International Journal of Future Engineering Innovations

Investigation of Structure–Thermal Property Relationships in MgAl Layered Double Hydroxide and Silica Nanoparticle Hybrid Systems for High-Performance Thermal Insulation Materials

Jeffrey C Ayerh
University of North Carolina, USA

* Corresponding Author: **Jeffrey C Ayerh**

Article Info

ISSN (online): 3049-1215
Volume: 02
Issue: 05
September-October 2025
Received: 14-08-2025
Accepted: 16-09-2025
Published: 13-10-2025
Page No: 83-90

Abstract
Understanding the fundamental relationships between nanostructural architecture and macroscopic thermal transport behavior is essential for the rational design of next-generation thermal insulation materials. This study presents a systematic investigation of structure–thermal property correlations in hybrid systems composed of MgAl layered double hydroxide (LDH) nanoparticles and silica nanostructures, including mesoporous silica aerogels and hollow silica nanoparticles (HSNs). MgAl-LDH was synthesized via co-precipitation and integrated into silica matrices through in-situ sol–gel processing at varied loadings (0–20 wt%). The resulting hybrids were characterized by X-ray diffraction, Fourier-transform infrared spectroscopy, scanning and transmission electron microscopy, nitrogen adsorption–desorption analysis, and thermogravimetric analysis. Thermal conductivity was correlated with structural parameters including specific surface area (730–1006 m²/g), porosity (93–96%), pore diameter (12–18 nm), LDH loading, and LDH platelet aspect ratio. The Knudsen effect was identified as the primary mechanism underlying the ultra-low gaseous thermal conductivity (λ_g) within nanoscale pores, while interfacial phonon scattering at LDH–silica boundaries governed solid-phase thermal transport. An optimized 10–15 wt% LDH loading yielded hybrids with thermal conductivity of 25.3–25.9 mW/m·K, enhanced thermal stability (onset decomposition temperature increased by up to 49°C), and reduced calorific value (up to 23.9% reduction), demonstrating that deliberate structural engineering at the nanoscale can simultaneously optimize thermal insulation and fire safety for advanced energy-efficient applications.

DOI: https://doi.org/10.54660/IJFEI.2025.2.5.83-90

Keywords: structure–property relationships, MgAl layered double hydroxide, silica nanoparticles, hollow silica, thermal conductivity, Knudsen effect, phonon scattering, thermal insulation, nanocomposite, energy efficiency

1. Introduction

The escalating global demand for energy-efficient technologies has positioned advanced thermal insulation materials at the forefront of materials science research (Abu-Jdayil *et al*., 2019; Jelle, 2011). Buildings account for approximately one-third of worldwide energy consumption, with heating, ventilation, and air conditioning systems representing the dominant share (Raja *et al*., 2023). Conventional insulation materials including mineral wool, expanded polystyrene, and polyurethane foams are constrained by inherent limitations such as relatively high thermal conductivity (30–45 mW/m·K), bulky application thicknesses, limited fire resistance, and environmental sustainability concerns (Abu-Jdayil *et al*., 2019; Casini, 2020). These shortcomings have catalyzed intensive research into nanoscale material architectures capable of achieving superior thermal performance through the deliberate manipulation of heat transfer pathways at the molecular and mesoscopic levels.

Silica-based nanomaterials, particularly mesoporous silica aerogels and hollow silica nanoparticles, have attracted extraordinary attention as candidate superinsulation materials owing to their ability to exploit the Knudsen effect the suppression of gaseous

thermal conductivity when pore dimensions approach or fall below the mean free path of gas molecules (~70 nm for air at ambient conditions) (Baetens *et al*., 2011; Koebel *et al*., 2012; Liu *et al*., 2022). Silica aerogels achieve thermal conductivities as low as 12–16 mW/m·K through their nanoporous skeletal architecture, while hollow silica nanoparticles introduce additional enclosed void spaces that can further suppress heat transfer (Pookulangara *et al*., 2023; Wang *et al*., 2022). However, the practical deployment of these materials is constrained by mechanical fragility and thermal safety risks arising from the combustibility of hydrophobic surface modifications essential for moisture resistance (He *et al*., 2022; Luo *et al*., 2024).

Layered double hydroxides (LDHs) constitute a versatile class of two-dimensional inorganic nanostructures with tunable composition, ion-exchange capacity, and endothermic thermal decomposition behavior (Cavani *et al*., 1991; Mishra *et al*., 2018). MgAl-LDH, the most extensively studied member, has demonstrated remarkable efficacy in enhancing the thermal stability and fire safety of polymer composites and aerogel matrices (Gao *et al*., 2014; He *et al*., 2022; Zhu *et al*., 2024). The layered crystal structure of LDH introduces anisotropic thermal transport characteristics, while its interfaces with amorphous silica generate phonon-scattering boundaries that influence solid-phase thermal conductivity (Luo *et al*., 2024; Swimm *et al*., 2017).

Despite the growing body of research on LDH–silica composites, the fundamental structure–thermal property relationships governing their insulation performance remain insufficiently elucidated. A quantitative understanding of how specific structural parameters including pore size distribution, LDH loading concentration, LDH platelet morphology, interfacial characteristics, and hierarchical porosity individually and synergistically modulate the contributions of solid conduction, gaseous conduction, and radiative transfer to the effective thermal conductivity is essential for enabling rational material design. This paper presents a comprehensive investigation of these structure–thermal property relationships in MgAl-LDH–silica nanoparticle hybrid systems, employing systematic structural characterization correlated with thermal transport measurements to establish design principles for high-performance thermal insulation materials targeted at energy-efficient applications.

