should be measured over the same temperature range used for electrical transport so that experimental ZT can be determined consistently.

Such an integrated framework would transform multifunctional materials discovery from a collection of independent calculations into a coordinated design process.

Integrated computational–experimental workflow (Figure 1). Candidate chemistry and 18-electron screening → enumerate atomic orderings → relax structures and compare total energies → competing-phase convex-hull assessment → elastic/phonon stability → electronic bands and density of states (with gap-method checks) → dielectric/absorption response → temperature- and doping-dependent electronic transport with justified scattering assumptions → anharmonic phonon transport and κ_l → estimate ZT with all thermal terms → synthesize selected candidates → XRD/Rietveld and microstructural/compositional verification → optical,

electrical and thermal measurement → iterate model against measured disorder and scattering. Every stage is a decision gate; failure at stability or reproducibility should stop claims of application readiness.

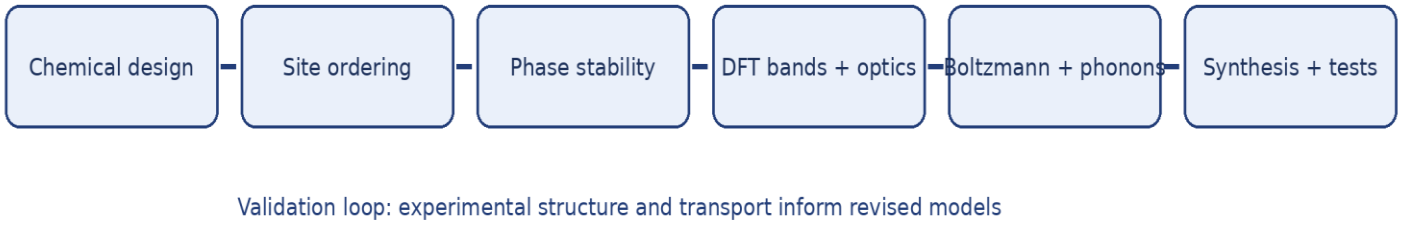

Figure 1. Proposed integrated computational–experimental research workflow

CONCLUSION

The literature reviewed in this work demonstrates a clear evolution in the design of lithium-containing and Heusler-type functional materials. Lithium-based oxides, particularly lithium niobate, have established the technological value of combining several physical responses within one crystal structure. Their strong ferroelectric, electro-optic, piezoelectric, and nonlinear-optical characteristics have enabled extensive photonic and acoustic applications. At the same time, their comparatively restricted and defect-sensitive electronic transport highlights the difficulty of extending conventional optical oxides toward efficient thermoelectric energy conversion.

Half-Heusler materials provide a complementary pathway. Their tunable electronic structures, thermal stability, and chemically adjustable lattices have supported significant progress in thermoelectric performance. Carrier optimization, band engineering, alloy scattering, nanostructuring, interfaces, and other phonon-control strategies demonstrate that transport properties can be deliberately engineered rather than regarded as fixed material constants (Li et al., 2024; Quinn & Bos, 2021; Zhang et al., 2024; Ai et al., 2025).

Quaternary Heusler semiconductors extend this flexibility further by introducing an additional chemically distinct atomic sublattice. High-throughput Density Functional Theory and electron-count-based design have established that semiconducting quaternary Heusler phases constitute a much broader materials family than previously recognized (He et al., 2018). Their predicted band gaps, dielectric properties, and transport characteristics make them particularly relevant to multifunctional materials research.

Despite these advances, the field remains fragmented. Optical studies, electrical-transport investigations, and thermoelectric analyses are frequently performed independently. Comprehensive studies correlating all three within the same lithium-containing ordered semiconductor framework remain limited. Experimental validation is even less developed, particularly for newly predicted quaternary phases.

The major opportunity for future research therefore lies in integrated multifunctional design. Structural stability, electronic bands, optical transitions, carrier transport, phonon dynamics, and defect chemistry should be investigated as interconnected aspects of the same material rather than as separate research problems. Advanced first-principles calculations, Boltzmann transport theory, anharmonic phonon modelling, high-throughput screening, machine-learning methods, and experimental validation should operate as complementary components of the same discovery process.

The long-term significance of lithium-containing quaternary semiconductor systems will ultimately depend not on whether individual calculations predict attractive optical or thermoelectric values, but on whether stable and reproducible materials can be produced in which optical activity, useful electronic transport, and controlled thermal conduction coexist. Establishing this correlation represents a promising research direction for future optoelectronic, sensing, and energy-conversion technologies.

Evidence-qualified conclusion. Established experimental evidence supports the optical/electro-optic utility of $LiNbO_3$ and thermoelectric improvements in several optimized half-Heusler families. High-throughput computational literature supports a broader pool of semiconducting quaternary Heusler candidates. However, no experimentally verified multifunctional performance is demonstrated here for LiNbRhGa or for lithium-containing quaternary Heuslers as a class. Their proposed optical–electrical–thermoelectric integration is therefore a testable research opportunity, not a demonstrated technological result.

Literature benchmarks and their limits. He et al. (2018) identified 99 lithium-containing semiconducting quaternary Heusler candidates with predicted band gaps of 0.3–2.5 eV; their work explicitly describes the LiMgSnPd structural prototype (space group F-43m, no. 216). These are computational predictions across a candidate family, not measured band gaps for LiNbRhGa. Quinn and Bos (2021) report that optimized half-Heusler materials can achieve $zT > 1$ at 773 K; this experimentally grounded family-level benchmark must not be transferred to an untested lithium-containing quaternary composition. Numerical values of σ, S, κ_l, and ZT for LiNbRhGa are not asserted here because a validated, composition-specific source has not been established. Cross-family comparisons therefore distinguish measured half-Heusler performance from screened quaternary candidates (He et al., 2018; Quinn & Bos, 2021).

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