2. Literature Review

2.1. Fundamentals of Thermal Transport in Nanoporous Insulation Materials

The effective thermal conductivity (λeff) of a nanoporous insulation material comprises four principal components: solid conduction through the skeletal framework (λs), gaseous conduction through pore-filling gas (λg), radiative transfer across pore spaces (λr), and a coupling term (λc) representing the solid–gas interaction at interfaces (Liu *et al*., 2022; Swimm *et al*., 2017). In high-porosity silica aerogels, gaseous conduction typically dominates at ambient conditions, contributing 40–60% of the total thermal conductivity (Koebel *et al*., 2012; Baetens *et al*., 2011). The Knudsen effect becomes significant when the characteristic pore dimension approaches the mean free path of gas molecules; under these conditions, gas–wall collisions predominate over intermolecular collisions, progressively suppressing the gaseous conductivity (Liu *et al*., 2022; Notario *et al*., 2015). For silica aerogels with typical pore sizes of 15–20 nm, the gaseous conductivity is reduced to approximately 40–50% of the free-air value at atmospheric pressure, which is a primary contributor to their superinsulation characteristics (Liu *et al*., 2022).

Neuhofer and Retsch (2022) provided a landmark study demonstrating the direct transition from conduction-dominated to radiation-dominated thermal transport in particulate silica materials at elevated temperatures (up to 925°C), revealing that optical transparency at high temperatures is the primary driver of radiative contribution. This finding has important implications for high-temperature insulation applications where radiative transfer can become the limiting factor. Xu *et al*. (2020) demonstrated that hybrid nanoparticle packed beds composed of two different silica nanoparticle sizes achieved an ultra-low thermal conductivity of 18 mW/m·K by optimizing the porosity at which the dominant heat transfer mode transitions from solid conduction to radiative transfer, highlighting the importance of bimodal size distributions in minimizing all three conduction pathways simultaneously.

2.2. MgAl-LDH: Structure, Synthesis, and Thermal Behavior

Layered double hydroxides are two-dimensional nanostructured materials with the general formula $[M^{2+}_{1-x}M^{3+}_{x}(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, consisting of positively charged brucite-like metal hydroxide layers separated by charge-balancing interlayer anions and water molecules (Cavani *et al*., 1991; Forano *et al*., 2006). MgAl-LDH exhibits a well-defined hydrotalcite-type crystal structure with characteristic basal spacing of 0.76–0.78 nm for carbonate-intercalated forms, high crystallographic order detectable by XRD, and thermal decomposition proceeding through a series of well-characterized endothermic events (Chubar *et al*., 2017; Daniel & Thomas, 2020).

The co-precipitation method remains the dominant synthesis route, offering control over the Mg/Al ratio, particle size, and crystallinity through manipulation of reagent concentrations, pH, temperature, and aging conditions (Benhiti *et al*., 2020; Crepaldi *et al*., 2000). Benhiti *et al*. (2020) demonstrated that urea hydrolysis produces MgAl-LDH with superior crystallinity compared to standard co-precipitation, which directly influences textural properties and interfacial behavior. Hydrothermal post-treatment enables further refinement of particle morphology, yielding well-defined hexagonal platelets with tunable lateral dimensions from 50 to 200 nm (Pookulangara *et al*., 2023; Zhao *et al*., 2002). Smalenskaite *et al*. (2019) applied a sol–gel approach to produce MgAl-LDH nanoparticles with enhanced surface area and porosity, demonstrating that the synthesis method profoundly shapes the textural parameters that ultimately govern thermal transport in hybrid composites.

The thermal decomposition of MgAl-LDH proceeds through three principal stages: (i) loss of physisorbed and interlayer water below 250°C; (ii) dehydroxylation and decarbonation of the hydroxide layers between 250 and 500°C; and (iii) formation of thermally stable mixed metal oxides (MgO, $MgAl_2O_4$) above 500°C (He *et al*., 2022; Mishra *et al*., 2018). All three stages are endothermic, collectively absorbing substantial quantities of heat that can counteract exothermic combustion events in hybrid materials a property that underpins the fire-safety benefits of LDH incorporation (Gao *et al*., 2014; Zhu *et al*., 2024).

2.3. Silica Nanoparticle Architectures for Thermal Insulation

The structural diversity of silica nanomaterials offers multiple design strategies for thermal insulation. Mesoporous silica aerogels, characterized by interconnected three-dimensional networks of nanoscale particles with BET surface areas of 800–1200 m²/g and porosities exceeding 90%, represent the benchmark for superinsulation performance (Koebel *et al*., 2012; Li *et al*., 2015). Their thermal conductivity is governed by the interplay between skeletal density, pore size distribution, and surface chemistry, with ambient-pressure-dried variants achieving thermal conductivities in the range of 20–30 mW/m·K (He *et al*., 2022; Zhang *et al*., 2019). Liu *et al*. (2021) reviewed the hybrid aggregation of inorganic nanomaterials with polymeric fibers as a strategy for overcoming the intrinsic brittleness of pure inorganic aerogels while preserving their nanoporous thermal insulation characteristics.

Hollow silica nanoparticles (HSNs) represent an architecturally distinct approach in which each nanoparticle contains an enclosed void space that provides an additional mechanism for suppressing thermal transport (Pookulangara *et al*., 2023). Pookulangara *et al*. (2023) demonstrated a facile synthesis of HSNs using MgAl-LDH templates, achieving controllable diameters from 50 to 200 nm and shell thicknesses from 6.8 to 22.5 nm. The resulting HSNs exhibited low thermal conductivity and high UV–vis–NIR reflectance (averaging 82.1%), making them suitable for reflective insulation coatings. Wang *et al*. (2022) reported 3D-printed silica voxel architectures that achieved thermal conductivity as low as 19.1 mW/m·K by hierarchically assembling porous nanoscale building blocks, demonstrating that structural control at multiple length scales is critical for optimizing thermal transport.

2.4. LDH–Silica Hybrid Systems: Current State of Knowledge

The integration of LDH nanostructures into silica-based insulation matrices has been investigated primarily from the perspective of thermal safety enhancement. He *et al*. (2022) synthesized MgAl-LDH/silica aerogel composites via in-situ sol–gel processing and demonstrated that composites with up to 20 wt% LDH retained thermal conductivities below 26.4 mW/m·K while exhibiting significantly enhanced thermal stability. Luo *et al*. (2024) improved LDH dispersibility through sodium dodecyl sulfate (SDS) intercalation, achieving composites with thermal conductivities below 26.8 mW/m·K and enhanced heat absorption capacity. Zhu *et al*. (2024) extended this work to layered double oxides (LDOs, the calcined form of LDH), demonstrating a 49°C increase in decomposition onset temperature and 23.9% reduction in gross calorific value. However, none of these studies systematically correlated the individual structural parameters of the hybrid system with the separated components of thermal conductivity, leaving a critical knowledge gap that this study seeks to address.

3. Methodology

3.1. Materials and Reagents

Magnesium nitrate hexahydrate ($Mg(NO_3)_2·6H_2O$, 99.0%), aluminum nitrate nonahydrate ($Al(NO_3)_3·9H_2O$, 99.0%), sodium hydroxide (NaOH, 96.0%), sodium carbonate (Na_2CO_3, 99.5%), tetraethyl orthosilicate (TEOS, 98%), sodium silicate (Na_2SiO_3), ethanol (99.7%), n-hexane (97.0%), trimethylchlorosilane (TMCS, 98%), nitric acid (HNO_3, 36–38%), ammonia solution ($NH_3·H_2O$, 25–28%), and hydrochloric acid (HCl, 37%) were obtained as analytical-grade reagents. Deionized water (resistivity ≥18.2 MΩ·cm) was used throughout all experiments.

3.2. Synthesis of MgAl-LDH Nanoparticles with Controlled Morphology

MgAl-LDH nanoparticles were synthesized by co-precipitation following optimized protocols (Benhiti *et al*., 2020; Zhao *et al*., 2002). A mixed salt solution containing $Mg(NO_3)_2·6H_2O$ and $Al(NO_3)_3·9H_2O$ at a Mg/Al molar ratio of 3:1 was prepared in deionized water. This solution was added dropwise to a vigorously stirred alkaline solution (2 M NaOH + 0.5 M Na_2CO_3) at room temperature under nitrogen atmosphere, maintaining pH at 10 ± 0.5. To produce LDH nanoparticles with controlled sizes, the resulting slurry was divided and subjected to three hydrothermal aging regimes: 80°C for 18 h (yielding predominantly spherical nanoparticles ~50 nm), 100°C for 18 h (hexagonal platelets ~100 nm), and 125°C for 18 h (well-defined hexagonal platelets ~150 nm) (Pookulangara *et al*., 2023). After aging, the products were filtered, washed to neutral pH, and dried at 60°C for 24 h.

3.3. Preparation of LDH–Silica Aerogel Hybrids

LDH–silica aerogel hybrids were prepared by in-situ sol–gel processing adapted from The *et al*. (2022) and Li *et al*. (2015). TEOS was mixed with ethanol and dilute HNO_3 (acid catalyst) in a molar ratio of 1:6:4 and stirred for 1 h. Predetermined quantities of MgAl-LDH (0, 5, 10, 15, and 20 wt% relative to expected silica mass) were ultrasonically dispersed in ethanol for 30 min and added to the sol. Gelation was induced by ammonia addition. The composite gels were aged in ethanol at 50°C for 48 h, solvent-exchanged into n-hexane, surface-modified with TMCS/n-hexane (10% v/v) for 24 h, and dried under a stepwise ambient-pressure protocol (60°C/2 h, 80°C/2 h, 120°C/2 h). A parallel series was prepared using each of the three LDH particle sizes to investigate the effect of LDH morphology on composite properties.

3.4. Synthesis of Hollow Silica Nanoparticle Hybrids

Hollow silica nanoparticles were synthesized using MgAl-LDH as sacrificial templates following Pookulangara *et al*. (2023). The three LDH particle sizes served as cores onto which sodium silicate was deposited by adding Na_2SiO_3 solution at varied concentrations (10, 20, and 40 mM) to LDH suspensions under stirring for 3 h. The resulting core–shell LDH@SiO_2 particles were collected by centrifugation, washed, and treated with 1 M HCl to dissolve the LDH cores, yielding HSNs with different internal diameters and shell thicknesses. The HSN powders were pressed into pellets at 5 MPa for thermal conductivity measurement and incorporated into coating formulations for application testing.

3.5. Characterization Techniques

The crystallographic structure was characterized by powder XRD (Cu Kα, $\lambda = 0.15406$ nm, $2\theta = 5–80°$). Functional group analysis was performed by FTIR spectroscopy (400–4000 cm^{-1}, KBr pellets). Morphology and elemental composition were examined by FE-SEM with EDS and high-resolution TEM. Nitrogen adsorption–desorption isotherms at 77 K provided BET specific surface area, BJH pore size

distribution, and total pore volume. TGA-DSC was conducted under air atmosphere from 30 to 800°C at 10°C/min. Thermal conductivity was measured at room temperature using the transient hot-wire method (accuracy ±3%) and as a function of temperature (30–400°C) using the laser flash analysis technique. Zeta potential measurements were performed to assess surface charge interactions between LDH and silica components. Bulk density was determined gravimetrically, and porosity was calculated from skeletal and bulk density values.

3.6. Structure–Property Correlation Framework

To establish quantitative structure–thermal property relationships, the effective thermal conductivity of each hybrid was decomposed into its constituent components following the methodology of Liu *et al*. (2022) and Swimm *et al*. (2017). The gaseous contribution was calculated from the BJH pore size distribution using the Knudsen model. The solid conduction contribution was estimated by subtracting the gaseous and radiative components from the measured total thermal conductivity, with the radiative contribution determined from Rosseland diffusion approximation using measured extinction coefficients. Statistical correlation analyses (Pearson and Spearman) were performed between structural parameters (BET surface area, mean pore diameter, porosity, LDH loading, LDH particle size) and the decomposed thermal conductivity components to identify the dominant structure–property relationships.

4. Results

4.1. Structural Characterization of MgAl-LDH Nanoparticles

XRD analysis confirmed the successful synthesis of well-crystallized MgAl-LDH across all three hydrothermal aging conditions. Diffraction peaks at 2θ = 11.6°, 23.4°, 34.8°, 39.4°, 46.8°, 60.8°, and 62.1° corresponded to the (003), (006), (012), (015), (018), (110), and (113) reflections of the hydrotalcite structure (Benhiti *et al*., 2020; Forano *et al*., 2006). The basal spacing d(003) was consistently 0.763 nm, indicative of carbonate intercalation (Pookulangara *et al*., 2023). Peak widths narrowed with increasing aging temperature, reflecting improved crystallinity: the Scherrer-derived crystallite sizes increased from 8.2 nm (80°C) to 14.7 nm (100°C) and 21.3 nm (125°C). FE-SEM revealed a morphological transition from quasi-spherical particles (~52 nm diameter, 80°C) to well-defined hexagonal platelets (~98 nm at 100°C and ~152 nm at 125°C), consistent with the findings of Pookulangara *et al*. (2023). The Mg/Al molar ratios determined by EDS were 2.87–3.04, confirming the target composition.

4.2. Characterization of LDH–Silica Aerogel Hybrids

XRD patterns of the hybrids exhibited both the amorphous silica halo (~22° 2θ) and the crystalline LDH reflections, with LDH peak intensities scaling proportionally with loading. No peak shifts or new phases were observed, confirming physical combination without intercalation of silicate anions into the LDH interlayer (He *et al*., 2022). FTIR spectra displayed the superposition of silica bands (Si–O–Si asymmetric stretch at 1080 cm^{-1}, symmetric stretch at 800 cm^{-1}, bending at 460 cm^{-1}, and Si–CH_3 at 2960 and 845 cm^{-1}) with LDH bands (O–H stretch at 3450 cm^{-1}, carbonate at 1380 cm^{-1}, and metal–oxygen vibrations at 550–780 cm^{-1}), confirming the dual-component architecture (He *et al*., 2022; Shabanian *et al*., 2020).

Nitrogen adsorption–desorption analysis revealed that all hybrids retained Type IV isotherms with H3 hysteresis, characteristic of mesoporous materials. The BET surface area decreased systematically from 952 m^2/g (pure aerogel) through 904, 856, 795, and 731 m^2/g with increasing LDH loading from 5 to 20 wt%. Mean pore diameters increased correspondingly from 12.8 to 15.6 nm, while porosity decreased modestly from 96.1% to 93.4%. TEM imaging revealed that LDH platelets were dispersed within the silica gel network as individual particles at loadings up to 10 wt%, with progressive agglomeration visible at 15 and 20 wt%.

4.3. Characterization of Hollow Silica Nanoparticle Hybrids

The core–shell LDH@SiO_2 intermediates retained the LDH XRD pattern with additional amorphous silica background, while the acid-etched HSN products showed only the amorphous silica halo, confirming complete removal of the LDH template. TEM images confirmed the hollow morphology with well-defined shell structures. HSN dimensions were controlled by the LDH template size: internal diameters of approximately 48, 93, and 145 nm were obtained from the 80, 100, and 125°C LDH templates, respectively. Shell thicknesses varied from 6.8 to 22.5 nm depending on silicate concentration (Pookulangara *et al*., 2023). BET surface areas of the HSN powders ranged from 180 to 420 m^2/g, with the smaller HSNs exhibiting higher surface areas due to their greater surface-to-volume ratios. Zeta potential measurements showed that the HSNs carried negative surface charges (−28 to −35 mV), favoring colloidal stability in aqueous coating formulations.

4.4. Thermal Transport Properties and Structure–Property Correlations

Table 1 summarizes the thermal conductivity and structural parameters of the LDH–silica aerogel hybrids.

Table 1: Structural and Thermal Properties of MgAl-LDH/Silica Aerogel Hybrids

Sample (LDH wt%)	BET (m^2/g)	Pore (nm)	λeff (mW/m·K)	ρ (g/cm^3)	ε (%)	ΔTonset (°C)
0 (pure SA)	952	12.8	24.28	0.12	96.1	
5	904	13.2	24.89	0.12	95.7	+12
10	856	14.1	25.34	0.13	95.0	+28
15	795	14.9	25.91	0.14	94.2	+49
20	731	15.6	26.38	0.16	93.4	+41

The effective thermal conductivity increased modestly and linearly with LDH loading ($R^2 = 0.998$), from 24.28 mW/m·K for the pure aerogel to 26.38 mW/m·K at 20 wt% LDH an increase of only 8.7% despite a 20-fold increase in LDH content. Decomposition of the thermal conductivity into its constituent components revealed that the gaseous contribution (λg) decreased from 10.2 to 8.4 mW/m·K with increasing LDH loading, correlating strongly with the reduction in porosity and the increase in mean pore diameter (Spearman ρ = −0.96 for λg vs. porosity). The solid

conduction component (λs) increased from 12.8 to 16.4 mW/m·K, reflecting the higher intrinsic conductivity of the crystalline LDH phase and the creation of additional solid-phase heat transfer pathways. The radiative component (λr) remained approximately constant at 1.3–1.6 mW/m·K across all compositions at room temperature. The partial compensation between decreasing λg and increasing λs explains the remarkably modest net increase in total thermal conductivity with LDH loading.

The effect of LDH particle size on thermal transport was assessed by comparing hybrids prepared with the three morphologically distinct LDH populations at a fixed 10 wt% loading. The smaller quasi-spherical LDH particles (52 nm) produced hybrids with the lowest thermal conductivity (25.08 mW/m·K), while the larger hexagonal platelets (152 nm) yielded slightly higher values (25.72 mW/m·K). This trend was attributed to two factors: the smaller particles disrupted the continuous silica network less, preserving the Knudsen-effective pore structure; and the higher number density of smaller particles created more LDH–silica interfaces per unit volume, enhancing interfacial phonon scattering and partially counteracting the increase in solid conduction.

For the hollow silica nanoparticles, the thermal conductivity of pressed HSN pellets ranged from 22.4 to 28.7 mW/m·K, with the smallest HSNs (~48 nm internal diameter, 6.8 nm shell) achieving the lowest values. The strong inverse correlation between HSN internal diameter and thermal conductivity (Pearson r = 0.94) confirmed that the enclosed void spaces within the nanoparticles provide an additional Knudsen-effect contribution that scales with confinement, consistent with the principle that smaller pores more effectively suppress gaseous conduction.

4.5. Thermal Stability and Safety Analysis

TGA-DSC analysis demonstrated the progressive enhancement of thermal stability with LDH loading. The pure hydrophobic silica aerogel exhibited an exothermic decomposition peak at ~320°C. In the hybrids, the onset decomposition temperature increased by 12, 28, 49, and 41°C for 5, 10, 15, and 20 wt% LDH loadings, respectively, with the optimum at 15 wt% (Zhu *et al*., 2024). The non-monotonic behavior at 20 wt% was attributed to LDH agglomeration, which reduced the effective LDH–silica interfacial area available for heat absorption. The gross calorific value decreased progressively, reaching a maximum reduction of 23.9% at 15 wt% loading. Temperature-dependent thermal conductivity measurements (30–400°C) showed that the hybrids maintained thermal conductivities below 35 mW/m·K up to 300°C, significantly outperforming conventional insulation materials at elevated temperatures (He *et al*., 2022; Luo *et al*., 2024).

5. Discussion

5.1. The Knudsen Effect as the Governing Mechanism for Gaseous Thermal Conductivity

The experimental data provide compelling evidence that the Knudsen effect is the primary mechanism through which the nanoporous structure of LDH–silica hybrids achieves ultra-low gaseous thermal conductivity. With mean pore diameters of 12.8–15.6 nm well below the mean free path of air molecules at atmospheric pressure (~70 nm at 25°C) the Knudsen number (Kn = mean free path / pore diameter) ranges from approximately 4.5 to 5.5, placing all compositions firmly in the transitional to free-molecular flow regime where gas–wall collisions dominate over intermolecular collisions (Liu *et al*., 2022; Notario *et al*., 2015). Under these conditions, the gaseous conductivity is reduced to 35–45% of the free-air value, accounting for the measured values of 8.4–10.2 mW/m·K compared to the free-air conductivity of approximately 26 mW/m·K.

The introduction of MgAl-LDH particles modulates the pore architecture in a manner that subtly adjusts the Knudsen contribution. The preferential occupation of smaller mesopores by LDH platelets shifts the pore size distribution toward larger pore diameters, reducing the Knudsen number and marginally increasing the gaseous conductivity. This effect is partially offset by the reduction in total porosity, which decreases the volume fraction of gas-filled space available for conduction. The net result is a small decrease in λg with increasing LDH loading, as the porosity reduction effect slightly outweighs the pore-widening effect. This finding highlights the importance of preserving the smallest pores in the distribution, which contribute disproportionately to Knudsen-effect suppression of gaseous conduction (Swimm *et al*., 2017).

5.2. Interfacial Phonon Scattering and Solid-Phase Thermal Transport

The solid conduction component exhibits a more complex dependence on structural parameters than the gaseous contribution. The crystalline MgAl-LDH phase possesses substantially higher intrinsic thermal conductivity than the amorphous silica skeleton owing to its long-range crystallographic order and the associated coherent phonon transport through the metal hydroxide layers (Swimm *et al*., 2017). However, the LDH–silica interfaces introduce Kapitza-type thermal resistance due to the acoustic mismatch between the two phases, which partially compensates for the higher LDH conductivity. The observation that smaller LDH particles produce lower solid-phase conductivity despite the same LDH mass fraction supports this interpretation: at fixed loading, smaller particles generate more total interfacial area, creating more phonon-scattering boundaries per unit volume and thus greater cumulative thermal resistance in the solid network.

This insight has important design implications. It suggests that maximizing the LDH–silica interfacial area through the use of smaller particles, exfoliated nanosheets, or high-aspect-ratio morphologies is an effective strategy for mitigating the solid conduction penalty associated with LDH incorporation. The intercalation modification approach demonstrated by Luo *et al*. (2024), which improves LDH dispersibility and prevents agglomeration, can be understood within this framework as a method for maximizing the effective interfacial area at a given loading level. Furthermore, the development of hierarchical architectures in which LDH nanoparticles are distributed within a multi-scale pore network combining macropores for mechanical compliance, mesopores for Knudsen-effect insulation, and LDH–silica interfaces for phonon scattering represents a promising direction for next-generation hybrid insulation materials.

5.3. The Role of Hollow Nanoparticle Architecture in Decoupling Thermal Transport Pathways

The hollow silica nanoparticle results reveal an architecturally distinct strategy for achieving low thermal conductivity that differs fundamentally from the bulk aerogel

approach. In HSN systems, the enclosed void within each nanoparticle acts as an isolated nanoscale gas cell in which the Knudsen effect suppresses gaseous conduction, while the thin silica shell minimizes the solid conduction path length. The strong inverse correlation between HSN internal diameter and thermal conductivity (r = 0.94) reflects the diminishing Knudsen contribution as the cavity size increases toward the mean free path of air. The thinnest shells (6.8 nm) simultaneously minimize the solid conduction path through individual particles, contributing to the lowest measured conductivities (22.4 mW/m·K for 48 nm internal diameter HSNs).

This finding aligns with the work of Neuhofer and Retsch (2022), who demonstrated that the structural parameters of particulate silica assemblies including particle size, shell thickness, and interparticle packing directly govern the temperature-dependent transition between conduction-dominated and radiation-dominated thermal transport. The ability to independently control the HSN internal diameter and shell thickness through the LDH template size and silicate concentration, respectively, provides a powerful tool for rational material design. By combining the LDH-templated HSN approach with aerogel matrix integration, it may be possible to create double-Knudsen-effect architectures in which both the inter-particle pores and the intra-particle voids contribute to gaseous conduction suppression, potentially achieving thermal conductivities substantially below those of either component alone.

5.4. Optimization Framework and Design Principles

Synthesizing the structure–property correlations established in this study, several evidence-based design principles emerge for optimizing MgAl-LDH–silica hybrid insulation materials. First, the LDH loading should be maintained in the range of 10–15 wt% to achieve the optimal balance between thermal safety enhancement and insulation performance. Below 10 wt%, the thermal stability improvement is insufficient to meet stringent fire safety requirements; above 15 wt%, LDH agglomeration degrades both the pore structure and the thermal stability due to reduced interfacial area. Second, smaller LDH particles (~50 nm) are preferable to larger platelets because they preserve the Knudsen-effective pore structure and generate more phonon-scattering interfaces per unit mass. Third, maintaining a mean pore diameter below 20 nm is critical for maximizing the Knudsen-effect suppression of gaseous conduction, which remains the dominant heat transfer pathway in these materials at ambient conditions.

Fourth, the combination of LDH–silica aerogel hybrids with hollow silica nanoparticle architectures offers a pathway to next-generation dual-mechanism insulation materials. By engineering both the interparticle porosity (aerogel network) and intraparticle porosity (HSN cavities) to exploit the Knudsen effect, while simultaneously utilizing the LDH–silica interfaces for phonon scattering, it should be possible to push the effective thermal conductivity below 20 mW/m·K while maintaining the thermal safety advantages conferred by LDH incorporation. These design principles provide a rational foundation for the continued development of high-performance insulation materials for energy-efficient buildings, industrial process equipment, and aerospace thermal protection systems (Casini, 2020; Jelle, 2011; Raja *et al*., 2023).

6. Conclusion

This study has established a systematic framework for understanding the structure–thermal property relationships in MgAl layered double hydroxide–silica nanoparticle hybrid systems, providing the quantitative foundation necessary for the rational design of high-performance thermal insulation materials. Through comprehensive structural characterization and thermal transport decomposition analysis, the following key findings were obtained:

The Knudsen effect was confirmed as the primary mechanism governing the ultra-low gaseous thermal conductivity in these hybrid systems, with mean pore diameters of 12.8–15.6 nm ensuring operation in the transitional-to-free-molecular flow regime. The incorporation of MgAl-LDH at 10–15 wt% loading produced an optimal balance between the competing effects of increased solid conduction and preserved Knudsen-effective porosity, yielding net thermal conductivities of 25.3–25.9 mW/m·K with simultaneous enhancements in thermal stability of up to 49°C and reductions in calorific value of up to 23.9%.

Interfacial phonon scattering at LDH–silica boundaries was identified as a significant mechanism for partially compensating the solid conduction penalty introduced by the higher-conductivity crystalline LDH phase. Smaller LDH particles generated more interfacial area per unit mass, producing lower solid-phase conductivity at equivalent loadings. Hollow silica nanoparticles synthesized from MgAl-LDH templates achieved thermal conductivities as low as 22.4 mW/m·K, with cavity size and shell thickness independently controllable through template dimensions and silicate concentration.

The design principles derived from these correlations including optimal LDH loading ranges, preferred particle sizes, critical pore diameter thresholds, and dual-mechanism architectures combining aerogel networks with hollow nanoparticle cavities constitute an evidence-based framework for engineering next-generation hybrid insulation materials. Future work should focus on validating the proposed dual-Knudsen-effect architecture through the integration of LDH-templated HSNs into aerogel matrices, conducting long-term durability and aging studies under realistic environmental conditions, and performing scale-up feasibility assessments and life-cycle analyses to advance these promising materials toward commercial deployment in energy-efficient building envelopes, industrial thermal management systems, and aerospace applications.

References

1. Abu-Jdayil B, Mourad AH, Hittini W, Hassan M, Hameedi S. Traditional, state-of-the-art and renewable thermal building insulation materials: An overview. Constr Build Mater. 2019;214:709-735. doi:10.1016/j.conbuildmat.2019.04.102
2. Baetens R, Jelle BP, Gustavsen A. Aerogel insulation for building applications: A state-of-the-art review. Energy Build. 2011;43(4):761-769. doi:10.1016/j.enbuild.2010.12.012
3. Benhiti R, Ait Ichou A, Zaghloul A, Aziam R, Carja G, Zerbet M, *et al*. Synthesis, characterization, and comparative study of MgAl-LDHs prepared by standard coprecipitation and urea hydrolysis methods for phosphate removal. Environ Sci Pollut Res. 2020;27(36):45767-45774. doi:10.1007/s11356-020-

10444-5
4. Casini M. Nanoinsulation materials for energy efficient buildings. In: Kharissova O, Martínez L, Kharisov B, editors. Handbook of nanomaterials and nanocomposites for energy and environmental applications. Springer; 2020. p. 1-32.
5. Cavani F, Trifirò F, Vaccari A. Hydrotalcite-type anionic clays: Preparation, properties and applications. Catal Today. 1991;11(2):173-301. doi:10.1016/0920-5861(91)80068-K
6. Chen BQ, Xia HY, Mende LK, Lee CH, Wang SB, Chen AZ, *et al*. Trends in layered double hydroxides-based advanced nanocomposites: Recent progress and latest advancements. Adv Mater Interfaces. 2022;9(22):2200373. doi:10.1002/admi.202200373
7. Chubar N, Gilber V, Gerda V, Szlachta M. The structure of layered double hydroxides: Layer stacking, interlayer anions, and water molecules. Appl Clay Sci. 2017;150:204-211. doi:10.1016/j.clay.2017.09.008
8. Crepaldi EL, Pavan PC, Valim JB. Comparative study of the coprecipitation methods for the preparation of layered double hydroxides. J Braz Chem Soc. 2000;11(1):64-70.
9. Daniel S, Thomas S. Layered double hydroxides: Fundamentals to applications. In: Thomas S, Daniel S, editors. Layered double hydroxide polymer nanocomposites. Elsevier; 2020. p. 1-76.
10. Forano C, Hibino T, Leroux F, Taviot-Guého C. Layered double hydroxides. In: Bergaya F, Theng BKG, Lagaly G, editors. Handbook of clay science. Elsevier; 2006. p. 1021-1095.
11. Gao Y, Wu J, Wang Q, Wilkie CA, O'Hare D. Flame retardant polymer/layered double hydroxide nanocomposites. J Mater Chem A. 2014;2(29):10996-11016. doi:10.1039/C4TA01030B
12. He S, Sun G, Shi X, Yang H, Zhang K, Li S, *et al*. In-situ synthesis of layered double hydroxide/silica aerogel composite and its thermal safety characteristics. Gels. 2022;8(9):581. doi:10.3390/gels8090581
13. Jelle BP. Traditional, state-of-the-art and future thermal building insulation materials and solutions - Properties, requirements and possibilities. Energy Build. 2011;43(10):2549-2563. doi:10.1016/j.enbuild.2011.05.015
14. Jelle BP, Baetens R, Gustavsen A. Aerogel insulation for building applications. In: Pacheco-Torgal F, Granqvist CG, Jelle BP, Vanoli GP, Bianco N, Kurnitski J, editors. Cost-effective energy efficient building retrofitting. Woodhead Publishing; 2015. p. 319-349.
15. Kalali EN, Zhang L, Shabestari ME, Crober J, Wang DY. Flame-retardant wood polymer composites as potential fire safe bio-based materials for building products. Fire Saf J. 2019;107:210-216. doi:10.1016/j.firesaf.2017.11.001
16. Kantor Z, Wu T, Zeng Z, Gaan S, Lehner S, Jovic M, *et al*. Heterogeneous silica-polyimide aerogel-in-aerogel nanocomposites. Chem Eng J. 2022;443:136401. doi:10.1016/j.cej.2022.136401
17. Khan AI, O'Hare D. Intercalation chemistry of layered double hydroxides: Recent developments and applications. J Mater Chem. 2002;12(11):3191-3198. doi:10.1039/B204076J
18. Koebel M, Rigacci A, Achard P. Aerogel-based thermal superinsulation: An overview. J Sol-Gel Sci Technol. 2012;63(3):315-339. doi:10.1007/s10971-012-2792-9
19. Li C, Wei M, Evans DG, Duan X. Layered double hydroxide-based nanomaterials as highly efficient catalysts and adsorbents. Small. 2014;10(22):4469-4486. doi:10.1002/smll.201401464
20. Li Z, Cheng X, He S, Shi X, Yang H. Characteristics of ambient-pressure-dried aerogels synthesized via different surface modification methods. J Sol-Gel Sci Technol. 2015;76(1):138-149. doi:10.1007/s10971-015-3760-y
21. Liu J, Buahom P, Lu C, Yu H, Park CB. Microscopic revelation of the solid–gas coupling and Knudsen effect on the thermal conductivity of silica aerogel with inter-connected pores. Sci Rep. 2022;12:21034. doi:10.1038/s41598-022-24133-5
22. Liu R, Dong X, Xie S, Jia T, Xue Y, Liu J, *et al*. Recent advances in novel aerogels through the hybrid aggregation of inorganic nanomaterials and polymeric fibers for thermal insulation. Aggregate. 2021;2(2):e30. doi:10.1002/agt2.30
23. Luo Y, He S, Chen G, Shi X, Li Z. Enhancing thermal safety of hydrophobic silica aerogels by incorporating sodium dodecyl sulfate intercalated layered double hydroxides. J Sol-Gel Sci Technol. 2024;111:459-470. doi:10.1007/s10971-024-06379-9
24. Mishra G, Dash B, Pandey S. Layered double hydroxides: A brief review from fundamentals to application as evolving biomaterials. Appl Clay Sci. 2018;153:172-186. doi:10.1016/j.clay.2017.12.021
25. Mohapi M, Sefadi JS, Mochane MJ, Magagula SI, Lebelo K. Effect of LDHs and other clays on polymer composite in adsorptive removal of contaminants: A review. Crystals. 2020;10(11):957. doi:10.3390/cryst10110957
26. Neuhöfer S, Retsch M. High-temperature thermal transport in porous silica materials: Direct observation of a switch from conduction to radiation. Adv Funct Mater. 2022;32(6):2108370. doi:10.1002/adfm.202108370
27. Notario B, Pinto J, Solorzano E, de Saja JA, Dumon M, Rodríguez-Pérez MA. Experimental validation of the Knudsen effect in nanocellular polymeric foams. Polymer. 2015;56:57-67. doi:10.1016/j.polymer.2014.10.006
28. Pookulangara LV, Kankanallu VR, Wunder SL. Controllable synthesis of hollow silica nanoparticles using layered double hydroxide templates and application for thermal insulation coating. ACS Omega. 2023;8(30):27289-27298. doi:10.1021/acsomega.3c03917
29. Prasad C, Tang H, Liu Q, Zulfiqar S, Shah S, Bahadur I. An overview of semiconductors/layered double hydroxides composites: Properties, synthesis, photocatalytic and photoelectrochemical applications. J Mol Liq. 2019;289:111114. doi:10.1016/j.molliq.2019.111114
30. Qu J, Zhang Q, Li X, He X, Song S. Mechanochemical approaches to synthesize layered double hydroxides: A review. Appl Clay Sci. 2016;119(1):185-192. doi:10.1016/j.clay.2015.10.018
31. Raja P, Barron AR, Murugan R. A review of sustainable bio-based insulation materials for energy-efficient buildings. Macromol Mater Eng. 2023;308(10):2300086. doi:10.1002/mame.202300086
32. Rives V. Layered double hydroxides: Present and future.

New York: Nova Science Publishers; 2001.
33. Shabanian M, Hajibeygi M, Raeisi A. FTIR characterization of layered double hydroxides and modified layered double hydroxides. In: Thomas S, Daniel S, editors. Layered double hydroxide polymer nanocomposites. Elsevier; 2020. p. 77-101.
34. Smalenskaite A, Vieira DEL, Salak AN, Kareiva A, Ferreira MGS. A sol-gel technique for the synthesis of MgAl-LDH nanoparticles with enhanced textural properties. J Sol-Gel Sci Technol. 2019;89(2):546-554. doi:10.1007/s10971-018-4889-2
35. Swimm K, Vidi S, Reichenauer G, Ebert HP. Coupling of gaseous and solid thermal conduction in porous solids. J Non-Cryst Solids. 2017;456:114-124. doi:10.1016/j.jnoncrysol.2016.11.010
36. Verdolotti L, Lavorgna M, Lamanna R, Di Maio E, Iannace S. Polyurethane–silica hybrid foam by sol-gel approach: Chemical and functional properties. Polymer. 2015;56:20-28.
37. Wang H, Liu J, Xu X, Ma Z. Tailoring thermal insulation architectures from additive manufacturing. Nat Commun. 2022;13:4313. doi:10.1038/s41467-022-32027-3
38. Wang Q, O'Hare D. Recent advances in the synthesis and application of layered double hydroxide (LDH) nanosheets. Chem Rev. 2012;112(7):4124-4155. doi:10.1021/cr200434v
39. Xu L, Jiang Y, Feng J. Reduced thermal conductivity of nanoparticle packed bed by hybrid design. Int J Heat Mass Transf. 2020;161:120306. doi:10.1016/j.ijheatmasstransfer.2020.120306
40. Yu J, Wang Q, O'Hare D, Sun L. Preparation of two-dimensional layered double hydroxide nanosheets and their applications. Chem Soc Rev. 2017;46(19):5950-5974. doi:10.1039/C7CS00318H
41. Zeng Q, Mao T, Li H, Peng Y. Thermally insulating lightweight cement-based composites incorporating glass beads and nano-silica aerogels for sustainably energy-saving buildings. Energy Build. 2018;174:97-110. doi:10.1016/j.enbuild.2018.06.031
42. Zhang W, Li Z, Shi L, Li Z, Luo Y, Liu Q, *et al.* Methyltrichlorosilane modified hydrophobic silica aerogels and their kinetic and thermodynamic behaviors. J Sol-Gel Sci Technol. 2019;89(2):448-457. doi:10.1007/s10971-018-4882-9
43. Zhao MQ, Zhang Q, Huang JQ, Wei F. Hierarchical nanocomposites derived from nanocarbons and layered double hydroxides: Properties, synthesis, and applications. Adv Funct Mater. 2012;22(4):675-694. doi:10.1002/adfm.201102222
44. Zhao Y, Li F, Zhang R, Evans DG, Duan X. Preparation of layered double-hydroxide nanomaterials with a uniform crystallite size using a new method involving separate nucleation and aging steps. Chem Mater. 2002;14(10):4286-4291. doi:10.1021/cm020370h
45. Zhu Q, Li L, Wang X, Ma S, Li J. Enhanced thermal safety of hydrophobic SiO_2 aerogels through introduction of layered double oxides. Gels. 2024;10(12):844. doi:10.3390/gels10120844